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STRUCTURAL, ELECTRONIC, VIBRATIONAL AND THERMODYNAMICAL PROPERTIES OF SURFACES AND NANOPARTICLES

by

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ABSTRACT

The main focus of the thesis is to have better understanding of the atomic and electronic structures, vibrational dynamics and thermodynamics of metallic surfaces and bi-metallic nanoparticles (NPs) via a multi-scale simulational approach. The research presented here involves the study of the physical and chemical properties of metallic surfaces and NPs that are useful to determine their functionality in building novel materials. The study follows the “bottom-up” approach for which the knowledge gathered at the scale of atoms and NPs serves as a base to build, at the macroscopic scale, materials with desired physical and chemical properties. We use a variety of theoretical and computational tools with different degrees of accuracy to study problems in different time and length scales. Interactions between the atoms are derived using both Density Functional Theory (DFT) and Embedded Atom Method (EAM), depending on the scale of the problem at hand. For some cases, both methods are used for the purpose of comparison. For revealing the local contributions to the vibrational dynamics and thermodynamics for the systems possessing site-specific environments, a local approach in real-space is used, namely Real Space Green’s Function method (RSGF). For simulating diffusion of atoms/clusters and growth on metal surfaces, Molecular Statics (MS) and Molecular Dynamics (MD) methods are employed.
To the memory of Grandmother, PASA
(Babaannemin Anisina)
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CHAPTER 1: INTRODUCTION

Nanoengineering which is becoming an increasingly emerging field involves nanoscale modeling and simulation methods that are capable of designing and guiding the development of functionalized nanoscale materials. Advancement in such experimental surface science techniques as Scanning Tunneling Microscopy (STM) [1] and Atomic Force Microscopy (AFM) [2] has provided valuable contributions to the understanding of these systems at the atomic scale. Determining the key factors behind their stability is one of the most important steps towards building functionalized materials. Recent advancements in theoretical approaches and computational resources have made it possible to carry out effective studies in which the bridge between experimental observations and theoretical results is concretely established. The aim is not to replace experimental observations by theoretical studies, rather for theory and simulation to provide support and rationale for experimental observations. The best picture that one achieves is the combination of the two to bring insight into the challenging problems. Theoretical approaches today have reached the accuracy that they can bring valuable contributions to experimental observations.

Nanoscale systems are of great importance in areas such as catalysis, biomedicine, and information technology that have direct influence in improving human life. The greatness of these materials originates from unusual electronic, magnetic, optical, thermodynamic and catalytic properties [3, 4]. The feature of their unusual stability -- energetically, thermodynamically, and electronically -- opens up the
The origin of the unusual properties of these nanostructures with respect to their extended counterparts is attributed to quantum size effects and the presence of large surface to volume ratio. As the size decreases, i) the surface to volume ratio and thus the concentration of low-coordinated atoms increases rapidly; and ii) quantum effects such as electronic and vibrational confinement become dominant [6]. Low-coordinated atoms are known to have striking electronic, vibrational and thermodynamical characteristics [7]. The effect of size has been shown to induce differences from bulk behavior in many physical and chemical properties [3, 8, 9]. It was shown for mono-metallic NPs that they have dissimilar vibrational properties as compared to extended systems -- population at the high frequency end of the spectrum, and enhancement at the low-frequency end of the spectrum [8, 9]. Thermodynamical properties also differ from those for the extended systems [10]. In consideration of the magnetic properties, small magnetic NPs have shown to have enhanced magnetic moments [11]. It was shown that once the band structure is achieved, these properties converge to those of the extended systems. Role played by size in inducing these unusual properties has been under investigation, and relatively good understanding has been achieved.

A more complicated picture appears when two elements are composed to build a NP. Alloying not only brings additional richness to their properties but also complexity in understanding the underlying reasons for their distinct features. To begin with the number of possible combinations resulting from the presence of different elemental components brings additional complexity in determining the most stable structures (the configuration
with the lowest total energy) [12]. Understanding their properties requires thorough examination of the relative ratio between the components, relative positions of the components, and possible charge transfer. In recent years the research in this area has intensified providing the basis for better understanding of their properties [12-14]. The structural stability of nanostructures is one of the most important concerns owing to the fact that once they are produced, the scale of their stability determines their response to any external perturbation such as temperature, pressure, electric, and magnetic fields. In consideration of structural stability, it was reported for the single-element NPs that vibrational dynamics contribute to their free energies [8]. For the binary alloys, the question arises to what extent the vibrational contribution is important, and whether it depends on a particular stoichiometry. For mechanical stability, a recent study examined the hardness of a particular binary alloy [15]. They showed that hardness of PtCu alloy NP has an oscillatory behavior, which depends on the total number of electrons in the system [15]. The thermodynamic stability -- based on melting temperature -- of small size binary transition metal NPs has been shown to be also influenced by alloying, and it is element dependent [16]. From the electronic point of view, it was shown that the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) gap of these nanostructures can vary widely; indicating differences in their electronic stability, hence chemical activity [17-19]. In addition, the role played by composition in controlling the physical and chemical properties of nanoparticles is still to be answered.

For determining the relative stability of extended systems such as surfaces, free energy is the key property that includes contributions from both the structural potential
energy and system’s vibrational and configurational entropy. Configurational entropy is important constituent for any system containing more than one type of element (hetero structures), while the vibrational entropy is the quantity to be evaluated for surfaces of both single and multi-elements. It may determine the equilibrium shape of the crystal surface and its preference to undergo structural transitions. Vibrational contribution to the stability of extended systems and its role in thermodynamics has been examined in earlier studies [20, 21]. Its role in nanoparticle will be considered here.

Understanding phenomena on surfaces has been one of the long term goals of material science because of their technological applications. For example, understanding of the underlying electronic factors governing chemical activity can be the key to the engineering of surfaces with such features. It has been shown that many chemical reactions are significantly enhanced when they occur on metallic surfaces. In order to study any particular reaction/adsorption on these systems, it is vital to examine their electronic structure, as the adsorption energies of atoms, molecules and small 2D clusters can vary dramatically depending on the electronic structure of the substrate [22]. Moreover, mixing of different metals may result in catalytically active and selective surface owing to the modification induced to its electronic structure. The change in chemical properties for such cases originates from the change induced in the bond lengths between metal atoms in the presence of another metal. Since these effects allow one to manipulate the chemical properties, they are very important for designing a novel catalyst. It is also reasonable to examine the role of vibrational contribution in chemical reaction since it may affect the rates for a particular event to occur. There is not much
examined along these lines owing to the difficulty in extracting these contributions accurately, for instance, using first-principles.

Diffusion of single atoms and clusters is another example of rare events. Understanding the basics of the phenomenon, evaluating both activation energies and the dynamics controlling diffusion processes are the initial steps towards determining the characteristics of the growth of thin films. Diffusion of multi-atom system is an important step of the early stages of nucleation. Since it involves the diffusion of more than a single-atom, cluster diffusion brings a bit more challenge originating from the competition between the interactions within the cluster atoms and that of the cluster-substrate. These interactions may affect diffusion energetics and diffusivity that ultimately controls nucleation. Moreover, the number of possible diffusion processes for a cluster is far more complex to determine as compared to that for a single-atom.

To study growth requires a multi-scale approach owing to the fact that growth proceeds in seconds and minutes in real observations, while the relevant atomistic processes are in the time scale of nanoseconds. There has been great effort for the last two decades towards a better understanding of the underlying principles governing the growth of thin metal films because of their technological applications [23]. It is now established that for some systems mass transport at step edges is the key parameter for the resulting growth morphology [24]. It was shown that the height of the barrier known as the Ehrlich-Schoewebel (E-S) -- difference between the diffusion barrier of adsorbates near step edge and that on the terrace -- can be correlated to the observed growth morphology [25, 26]. Systems with large E-S barrier are expected to grow rough films (3D) as mass transport is prohibitive. Conversely, small E-S barrier allows growth of
smooth films, and growth mechanism is layer-by-layer. It is also established that diffusion of single atoms on surfaces can occur via two different diffusion mechanisms, namely hopping and exchange [27]. It was shown for some metal surfaces that exchange is the governing mechanism for diffusion [28]. This is attributed to the fact that these surfaces inherently have tensile strain that favors an exchange mechanism over hopping. It is of great importance in evaluating growth morphology to consider both mechanisms for a complete picture of the controlling atomistic processes. Surface orientation is another factor dictating the observed growth morphology as difference in orientation leads to differences in atomic coordination, bonding and binding distribution that have direct influence on the energetics of adsorbate diffusion [29]. Recent studies have focused more on determining the role of electronic structure in governing the height of diffusion energetics by evaluating the binding energies of the adsorbates [30, 31].

Recently attention has also been paid to understanding hetero diffusion in which the atoms are deposited on a substrate of another element. Its relevance for better understanding the role of electronic structure modifications in catalysis seems to be speeding up its evolution [32]. Note that hetero diffusion is dissimilar to homo via two aspects. The first is the presence of the strain induced by the misfit between the adsorbate and substrate elements. The second is the electronic coupling between the two elements that is known to induce modifications in adsorption properties hence diffusion energetics [33]. It thus opens up ways to control reactions through the changes induced in adsorption energies. However, evaluating the role of each parameter is challenging experimentally since both effects are coupled. It is thus beneficial to employ accurate theoretical approaches to extract solely the role of each parameter. In this regard, first-
principles calculations have reached the level that they can accurately determine and predict these effects through careful analysis of the energetics. Activation energies can be evaluated up to certain accuracy by experiments, while dynamics are often difficult to extract via Arrhenius relation since several measurements have to be performed in a reasonable range of temperature. Such measurements quite often are difficult and their lack leads to the assumption of a constant prefactor -- measure of the vibrational contributions to diffusion [34]. From the theoretical point of view, an accurate evaluation of diffusion dynamics still stays as a challenge especially through first-principles. However, few attempts have been made to obtain these dynamics invoking certain assumptions to simplify its complexity [35].

As noted above, thorough understanding of thin film growth is challenging owing to the multi-scale nature of the problem. Each method undertaken to study growth has certain advantages and disadvantages. For instance, the temporal and temperature evolution of a system can be achieved via MD simulations. Perhaps it is the best approach to obtain the diffusion dynamics, activation barriers, as well as the atomistic processes. It is to be noted that anharmonic effects are inherent to the method. However, the time scale of a diffusion process -- rare event -- makes it impossible to perform simulations long enough to collect sufficient statistics for evaluating the parameters comparable to real observations. Moreover, MD simulations using first principles are confined for very small number of atoms and relatively short simulation times. With certain assumption taken to get around the time scale problem, the Kinetic Monte Carlo (KMC) method provides an opportunity for revealing the temporal and temperature evolution of a system. Appreciable attention has been paid recently for generation of such
methods with different accuracy and efficiency [36]. Perhaps, one of the most important inputs for such method is the accurate energetic profiles, which can be achieved nowadays by first-principles.

In an effort to build materials with novel properties, one can use nanostructures with unique intrinsic properties as building blocks. If that is not available, the alternative is to use manipulative tools with which one can induce properties that do not exist in nature. By modifying such process as diffusion and reaction, one can take control over the evolution of the atomistic processes. For instance, deposition of an overlayer of a catalytically active metal on a non-reactive metal can induce strong reactivity [37]. The opposite is also possible -- suppressing the reactivity of a metal substrate with a non-reactive material [37]. The same ideas can also be applied for diffusion processes -- diffusion can be enhanced or suppressed by surfactants [38]. The underlying process behind these effects is the modification induced to the electronic structure of the substrate. Another possibility in altering the electronic structure has been shown to be achieved by strain [39]. Applying either tensile or compressive strain can induce changes in the electronic structure of the substrate atoms. The effect of strain in altering the adsorption properties of small molecules on metal surfaces has been nicely illustrated using the so-called d-band model [40]. It was reported that when tensile strain -- increasing the distance between the neighbors -- is applied to the surface, the overlap between the wave functions become smaller leading to the shift in the position of the center of the d-band [39]. Under tensile strain, a strong shift of the center of the d-states towards higher binding energy is observed. Thus, making the substrate more reactive by changing the adsorption energy of the molecules hence enhancing the possibility of
reaction to occur [41]. Although the model is based on many assumptions, it seems to be capable of providing a measure of the changes induced to the electronic structure.

For diffusion of single atoms, studies have shown that strain can be used to modify diffusion barriers in the same spirit as for surface reactivity [42]. As noted above for hetero systems strain is inherently present along with electronic coupling; hence making it hard to separate one of the two effects from each other. Thus, the proposed alternative is to examine the changes induced to the diffusion parameters by studying self diffusion on strained layers [43]. Then by eliminating the electronic coupling one can obtain the information on the effect of strain solely. The studies mostly using semi-empirical methods have revealed that tensile strain increases diffusion barriers, while compressive strain induces the opposite [43]. The control over diffusion barriers is attributed to the changes induced to the binding energies of adsorbates relative to the substrate [43]. Since these studies were performed using semi-empirical approaches, they do not provide information on the electronic structure, thus the result were reported simply using geometric arguments -- change in surface corrugation in the presence of strain [43]. Note that only a single study paid attention to the changes in diffusion dynamics with strain, and concluded it to be small (a factor of two deviation from unstrained value) [44].

Altering diffusion barriers can also be achieved by manipulative tool such as STM tip. Earlier studies have shown that presence of tip alters the energy landscape in such a way as to reduce the diffusion barriers for single atoms [45]. The dependence of the observed trends on tip geometry and orientation has also been discussed providing the underlying processes of tip-induced modifications [46]. We examined the elemental
dependence of the extraction of single atoms and manipulation of clusters studying extraction/manipulation on two metal substrates [47]. The results revealed that there is a strong elemental dependence arising from the nature of the binding that the elements offer. The elemental dependence thus induces dissimilarities in the extraction and manipulation modes [47].

The ultimate goal of the studies undertaken in this dissertation is to gather knowledge that will help build materials with desired physical and chemical properties. The aim is to have a better understanding of the atomic and electronic structure, vibrational dynamics and thermodynamics of surfaces and bi-metallic NPs. Such a task requires examining local contributions (atomically-resolved) to the overall properties. Since each problem has to be treated in different time and length scales, a multi-scale simational approach is adopted. To date, the greatest computational accuracy can be achieved using DFT [48], by which the electronic structure of the system at hand is explicitly tackled. This computationally demanding theoretical approach is used for systems of relatively small length scale (of the order of 10 nm). DFT has been proven to be a robust method and applicable for studying physical and chemical properties of many systems. There are problems in which the method needs further improvement which are presently under way [49]. For more accurate description of the calculated properties and to reveal the electronic structure properties, we have employed DFT [48]. In order to study problems that require larger time and length scales, model potentials maybe preferred alternative to DFT methods. One of the most widely used potential for transition metals (the subject of the research presented here) is the one derived from the EAM [50]. The method has been widely tested [51], and shown to reliably produce the
properties of six transition metals, among which are those we extensively study here, namely, those of Cu and Ag and their alloys. The fact that for finite-sized systems, the properties of a single atom can influence the overall properties, thus revealing the site-specific properties is of great importance. For that reason for the calculation of the vibrational densities of states (VDOS), we have used RSGF method [52] -- a local approach that allows the determination of local contributions to the dynamics and thermodynamics of the systems possessing site-specific environments. For simulating diffusion of single metal atoms and clusters on metal surfaces, both MS [53] and MD [54] simulations are employed.

Chapter 1 describes the problems undertaken in this dissertation. It aims at clarifying the importance of the problems studied here for understanding the controlling parameters for building functionalized materials. It provides the related background for each problem, and the current state of each. It briefly mentions the theoretical methods used in this study, and discusses the reason(s) for their selection.

Chapter 2 introduces in detail each method employed in the study. The first two sub-sections discuss the energy models by which the interactions between the atoms in the systems are described. The third describes the method known as RSGF, adopted for calculating VDOS. Calculation of the thermodynamical functions within the Harmonic approximation, and the diffusion parameters will be the subject of sub-section 2.4. Details of the MS, MD simulations, and the Transition State Theory (TST) [55] will also be introduced in the chapter.

Chapter 3 discusses the vibrational and thermodynamical properties of the (100) surfaces of Cu, Ag, Au, Pd and Pt. The main goal of this part of the study is to reveal
local (atomically-resolved) contributions to vibrational dynamics and thermodynamics of these surfaces. Examination of the structural, dynamical and thermodynamical properties is crucial in understanding growth, catalysis and many other phenomena. The study also aims at examining the accuracy of the model potentials in describing the above mentioned properties by means of comparing their results to those obtained from DFT calculations.

Chapter 4 explores a multi-scale modeling of homo- and hetero-epitaxial growth on metal surfaces. MS, MD, TST and the thermodynamical functions are used to derive such diffusion parameters as activation energy barriers, diffusion prefactors and diffusion coefficients for single-atom and 2D-cluster diffusion. Knowledge of these parameters is necessary for understanding nucleation and growth through determination of the E-S [25, 26], which is the key parameter for atomic mass transport at step-edges. Studying homo and hetero diffusion, the aim is to understand the role of electronic interactions on the diffusion parameters.

In sub-chapter 4.1, I will discuss the diffusion of single metal atoms on flat and stepped metal surfaces of (100). The ultimate goal of the study is to derive insights into possible growth mechanisms for each surface by means of calculating the diffusion barriers both at terraces and near step edges, hence determine the so-called E-S barriers. By studying both possible diffusion mechanisms, namely hopping and exchange, we aim at obtaining an understanding of the role of these mechanisms in controlling the growth on these surfaces. Finally, the effect of electronic interactions in controlling the height of the calculated diffusion barriers is achieved by studying both homo and hetero diffusion via examining the binding energies. This part of the study helped us extending this study
into the examination of the strain role on the diffusion barrier heights that is the subject of the following sub-chapter.

The sub-chapter 4.2 is based on the idea of engineering the diffusion activation barriers by applying strain. Altering these parameters hence tuning material properties provides an opportunity in controlling microscopic events. In this chapter the effect of strain in altering diffusion barriers are examined, and the resulting effect on nucleation and growth is discussed. Studying diffusion parameters for cluster diffusion provides insights into the early stages of nucleation. This study is influenced by the results of the former section (sub-chapter 4.1) in which I present the diffusion of single metal atoms on metal surfaces both for homo and hetero diffusion. Comparison of the diffusion barriers for the hetero systems has revealed the difference between the two systems. As known, for the case of hetero diffusion, in addition to the existence of electronic coupling between the two elements, there is also presence of strain. It is not possible to reveal the effect of one of these parameters by means of studying the hetero systems thus we undertook an approach in which we study the self diffusion on the strained metal surfaces with an aim of directly revealing the role of strain on the diffusion barriers. By studying the diffusion near step edges, we aim at providing an understanding of the role of strain on growth by means of calculating the E-S barriers.

The subject of the sub-chapter 4.3 is the examination of the contribution of the vibrational entropy in the calculation of the prefactors for adatom diffusion via hopping mechanism on both terraces and near step edges. It is aimed at deriving an understanding of the effect of local environment on the prefactors. Comparisons between the results of different methods used for calculating the prefactors will also be discussed.
The motivation behind the study presented in sub-chapter 4.4 is based on the results of the earlier chapter in which we have found that the prefactors for several diffusion processes of single Cu and Ag atoms on Cu(100) and Ag(100) surfaces are the same within a factor of 2 at most. These calculations bring about the question of the role of vibrational dynamics in determination of the prefactors. It is also important to determine whether the prefactors change with the inclusion of dynamics from the substrate atoms. The reason(s) behind the quasi-constant prefactor will be revealed and discussed in detail.

The study presented in sub-chapter 4.5 derives the diffusion parameters of a compact hexagonal Cu heptamers and compares those for single atoms for both homo and hetero systems. The motivation behind the study is manifold. We aim at revealing the diffusion prefactor for compact 7-atom cluster and its comparison to that for the single atom. By studying the hetero diffusion, we are interested in determining the role of electronic interactions in controlling the energetics and dynamics of the 7-atom cluster. By employing several methods to study the diffusion parameters of such cluster, we are also interested in evaluating the accuracy of each method used in describing the diffusion parameters for multi-atom system. Performing dynamic simulations allows us to reveal the atomistic processes responsible for the diffusion of 7-atom cluster. In addition, the results are expected to provide insights into the contribution of full substrate dynamics in determining diffusion dynamics of multi-atom clusters.

Chapter 5 discusses the effect of progressive alloying on the bonding, vibrational and thermodynamical properties of the family of 34-atom bi-metallic Ag$_n$Cu$_{34-n}$ (n=0,1,2,…,34) NP. The goal is to derive insights into the interplay between
coordination and elemental environment in shaping the properties of these NPs. Controlling the properties at the nanoscale has been the growing interest for the last couple of years. Since alloying brings about an extra avenue to be exhausted for the creation of functionalized nanoscale materials, understanding its role in altering the material properties is of great importance. The knowledge gained from these analyses serves as a basis for the selection of the most stable NPs, to understand the role of composition, to determine the effect of relative atomic positions of each kind, and to reveal site-specific contributions into the above mentioned properties.

Chapter 6 reports the electronic structure of the Ag$_n$Cu$_{34-n}$ NP family. It discusses how the electronic structure is influenced by progressive alloying and what role is played by the Ag-to-Cu ratio on the electronic structure. More specially, the attention is paid to determine the change in the electronic densities of states (EDOS) both atomically-resolved (locally) and total (globally), the change in the center of the d-states of the atoms (for reactivity purposes) to build an understanding on the hierarchy between coordination, bond type and the strength of hybridization. In order to gain insights into metal to non-metal transition, the HOMO-LUMO gap for each NP is calculated. These analyses help to single out those NPs with specific compositions that present high electronic stability (degree of reactivity). Particular interest will be paid in understanding the relative composition of the core and the shell of the NPs in influencing the reactivity and metal to non-metal transition.

Chapter 7 presents the details of the atomistic processes that are responsible for the extraction of single Cu and Ag atoms from 3D mounds on Cu(111) and Ag(111), respectively. The study reveals that one can take control over atomistic processes. It
shows that manipulative techniques can be used to modify characteristics of the potential energy surfaces at hand that then directly influence diffusion and reaction. In the objective of building materials with desired physical and chemical properties, one may sometimes need to use manipulative techniques to control events such as growth and chemical reactions. In this chapter, we will present atomistic simulations motivated by the results of STM experiments to rationalize the capability of STM tip in extracting/manipulating single atoms and clusters on the closed-packed metal substrates. The present study not only aims at understanding the underlying reasons for atom extraction processes for a particular system, but also provides insight into the elemental dependence of extraction/manipulation processes.
CHAPTER 2: THEORETICAL METHODS

The chapter is devoted to introduce the theoretical methods that are employed to study the problems throughout the thesis. In the following two sections we begin with introducing the energy models with which the interactions between the atoms in the systems are described. These interactions set the level of accuracy of the calculations -- by means of describing the system total energy -- in obtaining the systems’ physical and chemical properties. The first model, which is considered to be the most accurate to date, belongs to the class of ab-initio methods. In principle, these methods do not rely on any experimental input. While the accuracy obtained using these methods in describing many physical and chemical properties of metals, semi-metals and even oxide systems, these methods have a serious limitation in realistically modeling of large number of atoms. A realistic modeling of several hundreds or thousands of atoms is necessary for properties that are time and temperature-dependent. For instance, the evolution of a system in time and space at a given temperature and pressure as the case for growth phenomena or the existence of disorder and defects that extend over several nm requires modeling of large number of atoms. Hence, a realistic simulation of such problems requires simplifications in describing the interactions between the atoms in the system. The simplifications are obtained by introducing parameterized expressions for the description of system total energy instead of solving the Schrödinger equation using approximations as is done in the case of ab-initio methods. The second model, called as semi-empirical interaction potentials [56, 57], is based on fitting the potential parameters to a set of well-known
material properties obtained from experimental observations. Among these potentials, the one derived from the EAM [50], which is used extensively throughout the thesis along with first-principles for the problems that require simulation of large number of atoms (Chapters 4.5 and 7) and for some cases for comparison purposes (Chapters 3, 4.4 and 6). The method was developed at the beginning of 80’s for six transition metals -- Cu, Ag, Au, Ni, Pd and Pt. During the last two decades, the accuracy of the method in describing the dynamical and thermodynamical properties of these metals and their alloys is extensively tested [51]. By comparing the results obtained from first-principles and the semi-empirical method, we assess how accurately the method describes the vibrations, dynamics and thermodynamics of the studied systems.

The initial goal of the thesis aims at a better understanding of the atomic and electronic structures, vibrational dynamics and thermodynamics of metallic surfaces and bi-metallic NPs. Once this understanding is achieved partially and/or completely through determination of the key factors controlling these above-mentioned properties, the next goal is to seek for ways with which these key factors can be altered so that man-made properties are induced (engineering). In order to achieve such a goal, a multi-scale simulativeal approach has to be taken. For revealing the vibrational dynamics of surfaces and mono- or bi-metallic NPs the determination of local (atomically-resolved site-specific) properties is vital in understanding the overall system dynamics [58]. Hence, for the calculation of vibrational dynamics (Chapters 3, 4.3, and 4.5), we have employed RSGF method [52], an approach that allows determination of local contributions to the dynamics of the systems possessing site-specific environments. The method has been successfully applied in early studies to reveal the local contributions for many extended
and finite-systems [59]. In Chapter 2.3, we will introduce the method and discuss how it excels in revealing these local contributions in comparison with the other available methods. In Chapter 2.4, we will present the details in calculating such system thermodynamical functions as lattice heat capacity, vibrational free energy and mean-square displacement that are obtained within the Harmonic Approximation. These thermodynamical functions are relevant in obtaining diffusion constants, and in understanding thermodynamical properties of extended and finite-systems of interest, particularly in the context of their stability.

A thorough understanding of the evolution of a system at a given time and a particular temperature -- such as growth of metal on metal -- starts with an examination of a flux of single atoms (later in time, cluster) diffusion on surfaces. Such diffusion parameters as diffusion energetics and dynamics (prefactors and diffusion constants) are the key parameters to understand the initial stages of nucleation and ultimately growth. The calculation of diffusion activation barriers requires mapping of the potential energy surface in order to determine the transition-state configuration for such a rare event. Search for the transition-state configuration can be done in many ways each with its own level of accuracy and computational cost. In Chapter 2.5, we will discuss MS simulations, which allow mapping of the potential energy surface in order to obtain transition-state configuration. We will introduce two particular methods employed in the thesis for transition-state search, namely Drag Method and Nudged-Elastic Band (NEB) Method [60]. MS simulations are employed in Chapters 4 and 7 in order to calculate the diffusion of single atoms and clusters on various flat surfaces and near-step edges. The
results of these simulations provide insights into the key factors affecting the initial stages of nucleation and growth on these surfaces.

MD is a simulation technique in which the time evolution of a set of interacting atoms is achieved by integrating their equations of motions. The technique has the ability to reveal possible set of atomistic processes that occur during the given simulation time and temperature. In addition, temperature-dependent diffusion parameters (effective) are also available from the resulted simulation via construction of an Arrhenius plot. In Chapters 4.5 and 7, we have employed MD simulations in order to study diffusion and manipulation/extraction of single atoms and 2D clusters on the (111) surfaces. These simulations reveal the atomistic processes (within given simulation time and temperature) that are responsible for these events. Although valuable insights can be driven from these simulations, the limitation emerges when these results are compared with those obtained from experiments. This originates from the fact that the time-scale of these simulations are far below those accessible to experimental observations. The way around the time-scale limitation is provided by KMC [36], which is based on TST [55] (Chapter 2.7). Because this method allows one to perform simulations for days even months, it provides valuable theoretical input, which is “directly” comparable to the experimental observations.

2.1 Embedded Atom Method (EAM)

Many problems of interest in surface and material sciences require a detailed understanding of the structure and the energetics of metal surfaces with defects and their alloys. A realistic simulation of the physical and chemical properties of such low
symmetric systems requires methods that are flexible in simulating large number of atoms. Clearly, *ab-initio* methods in their current state are not suitable for providing a realistic picture owing to their high computational cost. The alternative for such cases is to use semi-empirical potentials because their low computational cost makes it possible to simulate large number of atoms. There has been continuous effort in the community for the improvement of such potentials [61]. In the early 80s these potentials were confined to two-body cases and were employed mostly to study the properties of rare gases. One very widely-used potential is the Lennard-Jones potential. It was employed successfully in studying the properties of rare gases in which the atoms are attracted through Van der Walls forces. However, it was shown that the LJ potential does not provide accurate description of the properties of metals and semiconductors. In case of metals this is due to the fact that bond strength decreases as the local environment gets populated. The shortcoming of the two-body potentials originates from the absence of a volume-dependent term in the energy description. Studies have shown that the potential fails to reveal correctly the relaxation (of both magnitude and direction) of the surface atoms for transition metals such as Cu and Au. They predict expansion for the surface atoms, while the surface atoms of most metals contract (inward relaxation). Moreover, they lead to overestimation of the vacancy formation energy. They also failed correctly to describe the Cauchy relation (setting it as $C_{12}=C_{44}$ [elastic constants]) for most of the metals.

In order to improve the description of interactions between the atoms so as to provide the properties that realistically describe metals, an approach was proposed based on the inclusion of many-atom effects. It was shown that in order to describe the properties of such metallic systems; the potential should embrace both the many-body
and pair-wise interactions. Inclusion of the many-body interactions ensure that when the local environment differs from that of the bulk (as is the case for surfaces and grain boundaries), one can realistically describe the relaxations, reconstructions, and many other properties. During 80s significant progress was made in developing many-body potentials for metals on the basis of coordination and atomic density. The addition of an environment-dependent term to the potential has solved the shortcoming of the absence of volume-dependence. To date, the most widely used inter-atomic potential for the six fcc transition metals for which the potentials have been developed is the one derived from the EAM that was developed by Daw and Baskes [50], using an approach based on DFT.

The idea behind the model is based on earlier theories of the Quasi-atom [56] and Effective-medium theory (EMT) [57]. In the quasi-atom method one assumes that each impurity encounters a locally uniform environment and the associated energy is given by:

$$E_{quas} = E_Z (\rho_h(R))$$

(2.1)

where $\rho_h(R)$ is the electron density without the impurity at the position $R$ and $E_Z$ is the quasi-atom energy of an impurity with atomic number $Z$. The EAM scheme is constructed on the basis of the same assumption that each atom in the system is embedded in a host consisting of all the remaining atoms. Similar to the energy of an impurity, an embedding energy -- the energy to embed an atom within the host -- is described as being dependent on the electron density. The density dependence of the embedding energy thus ensures that the potential is volume dependent. The host energy for a system with an impurity is described as a functional of the (unperturbed) host...
electron density and a function of the impurity’s type and position [56] and is expressed as:

\[ E = F_{Z,R}(\rho_h(r)) \]  

(2.2)

where \( \rho_h(r) \) is the unperturbed host electron density and \( Z \) and \( R \) are the type and position of the impurity, respectively. Comparison to the Hohenberg-Kohn [48] theorem in which the total energy is a functional of the total electron density, indicates that two approaches (EAM and DFT) differ from each other. In the case of Hohenberg-Kohn theorem, there is an explicit self-consistent solution for density, while in the case of EAM, as is evident in equation 2.2 (not a variational theorem), there is no explicit self-consistent solution for density. The total energy of a system is described as the sum over all the contributions, and is given by:

\[ E_{\text{tot}} = \sum_i F_i(\rho_{h,i}) \]  

(2.3)

where \( F_i \) is the embedding energy, which is the energy to embed a positively-charged ion core \( i \) into a linear superposition of atomic densities, while \( \rho_{h,i} \) is the density of the host at the position \( R_i \) without the atom \( i \), and the total energy is the sum of the contributions of density from each individual atom.

There are two problems with this version of the formula. The first is the absence of the term for describing core-core repulsion a short-range pair-wise repulsion. The second is the unrealistic assumption that each atom experiences a locally uniform electron gas -- for a solid at which there is no uniform charge density -- as is the case for
a jellium. One can introduce non-uniformity into the charge density by limiting uniform charge density to a finite region around the impurity.

With these additional corrections, the total energy is expressed in the form given by:

$$E_{tot} = \sum_i F_i(\rho_{h,i}) + \frac{1}{2} \sum_{i,j (i \neq j)} \phi_{ij}(R_{ij})$$  \hspace{1cm} (2.4)

where $\phi_{ij}$ is the short-range pair potential ($\phi_{ij}(r) = Z_i(r)Z_j(r)/r$) and $R_{ij}$ is the distance between atoms $i$ and $j$. Further simplification is introduced by assuming that the host density ($\rho_{h,i}$) is a sum of the atomic densities ($\rho^a$) of the atoms, and thus given by:

$$\rho_{h,i} = \sum_{j (\neq i)} \rho^a_j(R_{ij})$$ \hspace{1cm} (2.5)

where $\rho^a_j$ is the contribution to the density from atom $j$. Connection to the atomic densities makes the total energy to be a function of the atomic positions. The system’s total energy given in equation 2.4 shows that it has two parts; an attractive part and a repulsive part. The former describes the embedding of a positively charged core into the electron density formed by the surrounding atoms, while the latter models the interactions between the ion cores.

For a system consisting of single elements, three functions -- the embedding function, a pair-wise interaction, and a function for describing the contribution from an electron cloud -- are necessary to construct the potential. In case of binary alloys, three pair-wise interactions, two embedding functions, and two functions for electron cloud contribution need to be specified. These functions are provided in a tabulated format and interpolated by cubic splines. For the construction of EAM potential, the first step is to
determine the embedding energy \((F(\rho))\) and the effective charge \((Z(r))\). The functions \(F\) and \(\phi\) are determined by empirical means from the physical properties of the solid in question. The fitting procedure must take into account the bulk lattice constant, elastic constant, vacancy formation energy, and sublimation energy in fcc and bcc phases. The constraints imposed on the embedding energy function \((F(\rho))\) are that it should have a single minimum, be linear at high densities, and go to zero at vanishing densities. Constraints for the effective charge \((Z(r))\) are that it should be monotonic and vanish beyond a certain distance. The cutoff distance employed for fcc metals is between the first and the second nearest neighbors. The atomic densities are obtained from the single-determinant Hartre-Fock calculations of Clementi et. al [62]. Note that in this formulation proper mixing between the electronic configurations is not allowed. Hence, the true ground state is obtained by introducing an empirical parameter \(N_s\) [50] that defines s-like content for atomic density. The atomic density for fcc transition metals is then determined by the summation of the s and d contributions, and given by:

\[
\rho^a(r) = N_s \rho_s^a(r) + (N - N_s) \rho_d^a(r)
\]

where \(N\) is the total number of outer electron. For the transition metals, Daw et. al [50] determine the empirical parameter \(N_s\) by fitting the heat of solution of hydrogen in the metal for which the potential is under construction. This provides the effective number of s-like electrons in the solid.

The last decade has witnessed several successful applications of the method in describing many physical properties of six fcc transitions metals (in particular Cu, Ag, Ni, Au, Pd and Pt) and their alloys [51]. A good review of EAM and other formulations
of metallic potentials are published by Voter [63]. Foiles, Baskes and Daw (FBD) fit the EAM potentials for Cu, Ag, Au, Ni, Pd, Pt and their alloys [64], while Voter and Chen (VC) have included diatomic information into the EAM to predict correctly the melting points [65].

2.2 Density Functional Theory (DFT)

Understanding of the electronic structure of the materials is of great importance for both scientific and technological applications. Particularly the materials at the nanoscale are of special interest owing to the fact there are indications for their possible usage in developing materials with desired useful properties. Revealing the variety of material properties requires treatment of the systems on different time and length scales. This can be achieved by using different classes of methods with which one accurately describes the properties. Above, we have discussed a semi-empirical interaction potential derived from EAM [50], which allows simulation of large number of atoms in the expense of obtained accuracy with respect to the first-principles (FP) methods [48]. In order to reveal the electronic structure of materials, a full quantum mechanical (QM) treatment is vital. The advantage of the FP methods (ab-initio) over semi-empirical schemes originates from the fact that the FP methods do not require any experimental input to perform the calculations. The only input in these calculations is the nature of the element of interest.

In order to accurately treat the systems at the nanoscale via the FP methods, it is important to remember that electrons are Fermions -- indistinguishable particles -- and their wave-functions should be anti-symmetric under the label interchange. The anti-
symmetric states give rise to the Pauli Exclusion Principle, which forbids the identical fermions to share the same quantum state. Many-particle systems can be understood via the interactions among the particles, which are introduced through the exchange and the correlation phenomena. The Thomas-Fermi [66], Hartree [67] and Hartree Fock (HF) [68] approaches were the early steps for describing the electronic structure. Later on, DFT [48] -- a powerful and widely used approach -- was proposed for full QM treatment of the systems. The HF method belongs to the class of wave-function methods in which the wave functions are used as the basic ingredients in describing the electronic structure. In the HF methods, the exchange is taken into account, while the correlations are ignored. On the other hand, DFT is an ab-initio method in which the only input is a minimal number of quantities; the atomic numbers of the nuclei. DFT comes as an alternative approach to the wave-function based methods, and it uses the charge density -- depends only on the Cartesian coordinates -- as the basic variable to describe the energies of the interacting system of Fermions. It uses approximations in order to include both the exchange and the correlation effects.

The majority of the problems of interest are many-electron systems in which the motion of every electron is coupled to the motion of all the other electrons as well as to the motion of nuclei. Since such a many-body problem involves all the interactions among the electrons, to treat it via many-body wave-functions is an impossible task due to the large number of degrees of freedom. The first approximations for solving such problem were proposed by Thomas and Fermi [66], and later by Hohenberg and Kohn (HK) [48]. The HK proved two theorems concerning the ground state of the many-particle system, and finally the development of Kohn and Sham [48] brought on today’s
most powerful method that reveals accurately the electronic structure of most of the materials. Let us remember that the Hamiltonian of a system consisting of \( N \) number of electrons and \( M \) number of ions interacting through the Coulomb forces can be defined in the following form:

\[
\hat{H} = -\sum_{i=1}^{M} \frac{\hbar^2}{2M_i} \nabla_i^2 - \sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 \nabla_i^2 + \frac{e^2}{2} \sum_{i=1}^{M} \sum_{j=1}^{M} \frac{Z_i Z_j}{R_i - R_j} + \frac{e^2}{2} \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{1}{r_i - r_j} - e^2 \sum_{i=1}^{M} \sum_{j=i}^{N} \frac{Z_i}{R_i - r_i} \]  

(2.7)

where \( R_1, \ldots, R_M = \hat{R} \) represents the nuclear coordinates, \( M_1, \ldots, M_M \) are the masses and \( Z_1, \ldots, Z_M \) are the atomic masses of the nuclear, and \( r_1, \ldots, r_N = \hat{r} \) is the coordinates and \( m \) is the mass of the electrons, respectively. The Hamiltonian consists of five components each of which either describes the electrons, nuclei, the electron-electron, nuclei-nuclei, and electron-nuclei interactions. In a more compact way, the Hamiltonian can be written in the following form:

\[
\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{nn}(\hat{R}) + \hat{V}_{ee}(\hat{r}) + \hat{V}_{ne}(\hat{r}, \hat{R}) \]  

(2.8)

where \( \hat{T}_n \) and \( \hat{T}_e \) are the kinetic energy operators of the nuclei and electrons, \( \hat{V}_{mn}(\hat{R}) \) operator describes the repulsion of nuclei, \( \hat{V}_{ee}(\hat{r}) \) is the electron-electron interaction, and \( \hat{V}_{ne}(\hat{r}, \hat{R}) \) is the electrostatic interaction between the nuclei and the electrons. In principle, all the properties of such a system consisting of \( N \) electrons and
ions can be derived from the many-body Schrödinger equation. The non-relativistic and time-independent version of the Schrödinger equation is expressed as:

\[ \hat{H} \Psi(R, r) = E \Psi(R, r) \]  

(2.9)

where \( \hat{H} \) is the many-body Hamiltonian operator. The solution of this equation provides the eigenenergies \( E \) and the many-body wave-functions \( \Psi(R, r) \). Practically, solving this many-body problem in a full QM framework is rarely possible [69]. The difficulty in solving the equation 2.9 arises from the fact that the motion of electrons and ions are coupled; hence the Schrödinger equation can not be decoupled into set of independent equations. Therefore, in the case of a coupled system of \( N \) electrons and \( M \) nuclei, one has to consider in total \( 3N + 3M \) coupled degrees of freedom. The first proposed simplification is to separate the motion of electrons from that of the nuclei. Thus, it reduces the number of degrees of freedom that has to be taken into account. The idea of separating the electron motion from that of the nuclei is based on the large difference between their masses (\( M_i \gg m \)) – the electrons move much faster than the nuclei, thus the nuclei can be treated as static in the time scale of the electronic motion. In this approach the electron motion can be separated from that of the nuclei that allow the nuclei kinetic energy to be set to zero. The repulsion between the nuclei is treated as constant. This approach is known as the Born-Oppenheimer (BO) or adiabatic approximation [70]. It corresponds to the case when the ions move on the potential
energy surface of the electrons in the ground state. Decoupling of the degrees of freedom thus leads to the many-body wave function that can be expressed as:

$$\Psi(\vec{R}, \vec{r}) = \Theta(\vec{R}) \Phi(\vec{r}, \vec{R})$$  \hspace{1cm} (2.10)$$

where \(\Phi(\vec{r}, \vec{R})\) is the electronic wave function, while \(\Theta(\vec{R})\) is the nuclear wave function.

The nuclear wave function is more localized than the electronic wave function \((\nabla \Theta \gg \nabla \Phi)\). Then, one can express the decoupled Schrödinger equation for the electrons within the BO approximation in the following form:

$$\hat{H}_e \Phi_m(\vec{r}, \vec{R}) = (\hat{T}_e + \hat{V}_{ee}(\vec{r}) + \hat{V}_{ne}(\vec{r}, \vec{R})) \Phi_m(\vec{r}, \vec{R}) = \epsilon_m(\vec{R}) \Phi_m(\vec{r}, \vec{R})$$  \hspace{1cm} (2.11)$$

where \(\hat{H}_e\) is the electronic Hamiltonian given by:

$$\hat{H}_e = -\sum_{i=1}^{N} \frac{\hbar^2}{2m} \nabla_i^2 + \frac{e^2}{2} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \frac{1}{|\vec{r}_i - \vec{r}_j|} - e^2 \sum_{i=1}^{M} \sum_{i=1}^{N} \frac{Z_i}{|\vec{R}_i - \vec{r}_i|}$$  \hspace{1cm} (2.12)$$

where \(\Phi_m(\vec{r}, \vec{R})\) is the mth-state electronic wave-function, and \(\epsilon_m(\vec{R})\) is the electronic eigenvalue, which depends on the nuclear positions \(\vec{R}\). The nuclear coordinates are treated as external parameters, not dynamical variables. The adiabatic approximation uses the fact that the nuclei move on the potential energy surface of the electrons in the ground state \((m=0)\).

Although the number of degrees of freedom has been reduced to \(3N\) with the BO approximation, the solution of the electronic Schrödinger equation is still complicated. Solving the problem of a system of \(N\) interacting electrons in an external field created by
a collection of the atomic nuclei is a very difficult problem of many-body theory. The exact solution for such a problem exists only for the uniform electron gas, atoms with small number of electrons and small molecules.

### 2.2.1 Hartree Approximation

The Hartree method belongs to the class of the wave-function methods. In this method, it is assumed that the many-body electronic wavefunction \( \Phi \) can be approximated by the product of one-electron wave functions \( \phi \) as:

\[
\Phi(r_1, r_2, r_3, ..., r_N) = \prod_{i=1}^{N} \phi_i(r_i) = \phi_1(r_1) \phi_2(r_2) \phi_3(r_3) ... \phi_N(r_N)
\]

(2.13)

where \( r_i \) are the coordinates (position and spin) of the i-th electron. These one-electron wave-functions are called orbitals. Regardless of being Fermions, the electrons are treated as independent -- their motion does not depend on each other. This then allows the many-electron wave-function to be written as the product of one-electron wave-functions, which results in a wrong symmetry of the many-electron wave function. In fact, the many-electron wave-function has to be antisymmetric under interchange of the indices of two particles due to the Pauli Exclusion Principle. Using the BO approximation, the electronic Hamiltonian operator can be expressed by separating the electron and nuclei degrees of freedom, and by taking into account the interactions with the other electrons through an effective potential, which results in:

\[
\hat{H}_{el} = \hat{T}_e + \hat{V}_{ion}(r) + \hat{V}_H(r)
\]

(2.14)
where \( V_{\text{ion}}(\mathbf{r}) = \sum_{i=1}^{M} \frac{-Z_i}{|\mathbf{r} - \mathbf{R}_i|} = V(\mathbf{R}, \mathbf{r}) \) represents the contributions from the ions, while \( V_H(\mathbf{r}) \) potential describes the electrostatic interaction with all other electrons. It was proposed that the electrons do not interact with each other, but the interaction is through the total density of the electrons. Defining the density corresponding to each electron as:

\[
\rho_i(\mathbf{r}) = \left| \phi_i(\mathbf{r}) \right|^2
\]

one can see that this definition includes the self-interactions, which has to be subtracted. For the \( j \)-th electron, the density \( \rho_j(\mathbf{r}) \) with which it interacts is determined by subtracting its own density from the total density. Using this density, the electrostatic potential generated by the interaction of the electron with the other electrons is expressed as:

\[
V_H(\mathbf{r}) = e^2 \sum_{j \neq i} \rho_j(\mathbf{r'}) \frac{\mathbf{r} - \mathbf{r'}}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'}.
\]

By using this equation for the electrostatic contribution, and adding it to the ionic potential, one finds the one-electron energy:

\[
V_{\text{eff}}(\mathbf{R}, \mathbf{r}) = V(\mathbf{R}, \mathbf{r}) + e^2 \sum_{j \neq i} \rho_j(\mathbf{r'}) \frac{\mathbf{r} - \mathbf{r'}}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'}.
\]

Now, the electronic Hamiltonian can be expressed in the following form:
\[
\hat{H}_{el} = \sum_{i=1}^{N} \left( -\frac{1}{2} \nabla_{r_i}^2 + V_{eff}^{(i)}(\vec{R}, \vec{r}) \right). 
\]  

(2.18)

At this point, the variational principle can be used to obtain the ground state energy of the electronic Hamiltonian using the many-body wave function defined in equation 2.13. This wave function can be used to determine the expectation value of the Hamiltonian,

\[
< \hat{H}_{el} > = \langle \Phi | \hat{H}_{el} | \Phi \rangle. 
\]

The variational principle requires the Hamiltonian to be stationary under the variations of the orbitals. The constraint for the normalization is given as \( \int d\vec{r} |\phi_i|^2 = 1 \), and defining the Lagrange multiplier for each orbital as \( \varepsilon_i \), this stationary condition takes the following form:

\[
\frac{\delta}{\delta \Phi} \left[ \langle \hat{H}_{el} \rangle - \varepsilon_i \int d\vec{r} \phi_i^* \phi_i \right] = 0. 
\]  

(2.19)

This then leads to the one-electron equations known as the Hartree equations given by:

\[
\left( -\frac{\hbar^2}{2m} \nabla^2 + V_{eff}^{(i)}(\vec{R}, \vec{r}) \right) \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r}) 
\]  

(2.20)

where \( \varepsilon_i \) is the eigenenergy of the \( i \)-th electron. This approach reduces the many-body problem to the problem of one-particle equation in an effective field. In order to solve this problem, one starts with some arbitrary orbitals (e.g. atomic orbitals), then calculates the effective potential using these orbitals, and solves \( N \) equations to obtain new orbitals. The process is repeated until there is no difference between the new orbitals obtained for two consecutive iterations (the self-consistent field orbitals). These orbitals are then used...
to construct the many-electron wave function (equation 2.13). The energy of the many-body system can be obtained as:

$$E_{H} = \sum_{i=1}^{N} \epsilon_i - \frac{e^2}{2} \sum_{i \neq j}^{N} \int \rho_{i}(\mathbf{r})\rho_{j}(\mathbf{r}') \left| \mathbf{r} - \mathbf{r}' \right| dr \, dr'. \quad (2.21)$$

The term that is subtracted on the right hand side of the equation is due to the fact that the electron-electron interaction is counted twice in the effective potential; hence it is corrected by the subtraction. One electron wave functions allow one to construct an approximate wave function for the whole atom. However, the fact that the wavefunctions do not change the sign when interchanging their labels is the drawback of the method, which ignores the fact that for the system consists of Fermions (electrons), two particles can not be described by the same one-particle wave function.

### 2.2.2 Hartree-Fock (HF) Approximation

Corrections to the Hartree method are introduced by employing the true symmetry constraints on the eigenfunction. In other words, the method treats the electrons as Fermions, as they should be, and ensures that the total wave function is antisymmetric with respect to the interchange of any of two electrons. It includes the correlation of electrons, which in Hartree approximation were treated as indistinguishable. Thus, in the HF method the electrons satisfy the Pauli Exclusion Principle. The total wave function is constructed by using the one-electron wave functions as an antisymmetrized sum of all their products. An antisymmetric wave function can be represented as a determinant by:
which is the Slater determinant representation of the total wave function. One can reveal that the exclusion principle is satisfied in this case -- if any of two orbitals are equal ($i = j$), the determinant is equal to zero. Describing the wave function as an antisymmetric one, the method takes into account basic Fermionic characteristics that were missing in the Hartree approximation.

The assumption in the HF method is that every electron moves in the potential created by the nuclei, and the average potential of all other electrons. This is known as independent-particle method. The method reduces the complex many-electron problem to the problem of coupled one-electron ones. However, the computational cost of this method is very high.

Once again, applying the variational principle with the constraint of normalization for each orbital as is done above in the Hartree approximation, one can construct the one-electron ground-state HF equation given by:
\[-\frac{\hbar^2}{2m} \nabla_r^2 + \hat{V}(\vec{R}, \vec{r}) + \sum_{\sigma', j=1}^N e^2 \int \frac{\phi_j^*(\vec{r}', \sigma') \phi_j(\vec{r}', \sigma')}{|\vec{r} - \vec{r}'|} d\vec{r}' \phi_j(\vec{r}, \sigma) \\tag{2.23}\]

\[-\sum_{j=1}^N \left( \sum_{\sigma'} e^2 \int \frac{\phi_j^*(\vec{r}', \sigma') \phi_j(\vec{r}', \sigma')}{|\vec{r} - \vec{r}'|} d\vec{r}' \right) \phi_j(\vec{r}, \sigma) = \varepsilon_j \phi_j(\vec{r}, \sigma) \\tag{2.24}\]

where the sum over \( j \) runs over all occupied states. The eigenvalue equation in a more compact way can be written as:

\[ h_i(\vec{r}) \phi_i(\vec{r}, \sigma) + (V_{ee}(\vec{r}) - V_x(\vec{r})) \phi_i(\vec{r}, \sigma) = \varepsilon_i \phi_i(\vec{r}, \sigma) \]  

where \( h_i \) is the Hamiltonian (Hartree) for the non-interacting electrons. It represents the kinetic energy contribution and the electron-ion potential. The second terms in the parenthesis -- Hartree-Fock potential -- arise from the inclusion of the electron-electron interactions. The \( V_{ee}(\vec{r}) \) represents the electrostatic repulsion between the electrons, while \( V_x(\vec{r}) \) is the exchange term, which leads to a non-local potential. This term comes from the Pauli Exclusion Principle ensuring that the electrons with like-spin avoid each other. This is achieved by surrounding each electron with an exchange hole (a small volume).

### 2.2.3 Hohenberg-Kohn (HK) Theorem

The basics of the modern density functional theory were formulated by Hohenberg and Kohn (HK) in 1964 [48]. Two remarkable theorems were proved to show that the electron density is the useful quantity to describe the electronic interactions. The
HK theorems correspond to system that consists of electrons moving in an external potential $V_{\text{ext}}(r)$. The first HK theorem states that, every observable in a stationary QM system can be obtained from the ground-state density of the system of interacting electrons. In other words, the ground-state density uniquely determines the external potential. The ground state energy of many-electron system is unique functional of the density and is given by:

$$E_0 = E[(\rho(r))]$$  \hspace{1cm} (2.25)

where $E_0$ is the ground state energy, while $\rho(r)$ is the particle density. The energy functional has an extremum with respect to the variations of the particle density ($\delta \rho(r)$) at the equilibrium density $\rho_0(r)$ and is given by the condition:

$$E = E[(\rho_0(r))] = \min \{E[(\rho(r))]\}$$  \hspace{1cm} (2.26)

$$\frac{\delta E[(\rho(r))]}{\delta \rho(r)}_{\rho(r) = \rho_0(r)} = 0$$  \hspace{1cm} (2.27)

The second theorem states that the ground-state density can be calculated, in principle by using the variational method. These theorems are based on the fact that within the BO approximation, the kinetic energy of the electrons ($E_{\text{el}}$) and the interaction between the electrons ($V_{\text{ee}}$) adjust themselves to the external potential. If $V_{\text{ext}}$ is known then the electron density can be evaluated. The HK approach is based on the opposite -- the density in ground-state may be used to obtain $V_{\text{ext}}$. If this is correct, then one can find
all the information regarding the system using this density. Let us start with an electronic Hamiltonian that describes a many-electron system in an external potential \( (V_{\text{ext}}) \) and with an electron-electron interaction \( (V_{\text{ee}}) \). Such an electronic Hamiltonian can be written as:

\[
H_{\text{el}} = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}
\]

Let us define the ground state energy of such a system as \( E_0 \), which comes from the expectation value of the Hamiltonian \( (E_0 = \langle \psi_0 | H_{\text{el}} | \psi_0 \rangle) \). The ground state density \( (\rho_0(r)) \) of such a system is \( \rho_0(r) = |\psi_0(r)|^2 \). It is assumed that the ground-state is non-degenerate -- only one wave-function corresponds to the ground-state. The assumption that a different external potential \( (V'_{\text{ext}}) \) leads to a different ground-state wave function \( (\psi'_0) \) satisfying \( E'_0 = \langle \psi'_0 | H'_{\text{el}} | \psi'_0 \rangle \), however results in the same ground-state density, \( \rho'_0(r) = |\psi'_0(r)|^2 = \rho_0(r) \).

The variational principle for the expectation value gives the following:

\[
E'_0 < \langle \psi_0 | H'_{\text{el}} | \psi_0 \rangle = \langle \psi_0 | (\hat{T} + \hat{V}_{\text{ee}} - \hat{V}_{\text{ext}}) | \psi_0 \rangle = E_0 + \langle \psi_0 | (\hat{V}_{\text{ext}} - \hat{V}_{\text{ext}}) | \psi_0 \rangle = E_0 + \int \rho_0(r) (V_{\text{ext}} - V_{\text{ext}}) dr.
\]
The same procedure is repeated for the variational principle of the Hamiltonian $\hat{H}_{el}$, and remembering that $\rho'_0(r) = \rho_0(r)$, the procedure then results in the following:

$$E_0 < \langle \psi'_0 | \hat{H}_{el} | \psi'_0 \rangle = \langle \psi'_0 | (\hat{H}_{el}^t + V_{ext}^t - V_{ext}^t) | \psi'_0 \rangle = E'_0 + \langle \psi'_0 | (\hat{V}_{ext}^t - V_{ext}^t) | \psi'_0 \rangle$$ \hspace{1cm} (2.31)

$$E_0 < E'_0 + \int \rho'_0(r)(\hat{V}_{ext}^t - V_{ext}^t) dr$$ \hspace{1cm} (2.32)

$$E_0 < E'_0 + \int \rho_0(r)(\hat{V}_{ext}^t - V_{ext}^t) dr$$ \hspace{1cm} (2.33)

The result contradicts the conclusion obtained in the equation 2.30, and leads to an inconsistency; $E_0 + E'_0 < E'_0 + E_0$ indicating that the densities should be different ($\rho'_0(r) \neq \rho_0(r)$), and the external potential is a unique functional of the density. Therefore, from this result, one concludes that there are no two external potential ($V_{ext}^t \neq V_{ext}^t$) that correspond to the same electronic density for the ground-state. This proof adjusts that the density determines the external potential, and the number of electrons can be obtained as $N = \int \rho(r) dr$. From the external potential, one can obtain the Hamiltonian $\hat{H}_{el}$, which can be used to determine the wave functions. All the ground-state properties are then determined from these functions. The ground-state energy can be expressed as a functional of the density and is given by:

$$E[\rho] = V_{ext}[\rho] + F_{HK}[\rho] = \int \rho(r)V_{ext}(r) dr + F_{HK}[\rho]$$ \hspace{1cm} (2.34)
where \( F_{\text{HK}}[\rho] \) is a universal functional -- the HK functional -- which does not depend explicitly on \( V_{\text{ext}} \), and depends only on the electron density. If this functional was known, such ground state properties as the density and the total energy could be determined easily via minimization of the functional of the three-dimensional density. For any given external potential, the system ground-state energy is defined as the global minimum of the energy functional, and the density minimizing that functional is the exact ground-state density \((\rho_0(r))\). Let the trial density \( \tilde{\rho}(r) \) such that \( \tilde{\rho}(r) \geq 0 \) and satisfies the relation \( \int \tilde{\rho}(r) dr = N \). Then if this trial density corresponds to the exact number of electrons, the calculated total energy can not be lower than the ground-state energy.

\[
E_0 \leq E[\tilde{\rho}] \tag{2.35}
\]

The total energy minimization is obtained under the N-representability constraint -- the conservation of number of electron -- which is given by the following condition (by using the Lagrange’s method of undetermined multipliers):

\[
\int \rho(r) dr - N = 0 . \tag{2.36}
\]

Multiplying it by the Lagrange multiplier \((\mu)\) and by adding it to the minimized energy functional \( E[\rho] \), the following functional is obtained:

\[
E[\rho] - \mu \left[ \int \rho(r) dr - N \right] . \tag{2.37}
\]

The minimum of this expression corresponds to the case when the differential of the expression is zero. This condition is expressed as the following:
\[ \delta \left\{ E[\rho] - \mu \left( \int \rho(r) dr - N \right) \right\} = 0 \]
\[ \delta E[\rho] - \mu \delta \left\{ \int \rho(r) dr \right\} = 0 \]

Applying the differential of a functional, the equation 2.38 leads to the following:

\[ \int \left( \frac{\delta E[\rho(r)]}{\delta \rho(r)} - \mu \right) \delta \rho(r) dr = 0 \]

which results in the Lagrange multiplier \( \mu \):

\[ \mu = \frac{\delta E[\rho(r)]}{\delta \rho(r)} = \nabla \cdot \nabla (\text{int}) + \frac{\delta F_{\text{HK}}[\rho(r)]}{\delta \rho(r)} \]

which is the chemical potential of the electrons. The HK functional is then expressed as:

\[ F_{\text{HK}}[\rho] = T_e[n] + V_{ee}[n] \]

It includes the kinetic and potential energies of the interacting system, and is universal -- the same for all electron systems -- and independent of \( V_{\text{ext}}(r) \) owing to the fact that the kinetic and potential energies are functionals of only the density.

Although the HK theorems greatly simplified the many-body problem by proposing the density to be the basic quantity describing the electronic structure, however, they only prove the existence of a universal density functional, but do not show how to construct it.
2.2.4 Kohn-Sham (KS) Approach

The method proposed by Kohn and Sham [48] forms the basis of DFT, which became a practical tool for calculating the electronic structure. The Kohn-Sham (KS) approach has replaced the problem of interacting many-body system with the problem of non-interacting particles. They introduced the KS equations that are one-particle equations similar to the time-independent Schrödinger equation, with a difference that the potential experienced by electrons is a functional of density. Earlier methods proposed to minimize the total energy with respect to density; however, the relation between the kinetic energy and density was not transparent. Kohn and Sham has introduced orbitals in such a way that the kinetic energy functional $T_{\text{e}}[n]$ can be computed within a good accuracy.

Note that choice of a system of non-interacting particles is not unique. Hence further ansatz proposed in the KS approach is that the ground-state density of the interacting system is the same as that of the non-interacting (reference) system. In the resulting independent-particle equations, the many-body terms are incorporated into the term known as the exchange-correlation potential. The solution of these equations provides the ground-state density and the energy of the interacting system. Obviously, the accuracy of the solution depends on the choice of the exchange-correlation potential. Two assumptions summarize the KS method; i) the ground-state density can be described by the ground-state density of the system of non-interacting particles; ii) the Hamiltonian
describing the system consists of a kinetic energy operator and an effective local potential $V_{\text{eff}}^\sigma(\vec{r})$ that acts on an electron with spin $\sigma$ at position $\vec{r}$.

Let us define a Hamiltonian describing an independent-particle system (non-interacting reference system) as the following:

$$\hat{H}_{\text{REF}} = \sum_{i=1}^{N} \left( -\frac{\nabla_i^2}{2m} + V_{R}(\vec{r}) \right)$$

(2.42)

where the first term is the kinetic energy operator, while the second term $V_{R}(\vec{r})$ ensures that the ground-state density of this reference system is equal to $\rho(\vec{r})$ -- the ground state density of the interacting system -- and the ground state total energy of the reference system is the same as that of the interacting system. Such a density of the reference system is the sum of the squares of the lowest ($N_e$) single-particle orbital amplitudes, and is given by:

$$\rho(\vec{r}) = \sum_{i=1}^{N} | \phi_i(\vec{r}) |^2 .$$

(2.43)

and the kinetic energy of this independent-particle system ($T_R$) is expressed as:

$$T_R[\rho] = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \left\langle \phi_i(\vec{r}) \left| \nabla_i^2 \phi_i(\vec{r}) \right\rangle .$$

(2.44)

Independent-particle orbitals $\phi_i(\vec{r})$ are the $N_e$ lowest eigenfunctions of the given Hamiltonian in equation 2.42, and a one-particle equation can be written as:

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V_R(\vec{r}) \right) \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

(2.45)
The density functional can be expressed by using the kinetic energy as:

\[
F[\rho] = T_k[\rho] + \frac{e^2}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} drdr' + E_{xc}[\rho] \tag{2.46}
\]

where \(T_k[\rho]\) is the kinetic energy of the non-interacting electron gas with the density \(\rho(r)\) that is equal to that of an interacting system. The kinetic energy term lacks the correlation owing to the fact that for independent-particle system, there is no explicit electron-electron interaction. The second term in the equation is the Hartree energy, which is the largest part of the interaction energy. The third term is the exchange-correlation (\(xc\)) energy that contains all the interactions beyond the Hartree one. It includes the energy contributions of the electron exchange, the correlation, a correction to the kinetic energy of non-interacting electrons, and the correction for self-interaction introduced via the Coulomb potential. The exchange-correlation energy is the most complicated part of energy for which the exact form is not known explicitly.

Using the density functional, the KS energy functional is obtained as the following:

\[
E_{KS}[\rho] = T_k[\rho] + \int \rho(r) v(r) dr + \frac{e^2}{2} \iint \frac{\rho(r) \rho(r')}{|r - r'|} drdr' + E_{xc}[\rho] \tag{2.47}
\]

or

\[
E_{KS}[\rho] = T_k[\rho] + \int (V_{ext}(r) + \frac{1}{2} V_{ht}(r)) \rho(r) dr + E_{xc}[\rho]. \tag{2.48}
\]
Let us assume that the form of the exchange-correlation functional is known, then using the variational principle leads to the following equation:

\[
\mu = \frac{\delta E_{\text{KS}}[\rho]}{\delta \rho(r)} = \frac{\delta T_{\text{K}}[\rho]}{\delta \rho(r)} + V_{\text{ext}}(r) + V_{\text{H}}([\rho(r)]) + \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)} \quad (2.49)
\]

where \( V_{\text{xc}}[\rho] = \frac{\delta E_{\text{xc}}[\rho]}{\delta \rho(r)} \) is the exchange-correlation potential (the functional derivative of the exchange-correlation energy). Combining the last three term of the equation 2.49, one can find:

\[
V_{\text{eff}}([\rho(r)]) = V_{\text{ext}}(r) + V_{\text{H}}([\rho(r)]) + V_{\text{xc}}([\rho(r)]) \quad (2.50)
\]

where \( V_{\text{eff}}([\rho(r)]) \) is the effective external potential. The Euler-Lagrange equation with the constraint \( \delta \left\{ E[\rho] - \mu \int \rho(r) dr - N \right\} = 0 \) has the same solution as a system of equations of non-interacting particles in an external potential \( V_{\text{K}} = V_{\text{eff}} \). Considering non-interacting electrons in an external potential equal to \( V_{\text{eff}}([\rho(r)]) \), and rewriting the equation 2.49 in terms of the kinetic energy term for the non-interacting electrons and the effective potential, the chemical potential can be written as:

\[
\mu = \frac{\delta T_{\text{K}}[\rho]}{\delta \rho(r)} + V_{\text{eff}}([\rho(r)]). \quad (2.51)
\]

In case of such a system of non-interacting electrons in an effective potential, in order to find the ground-state density and the energy, one has to solve the one-electron equations given by:
$(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}([\rho(r)]) \phi_i(r) = \varepsilon_i \phi_i(r)$ \hspace{1cm} (2.52)

where the density $\rho(r) = \sum_{i,\text{occ}} \phi_i^* \phi_i$ is the summation over all the occupied KS states -- states that correspond to $N_e$ lowest eigenvalues. The equation 2.52 known as the KS equation that is similar to the one-particle equation of the HK method. The total energy is written in terms of the sum of the orbital energies by subtracting the double counted terms and is expressed as:

$$E[\rho] = \sum_{i=1}^{N} \varepsilon_i - \frac{e^2}{2} \iint \frac{\rho(r)^* \rho(r')}{|r-r'|} drdr' + E_{xc}[\rho] - \int V_{xc}(\rho(r)) \rho(r) dr. \hspace{1cm} (2.53)$$

The solution to the KS equations can be obtained by using an iterative procedure since the effective potential depends on the density through the exchange-correlation potential. The procedure starts with an initial guess for the KS orbitals that are used to generate the density, and then this density can be used to construct the effective potential and the total energy. With this information, the equations are solved to generate the new set of the KS orbitals, and they are used to obtain new density, the effective potential and the total energy. This cycle is repeated until the convergence is reached. The main issue in this approach is the need of the explicit form of exchange-correlation functional, which is usually approximated by different expressions.

In summary, the KS equations can be used to calculate the density by solving a non-interacting Hartree-type problem with the same ground-state density as the interacting system. The density and the kinetic energy are obtained from the single-
particle Hartree-type equations named as the Kohn-Sham equations. A typical Kohn-Sham self-consistent scheme is defined in Figure 2.1.

![Figure 2.1 Self-consistent Kohn-Sham (KS) scheme](image-url)
2.2.5 Exchange-Correlation Functional(s)

The success of the KS approach emerges from the idea of separating out the kinetic energy of independent-particle and the long-range Hartree terms. The remaining component, the exchange-correlation functional, can be approximated by a functional of local density. Several approximations are available for the exchange-correlation functional, and can be classified as empirical and non-empirical functionals. In derivation of the class of empirical functionals, one uses experimental results for particular materials. The non-empirical functionals are defined from the results of first-principles calculations. We will here discuss the non-empirical exchange-correlation functionals.

The total exchange-correlation energy can be expressed as:

\[ E_{exc}[\rho] = \int dr \rho(r) \varepsilon_{xc}([\rho(r)]) \]  \hspace{1cm} (2.54)

where \( \varepsilon_{xc}([\rho(r)]) \) is the exchange-correlation energy per electron of a homogenous electron gas with density \( \rho(r) \). It is a functional of the density at every point in space. Every electron is surrounded by an exchange-correlation hole that leads to the reduction of its potential energy. The relation of \( \varepsilon_{xc}([\rho(r)]) \) to the exchange-correlation hole -- the change in electron density induced by the existence of an electron at a position \( r \) -- is obtained through the coupling constant integration formula, in which by varying the charge from 0 to 1, while keeping the density constant, the exchange-correlation energy can be rewritten as the following:
\[
E_{xc}[\rho] = \frac{1}{2} \int dr \rho(r) \int dr' \frac{\tilde{h}_{xc}(r, r')}{|r - r'|}
\]  
(2.55)

where \( \tilde{h}_{xc}(r, r') \) is the coupling constant averaged exchange-correlation hole. Comparing the equations 2.54 and 2.55, the exchange-correlation potential per electron can be written as:

\[
\varepsilon_{xc}(\rho[r]) = \frac{1}{2} \int dr' \frac{\tilde{h}_{xc}(r, r')}{|r - r'|}
\]  
(2.56)

which can be viewed as the potential generated by the interaction between an electron and its exchange-correlation hole. The exchange-correlation potential \( V_{xc}(r) \) can be obtained from the functional derivative of the exchange-correlation energy and expressed as:

\[
V_{xc}(r) = \varepsilon_{xc}(\rho(r)) + \rho(r) \frac{\delta \varepsilon_{xc}(\rho(r))}{\delta \rho(r)}
\]  
(2.57)

The term in the right of the equation 2.57 represents the change in exchange-correlation hole with density.

Exchange arises from the Pauli principle, which states that no two electrons with parallel spins can occupy the same region in space. The correlations take place due to the motion of electrons, which is not independent. The exchange energy term is exactly known from the HF theory [68], while the correlation term is known only in parameterized forms, and can be obtained for some limiting cases from the quantum Monte Carlo (QMC) methods [71]. Below, a summary of the exchange and correlation
schemes are presented. The attention will be given mostly to the generalized gradient approximation (GGA) [72] since it is frequently used in the present calculations. The local density approximation (LDA) [73] will also be discussed.

2.2.5.1 Local Density Approximation (LDA)

The simplest and the most commonly used exchange-correlation functional were proposed by using the local approximations. There are two methods known as Local Density Approximation (LDA) [73] and spin-polarized Local Density Approximation (LSDA). Let us first define the LDA exchange-correlation energy as:

\[
E_{xc}^{LDA} = \int \rho \rightarrow \rho \epsilon_{xc}^{LDA}[\rho] dr
\]

(2.58)

where \( \epsilon_{xc}^{LDA}[\rho] \) is the exchange-correlation energy per electron. In this method it is assumed that \( \epsilon_{xc}^{LDA}[\rho] \) is a functional of the local density, and is expressed as:

\[
\epsilon_{xc}^{LDA}[\rho] = \epsilon_{xc}^{hom}[\rho]
\]

(2.59)

where \( \epsilon_{xc}^{hom}[\rho] \) is the energy density of a homogenous electron gas per particle of the density \( \rho \). Thus in this approximation, the exchange-correlation energy and the exchange-correlation potential are replaced by the corresponding expressions for the homogenous electron gas. The homogenous electron gas is a system with a uniform density in its ground state; hence it is defined by this density. Notice that the accuracy of the LDA is good for the systems in which the density varies slowly.

Within this approximation, the exchange-correlation energy per particle is defined as the following:
\[ e_{xc}^{LDA}[\rho] = \frac{1}{2} \int \frac{h_{xc}^{LDA}(r, r')}{|r - r'|} dr'. \tag{2.60} \]

Since the exchange-correlation energy for an electron depends on the other particles around through the exchange-correlation hole, it is non-local. The exchange-correlation potential within this approach is expressed as:

\[ V_{xc}^{LDA}(r) = e_{xc}^{LDA}(\rho(r)) + \rho(r) \frac{\delta e_{xc}^{LDA}([\rho(r)])}{\delta \rho(r)} \tag{2.61} \]

The exchange energy of the homogenous electron gas can be found analytically, while the correlation energy is obtained by means of QMC calculations [71]. The form of the exchange energy density is adopted from the Dirac [74] and is given by:

\[ e_x[\rho] = -\frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3} \rho^{4/3} \tag{2.62} \]

where \( 1/\rho = 4\pi r_s^3 \) and \( r_s \) is the radius of the sphere containing one electron. The most widely used approximation for the correlation is the parameterization by Perdew and Zunger’s [75] of the QMC results of Ceperley and Alder [76], and is given by:

\[ e_c[\rho] = \begin{cases} 
A \ln r_s + B + Cr_s \ln r_s + Dr_s, & r_s \leq 1 \\
\gamma / (1 + \beta_1 \sqrt{r_s} + \beta_2 r_s), & r_s \geq 1
\end{cases} \tag{2.63} \]

LDA was successfully applied for many systems like the bulk metals for which the density is quite smooth. Although there are cases for which LDA works well, there are inherent problems with the approximation. These can be summarized as the following:

i) binding energies for solids are often over-estimated (about 30%)
ii) dielectric constants are over-estimated for system with covalent, ionic and metallic bond nature

iii) for weakly bound small systems (i.e. hydrogen atom), the binding is too strong

iv) lattice constant for solids are often reported to be smaller than that from the experiments, as a result bulk compressibility or bulk modulus are found too large

v) LDA fails for atomic systems where the density largely varies

vi) magnetic properties are often not satisfactory

2.2.5.2 Generalized Gradient Approximation (GGA)

LDA failure in describing accurately the cases in which the density varies sharply led to a need to find more accurate exchange-correlation functionals. The first approach proposed, which can be seen as an extension to the LDA, was the generalized expansion approximation (GEA) [77]. The idea behind this method is based on the fact that the correction to the density should be such that any inhomogeneity in density should be correctly captured. Thus, the GEA approximation concentrated on including not only the density but also the gradient of the density. The first approach is to start with some sort of expansion such as a first order Taylor expansion around a constant density. Low-order Taylor expansion could be suitable if the inhomogenities are small or slowly varying. The condition for such an expansion to be successful is given by:
where the term $\frac{\nabla \rho(r)}{2 \rho(r)}$ is the dimensionless gradient density, and $k_f(r) = (3\pi^2 \rho(r))^{1/3}$ is the Fermi-wave vector. Testing of the GEA showed that many properties are less accurately described by this method even for molecules and atoms. The failure of the method was attributed to the facts that it violates the sum rule condition on the correlation hole ($\int \rho_c(r,r')dr' = 0$), and also the negativity constraint on the exchange hole (for $r = r'$, $\rho_x(r,r) = -\rho(r)$). These are important conditions for well defining a spatial range for the exchange hole.

An alternative approximation proposed to include the gradient of the density that is known as the Generalized Gradient Approximation. A functional proposed is not based on an exact gradient expansion. Perdew and co-workers proposed that in order to ensure the sum rule and the negativity constraint conditions to hold, the GEA exchange-correlation hole is to be terminated by a cutoff procedure. Thus, the functional ($F_{xc}$) named as enhancement factor is introduced and the resulting exchange-correlation energy is expressed as the following:

$$E_{xc}^{GGA}[\rho] = \int \rho(r) e_{xc}^{GGA}[\rho(r)] dr = \int \rho(r) e_{xc}^{hom}[\rho(r)] F_{xc}[\rho(r), \nabla \rho(r)] dr \quad (2.65)$$

where the enhancement factor satisfies the conditions such as sum rules and long range decay. The form of this functional is not unique, and until today several functional forms
have been proposed and applied. It is usually defined in terms of the Seitz radius ($r_s$) and the dimensionless density gradient $s(r) = \left| \nabla \rho(r) \right| / 2k_f(r)\rho(r)$. Since there is no exact form of the $\epsilon_{xc}^{GGA}[\rho(r)]$, it is chosen according to the nature of system under study. The most widely used GGA functionals are the ones proposed by Perdew and Wang, known as PW91 [78], and the modified version by Perdew-Burke-Ernzerhof (PBE) [79]. In the present study, we have employed mostly PW91 functional and for comparisons PBE functional.

In the PW91, the exchange enhancement factor is expressed as the following:

$$F_x^{PW91}(s) = \frac{1 + a_1 s \sinh^{-1}(a_2 s) + (a_3 + a_4 e^{-100s^2})s^2}{1 + a_1 s \sinh^{-1}(a_2 s) + a_5 s^4}$$  \hspace{1cm} (2.66)

where $a_1 = 0.19645$, $a_2 = 7.7956$, $a_3 = 0.2743$, $a_4 = -0.1508$, and $a_5 = 0.004$.

Notice that there is no $r_s$ dependence. The correlation functional is expressed as:

$$E_C^{PW91} = E_C + \rho H[\rho, s, t]$$ \hspace{1cm} (2.67)

where

$$H[\rho, s, t] = \frac{\beta}{2\alpha} \ln(1 + 2\frac{\alpha}{\beta} \frac{t^2 + At^4}{1 + At^2 + A^2t^4} + C_c [C_c(\rho) - C_{cl}] t^2 e^{-100r^2})$$ \hspace{1cm} (2.68)

with $A = \frac{2\alpha}{\beta} [e^{-2\alpha C_c(\rho)} \beta^2 - 1]^{-1}$. The parameters are defined as follows:
\[ \alpha = 0.09, \beta = 0.0667263212, C_{c0} = 15.7559, C_{s} = 0.003521, t = \frac{\nabla \rho(r)}{2k_r \rho(r)}, \] \hspace{2cm} (2.69)

\[ k_s = (4k_F / \pi)^{1/2}, \text{and } \rho E_C[\rho] = E^{LDA}_C[\rho]. \] \hspace{2cm} (2.70)

Some of the general properties of the solutions obtained by using PW91 and PBE functionals are:

i) Lattice constants are generally overestimated, the LDA results are closer to the experiments

ii) Improvement obtained for the binding energies

iii) Bulk modulus of solids are generally underestimated, probably resulting from an overestimation of the lattice constants

iv) Work functions for the surfaces are usually underestimated

v) Surface energies are often lower than that of the experiments and LDA

vi) Ground state properties of iron is accurately described by GGAs

### 2.2.6 Solving the Kohn-Sham (KS) equations

In the previous sections, we have shown that by separating the degrees of freedom of electrons from that of the nuclei through BO approximation [70]; one can reduce the many-body problem to solve N one-particle KS equations [48], where N is the number of electrons. Still additional methods have to be applied to approach to this computationally costly problem -- the real materials have very large number of electrons. One performs the calculation for a periodic system, and uses some sort of basis set to expand the KS
orbitals, and mimics the electronic wave functions that extend over the entire solid. In the choice of the basis set, one considers efficiency, simplicity, and completeness. The most commonly used basis sets are the plane wave (PW), linear combination of atomic orbitals (LCAO) and atomic sphere methods. Each method has its own advantages, and the choice can be made based also on the nature of the problem. The method used in the present study is based on plane wave representation.

When choosing a basis set, one also needs to take into account both the core states (localized, atomic-like) and the valence states (delocalized, Bloch waves). Most of the physical properties are determined by the outer shell since it contributes most to the chemical bonding and dynamics. In addition, the behavior of the effective potential differs in different regions -- deep potential wells close to the nuclei, and smooth potential between the atoms. In order to treat these issues, the Muffin-Tin and Pseudopotential approximations [80] were proposed. In the latter, the deep wells are replaced by a smooth potential, while keeping the same scattering properties. We will address the pseudopotential approximation in this section below. Now, let us discuss the application of the Bloch’s theorem to the KS orbitals.

2.2.6.1 Bloch’s Theorem

Bloch’s Theorem is based on the translational invariance of the system [81]. In a crystal, nuclei are arranged in a regular periodic array defined by a set of Bravais lattice vectors (\( \mathbf{R}_i \)). Using this feature, one can show that for an infinite system, the external potential and the charge density at each point \( r \) are invariant under translations by these
lattice vectors. Since the crystals are periodic atomic structures, the potential should also be periodic. Let us rewrite the KS equation in the following form:

$$\left(-\frac{\hbar^2}{2m}\nabla^2_j + V_{\text{eff}}(\vec{r})\right)\phi(\vec{r}) = \varepsilon \phi(\vec{r})$$  \hspace{1cm} (2.71)$$

where the effective KS potential \(V_{\text{eff}}\) is a periodic function:

$$V_{\text{eff}}(\vec{r} + \vec{R}_i) = V_{\text{eff}}(\vec{r}) \text{ for } \forall \vec{R}_i.$$  \hspace{1cm} (2.72)$$

Let \(\hat{T}(\vec{R}_i)\) be the translation operator of the vector \(\vec{R}_i\) that acts on a position-dependent \(f(\vec{r})\) function and leads to:

$$\hat{T}(\vec{R}_i) f(\vec{r}) = f(\vec{r} + \vec{R}_i)$$  \hspace{1cm} (2.73)$$

indicating that the function \((f(\vec{r}))\) is periodic. Since the KS Hamiltonian is also periodic, the translation operator and the Hamiltonian commute. Also, the translation operators commute with each other:

$$\hat{T}(\vec{R}_i) \hat{T}(\vec{R}_j) = \hat{T}(\vec{R}_i + \vec{R}_j).$$  \hspace{1cm} (2.74)$$

Therefore, the eigenfunctions of \(\hat{T}(\vec{R}_i)\) operator are also those of the Hamiltonian. Let \(\lambda(\vec{R}_i)\) be the eigenfunction of the translation operator, and then the following relation can be found:

$$\hat{T}(\vec{R}_i) \Phi(\vec{r}) = \Phi(\vec{r} + \vec{R}_i) = \lambda(\vec{R}_i) \Phi(\vec{r}).$$  \hspace{1cm} (2.75)$$

By using equation 2.74, one obtains the following property:
\[ \hat{T}(\vec{R}_i) \hat{T}(\vec{R}_j) \Phi(r) = \hat{T}(\vec{R}_i + \vec{R}_j) \Phi(r) = \lambda(\vec{R}_i) \lambda(\vec{R}_j) \Phi(r) = \lambda(\vec{R}_i + \vec{R}_j) \Phi(r) \] (2.76)

where \( |\lambda(\vec{R}_i)|^2 = 1 \). The equation can be satisfied if:

\[ \hat{T}(\vec{R}_i) \Phi(r) = e^{i \vec{k} \cdot \vec{R}_i} \Phi(r), \] (2.77)

therefore:

\[ \hat{T}(\vec{R}_i) \Phi(r) = \Phi(r + \vec{R}_i) = e^{i \vec{k} \cdot \vec{R}_i} \Phi(r). \] (2.78)

where \( e^{i \vec{k} \cdot \vec{R}_i} \) are the eigenvalues of \( \hat{T}(\vec{R}_i) \). The Bloch’s theorem states that in a periodic potential, the wave function of an electron can be expressed by the product of a wave-like part and a part defining the periodic lattice. Such a function is given by:

\[ \Phi_{n,k}(r) = e^{i \vec{k} \cdot \vec{r}} u_n(\vec{r}) \] (2.79)

where \( n \) indicates the band index, and \( \vec{k} \) is the wave vector. Note that \( u_n(\vec{r}) \) has the periodicity of the lattice, thus satisfies the following condition, \( u_n(\vec{r}) = u_n(\vec{r} + \vec{R}_i) \).

### 2.2.6.2 Kohn-Sham (KS) Orbitals in Plane-wave Description

Let us start with the periodic function \( u_n(\vec{r}) \). Its periodicity (by using the equations 2.77 and 2.79) leads to the following:
\[
\begin{align*}
\Psi_{n,k}(r + R_i) &= e^{-i\mathbf{k} \cdot (r + R_i)} \Phi_{n,k}(r + R_i) = e^{-i\mathbf{k} \cdot r} e^{i\mathbf{k} \cdot R_i} \Phi_{n,k}(r) \\
&= e^{-i\mathbf{k} \cdot r} \Phi_{n,k}(r) = \Psi_{n,k}(r)
\end{align*}
\] (2.80)

Since \( \Psi_{n,k}(r) \) has the periodicity of the lattice, it can be expressed by a discrete plane wave basis set with wave vectors \( \mathbf{G}_j \) of the reciprocal lattice that satisfying the condition 

\( \mathbf{G}_j \cdot R_i = 2\pi m, \) \( m \) is integer. Now, we rewrite \( \Psi_{n,k}(r) \) in terms of these basis set vectors, and obtain the following:

\[
\Psi_{n,k}(r) = \sum_{\mathbf{G}_j} C_{(k,\mathbf{G}_j)} e^{i\mathbf{G}_j \cdot r}.
\] (2.81)

Following equation 2.79, we can expand the electron wave-function \( \Phi_{n,k}(r) \) as a linear combination of the plane-waves:

\[
\Phi_{n,k}(r) = \sum_{\mathbf{G}_j} C_{(k,\mathbf{G}_j)} e^{i(k + \mathbf{G}_j) \cdot r}.
\] (2.82)

Expanding the electron wave-functions in terms of a linear combination of the plane waves has the advantages such as independence of the basis set on type of crystal, and on the nuclear-positions. Thus, the KS orbitals can also be represented by a set of plane waves.

Inserting equation 2.82 into the KS equations --

\( \begin{align*}
\frac{-\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \Phi(r) &= \varepsilon \Phi(r) 
\end{align*} \) --

multiplying it by \( e^{i(k + \mathbf{G}_j) \cdot r} \) from the left and using the plane wave orthogonality condition
\[
\left( \int e^{-i \mathbf{G}_i \cdot \mathbf{r}} e^{i \mathbf{G}_j \cdot \mathbf{r}} d\mathbf{r} = \delta_{ij} \right), \text{ we find the following relation for the coefficients } C_{(k+\mathbf{G}_j)}:
\]

\[
\frac{1}{2} \left| \mathbf{k} + \mathbf{G}_j \right|^2 C_{(k+\mathbf{G}_j)} + \sum_{\mathbf{G}_i} V_{\mathbf{G}_i, \mathbf{G}_j} C_{(k+\mathbf{G}_j)} = E(k) C_{(k+\mathbf{G}_j)}
\]

(2.83)

where \( V_{\mathbf{G}_i, \mathbf{G}_j} = \int \psi_{\text{eff}}(r)e^{i(\mathbf{G}_j - \mathbf{G}_i) \cdot \mathbf{r}} d\mathbf{r} \).

In the calculations, the dimension of the plane wave basis set is required to be infinite for expending the electron wave-function. The plane waves with low kinetic energy are usually more important. Thus, the solution can be found by truncating the basis set to at a finite number of the plane waves. The Fourier expansion (2.82) is truncated at some \( \left| \mathbf{G}_{\max} \right| \) corresponding to the cutoff energy \( E_{\text{cut}} = \frac{\hbar^2}{2m} \left| \mathbf{G}_{\max} \right|^2 \). The condition for truncation of the basis set is given by:

\[
\frac{1}{2} \left| \mathbf{k} + \mathbf{G} \right|^2 \leq E_{\text{cut}}
\]

(2.84)

One can increase the cutoff energy to improve the accuracy of the calculations. The energy cutoff depends on the properties of studied system. The choice of the cutoff energy is important in terms of the convergence procedure.

The disadvantage of this type of plane wave description is that in order to model the wave functions around the core regions one needs a large number of plane waves. Using the pseudopotential approximation, this problem can be overcome.
2.2.7 Pseudo-potential Approximation

Although the idea to use the plane waves to express the KS orbitals by using the Bloch’s theorem, simplified the solution of the KS equation, calculations by using a basis set consisting of both the core and valence electrons is very expensive. The computational cost originates from the facts that strong interaction near the core makes it hard to describe the wave-functions by using a plane wave basis set, and highly oscillatory valence wave functions near the core due to the strong ionic potential. The fact that an accurate description of the properties requires large number of plane waves and high energy cutoff causes the calculations to be extremely costly. The main motivation behind the generation of the pseudo-potentials is due to a need to reduce the computational cost.

In order to solve this problem, one needs to use the fact that the main contribution to the chemical bonding comes from the valence electrons. Thus, it is sufficient to concentrate only on these chemically active electrons, while keeping the core electrons frozen. An effective potential due to the core electrons known as pseudo-potential can be generated. It replaces the core electrons and the ionic potential within a cutoff radius around the core by a smoother potential. By doing that the core states can be eliminated and the valence electrons can be described by nodeless pseudo-wavefunctions. These wave-functions are different from the exact ones only in the region near the core. They are the same outside the chosen cutoff radius. Thus, this approach reduces the number of required plane waves and hence the computational cost.
2.2.8 k-point Sampling

Above, we have discussed that the ground state properties of a system of interacting electrons can be determined from the solutions of the KS equations [48]. In practice, application of the method is expensive due to the fact that one has to solve the KS equations for an extremely large number of electrons. Using the Bloch’s theorem [81] one finds a way to represent large number of electrons by much smaller number of electrons by expanding the KS orbitals in terms of plane waves. Solving the KS equation for a single k-point is simple. However, determining the total energy requires calculations for infinite number of k-points. To reduce the number of k-points, one invokes the fact that the wave-functions do not change much over a small distance in k-space. The properties are similar for the two wave functions with close values of k. Thus, this assumption makes it possible to perform integrations as summations over a finite mesh of k-points. The infinite number of k-points is then replaced by a finite number of k-points lying within the first Brillouin zone (BZ).

The popular methods for choosing the k-points in the BZ include tetrahedron [82] and the special points method [83]. In the present study, the set of k-points -- chosen to sample the BZ -- is obtained by using the Monkhorst and Pack method. Using the symmetry arguments, one determines those special k-points that reflect the properties of the whole BZ. Then, the integration is performed as the weighted sum over a grid of these special k-points. The k-points are distributed uniformly throughout the space as:

$$\vec{k}_j = x_{j1} \vec{b}_1 + x_{j2} \vec{b}_2 + x_{j3} \vec{b}_3$$  \hspace{1cm} (2.85)
where the $\mathbf{b}_j$'s are the reciprocal lattice vectors, and $x_j = \frac{l_j}{n_j}$, $j = 1, \ldots, n_j$, $l_i$'s are the length of the reciprocal lattice vector components, while the $n_j$ represents the number of special points in the set.

By representing an integral as a sum over a finite number of $k$ points one performs numerically the integration over the BZ, given by:

$$
\int_{BZ} \frac{1}{V_{BZ}} dk \rightarrow \sum_j \omega_j
$$

(2.86)

Then an integral over the over the BZ can be expressed as:

$$
\frac{V}{(2\pi)^3} \int_{BZ} F(\mathbf{k}) dk = \sum_j \omega_j F(\mathbf{k}_j)
$$

(2.87)

where $F(\mathbf{k})$ is a function of momentum, $V$ is the unit cell volume and $\omega_j$'s are the weight factors.

In practice, it is important to perform the calculations with a sufficient number of $k$-points. For metals, special attention has to be paid, since the bands cross the Fermi energy leading to a discontinuity in the occupation, which complicates the integration over the Fermi surface. For these special cases, a large number of $k$-points are needed for an accurate description of the properties. However, the computational time scales linearly with the number of $k$-points. Therefore, one needs to decide whether the reasonably large number of $k$-points used in the calculations is sufficient through a procedure known as $k$-point sampling. Several calculations can be performed by increasing the $k$-point mesh density. In the present study, a large number of additional calculations is performed to ensure convergence.
2.3 Real Space Green’s Function (RSGF) Method

In lattice dynamics a crystal lattice is an array of atoms that are in motion, which is seen as the superposition of atomic vibrations around their equilibrium. The normal modes of vibrations are treated to be particle-like with discrete energies. For instance, for a molecule the vibrational energy is quantized and treated as quantum harmonic oscillator with equally spaced energy levels. For a periodic lattice, these energy quanta are known as phonons.

Experimentally, the measurements of lattice dynamics are performed using vibrational spectrosopes of which there are two kinds. The first -- consisting of Brillouin, Raman, Infrared Absorption Spectroscopes and Inelastic X-ray Scattering -- uses light as the probe, while the second -- Electron Energy Loss, He-atom Scattering, and Inelastic Neutron Scattering -- uses particles as probes. Both sorts of measurements, by providing insights into characterization of atomic vibrations, supply valuable information related to thermodynamic and mechanical properties of materials. Such measurements, because they are performed on periodic systems, provide the modes in wave-vector representation. The modes present in phonon dispersion are associated with a specific point in the BZ. In contrast measurements of the vibrational densities of states (VDOS) for finite-sized systems such as NPs have been performed using Neutron Scattering and Nuclear Resonant Inelastic X-ray scattering (NRIXS).

From the theory side, the VDOS can be obtained from the lattice dynamics [84]. The objective is to determine phonon frequencies as a function of the wave vector, in other words, to derive the dispersion relation. Since these calculations are performed in
wave-vector representation, they offer the prospect of one to one comparison with experimental observations. The slab method [84], which uses this lattice dynamic approach, has been proven to be successful in revealing the vibrational properties, particularly for systems with no or only partial long-range order (LRO). In this method, the system is treated as consisting of virtually infinite stacks of infinitely wide 2D layers with a vacuum separating the surfaces of the lowers of upper stack from the uppers of the lower. In order to determine accurately the vibrational modes of a crystal, large number of layers must to be used in the calculations in order to ensure elimination of the interactions between the surfaces above and below the upper stack. The calculation of vibrational frequencies involves the construction of the dynamical matrix for a specific point in the BZ, and solving the secular equation by diagonalizing the dynamical matrix. The resulting eigenvectors represent the displacement fields, while the eigenvalues are the phonon frequencies. Such calculations are computationally very expensive, owing to the involvement of large number of degrees of freedom. The VDOS can also be calculated using MD simulations by means of the Fourier transform of the velocity autocorrelation function [85]. This method has been employed to study the vibrational properties of nanoscale materials [86].

Calculation of VDOS via the slab method is computationally costly. An alternative approach is based on the realization that for systems with no LRO (such as surfaces, interfaces, and NPs), the local environment may reveal the VDOS of the whole system [52]. This makes it possible to treat these systems in real-space instead of wave-vector space. Throughout the study, one of the interests is to determine local contributions to the vibrational and thermodynamical properties of surfaces and NPs.
Hence, for the calculation of vibrational properties of such systems, we employ a local approach in real space that reveals site-specific contributions and their effect on other physical properties. One such method known as real-space Green’s function was developed by Wu and co-workers [52], especially for systems with low symmetry, to calculate the local Green’s function in order to determine the local densities of states (LDOS). The approach is based on constructing the resolvent matrix of an infinite block-tridiagonal matrix [87]. The Green’s function is defined as the matrix representation of the resolvent operator that yields the LDOS via its matrix elements. Such a matrix must be constructed in a block tridiagonal form, and the interactions should be in finite range. The system is divided into the regions in such a way that the Hamiltonian can be written in a block-tridiagonal matrix as given below:

\[
H = \begin{pmatrix}
    \ddots & & & \\
    \nu_{i,i-1} & h_i & \nu_{i,i+1} & \\
    & \nu_{i+1,i} & h_{i+1} & \nu_{i+1,i+2} & \\
    & & \ddots & \\
\end{pmatrix}
\]  

(2.88)

where \( h_i \) sub-matrices along the diagonal are \( 3n_i \times 3n_i \) square matrices, \( \nu_{i,i+1} \) matrices along the off-diagonals have dimension \( 3n_i \times 3n_{i+1} \), and \( n_i \) is the number of particles in the chosen locality. Figure 2.2 shows such a system divided into three regions (localities labeled as \( L_1 \) to \( L_3 \)). For each locality, there is a sub-matrix \( (h_1, h_2, h_3) \) describing the interactions within the associated locality. The sub-matrices \( (\nu_{12} \text{ and } \nu_{23}) \) describe the interactions between localities. The interactions beyond these localities are considered to be bulk-like.
Note that in our calculations the system Hamiltonian is described by the force constant matrix, which is obtained from the second derivative of the interaction potential. The eigenvalue can be derived by means of the Green’s function that is associated with the matrix $H$ and is given by:

$$G(z) = (zI - H)^{-1}$$  \hspace{1cm} (2.89)  

where $z = \omega^2 + i\epsilon$, $\epsilon$ is the width of the Lorentzian representing the delta function at $\omega^2$, and $I$ is a unit matrix of the same dimension as that of $H$. The diagonal element of the Green’s function matrix corresponding to a chosen locality is expressed as:

$$G_{ii} = \left[ (zI - h_i) - \nu_{i,i+1} \Delta^+_i + \nu_{i,i+1} \nu_{i,i+1} \Delta^-_i - \nu_{i,i-1} \Delta^-_i \nu_{i,i-1} \right]^{-1}$$  \hspace{1cm} (2.90)  

$\Delta^+_i$ and $\Delta^-_i$ are defined as forward and backward partial Green’s functions and described by:
\[ \Delta_i^+ = \left( zI - h_i - \nu_{i,i+1}\Delta_{i+1}^+\nu_{i+1,i} \right)^{-1} \]  
(2.91)

\[ \Delta_i^- = \left( zI - h_i - \nu_{i,i-1}\Delta_{i-1}^-\nu_{i-1,i} \right)^{-1} \]  
(2.92)

The relation between the successive diagonal elements of the Green’s function matrix \( G \) is obtained by the following equation:

\[ G_{ii} = \Delta_i^+ \Delta_{i-1,1} \Delta_{i,21} G_{i+1,1} \Delta_{i+1,1} \],  
(2.93)

As seen above the calculation of the Green’s function mainly depends on the forward and backward Green’s functions (\( \Delta_i^\pm \)), which are the inverses of matrices with the dimensions same as that of \( h_i \). The convergence procedure for the calculation of \( \Delta_i^\pm \) for an infinite system starts with the condition as:

\[ \Delta_i^{+(1)} = \lim_{m \to \infty, c \to 0} \Delta_i^{+(m)}(z) \]  
(2.94)

where,

\[ \Delta_i^{+(m)} = \left\{ (zI_1 - h_1) - v_{12}([zI_2 - h_2] - \ldots - [v_{m-1,m}(zI_m - h_m)]^{-1}v_{m,m-1}]^{-1} \ldots]^{-1}v_{21} \right\}^{-1} \]  
(2.95)

From this equation, one can define the forward Green’s function for any chosen regime as:

\[ \Delta_i^{+(1)} = (zI_1 - h_1)^{-1} \]  
(2.96)

\[ \Delta_i^{+(2)} = \left\{ (zI_1 - h_1) - v_{12}([zI_2 - h_2]^{-1}v_{21}]^{-1} \right\}^{-1} \]  
\[ \Delta_i^{+(3)} = \left\{ (zI_1 - h_1) - v_{12}([zI_2 - h_2]^{-1}v_{23}(zI_3 - h_3)]^{-1}v_{32} \right\}^{-1}v_{21} \}^{-1} \]  
(2.97)

\[ \vdots \]  
(2.98)

\[ \Delta_i^{+(m)} \]
The convergence procedure shows that the information obtained at previous steps cannot be used to calculate $\Delta_{1}^{(m)}$ for the current step; hence for each step, the sequence must be repeated independently. This requires excessive computing time. In order to make use of the information obtained at the previous step ($\Delta_{1}^{(m-1)}$) and the current one ($\Delta_{1}^{(m)}$), a recursive method is introduced that defines the forward Green’s function for the localities ($\Delta_{1}^{(1)}, \Delta_{1}^{(2)}, \Delta_{1}^{(3)}, \ldots, \Delta_{1}^{(m)}$) for a finite system as:

$$
\Delta_{1}^{(1)} = (zI_1 - h_1)^{-1} \equiv \Delta_1^{-1}
$$

$$
\Delta_{1}^{(2)} \equiv G_{11}^{(2)}
$$

$$
\Delta_{1}^{(3)} \equiv G_{11}^{(3)}
$$

$$
\vdots
$$

$$
\Delta_{1}^{(m)} \equiv G_{11}^{(m)}
$$

where $G_{11}^{(m)}$ is the (1,1) diagonal block of the Green’s function corresponding to the matrix $H^{(m)}$. Using the equation 2.97, $\Delta_{1}^{(2)}$ and $G_{22}^{(2)}$ are given by:

$$
\Delta_{1}^{(2)} = C_{11}^{(2)} = \Delta_1^{-1} + \Delta_1^{-1}v_{12}G_{22}^{(2)}v_{21}\Delta_1^{-1}
$$

$$
G_{22}^{(2)} = \Delta_2^{-1} = \left\{ (zI_2 - h_2) - v_{21}\Delta_1 v_{12} \right\}^{-1}
$$

So that the relation between the successive forward Green’s functions is obtained as:

$$
\Delta_{1}^{(2)} = \Delta_{1}^{(1)} + A_1\Delta_2^{-1}B_1
$$

where $A_1 = \Delta_1^{-1}v_{12}$ and $B_1 = v_{21}\Delta_1^{-1}$. Repeating the same steps, general recursive relation can be obtained thus:
This method thus simplifies the calculation of the Green’s functions to inversion and multiplication of matrices whose dimensions are much smaller than the total number of degrees of freedom of the system. The diagonal element of the Green’s function represents the entire system. The method ensures that the Green’s function associated with a particular locality in the system can be reasonably calculated.

In calculating the VDOS for surfaces of the systems under study here we have brought this method to bear by considering each system as consisting of infinite number of layers with in-plane periodicity, and specifying a certain number of layers as constituting a locality. The sub-matrix elements of the block tridiagonal matrix represent the force constants between the atoms, within and between the chosen localities. We then determine the normalized VDOS \( N_s(\omega) \) from the trace of Green’s function by employing the following equations:

\[
g(\omega^2) = -\frac{1}{3n\pi} \lim_{\varepsilon \to 0} \text{Im} \text{Tr}[G(\omega^2 + i\varepsilon)]
\]

\[
N(\omega) = 2\omega g(\omega^2)
\]

The method has been applied successfully to both high and low-symmetry systems [59] such as bulk, flat and vicinal surfaces and single-element and bi-metallic NPs. These studies have proved that it can accurately reveal the vibrational properties, especially for low-symmetric systems. Recent applications of the method have provided
insights into the effect of coordination and alloying on vibrational and thermodynamical properties of such low-symmetry systems [8, 88].

2.4 Thermodynamical Functions

At a given temperature T, a system is in contact with a heat source that yields heat exchange. From the thermodynamic point of view, such a system can be described by its free energy, which is expressed as:

\[ F = U - TS \]  \hspace{1cm} (2.112)

where U is the internal energy, T and S are temperature and entropy, respectively. From the statistical mechanics point of view, a crystal (C) can be represented by an ensemble of 3N harmonic oscillators of frequencies \( \omega(q, j) \). The heat source (S) is expressed by a large number of atoms or molecules \( 3N' \gg 3N \). The system formed by the crystal and the source (S+C) is isolated, and its energy is constant. Suppose that at some instant in time the source (S) is in a state described by \( |s\rangle \), and the crystal (C) is in the state described by \( |n\rangle \), and their corresponding energies are \( E_s \) and \( E_n \), respectively. The Hamiltonians \( (H_s, H_n) \) describing these sub-systems and the corresponding secular equations are expressed as:

\[ H_s |s\rangle = E_s |s\rangle \]  \hspace{1cm} (2.113)
\[ H_c |n\rangle = E_n |n\rangle \]  \hspace{1cm} (2.114)

and the total energy is \( E = E_s + E_n \). At some point later in time, a molecule hits the crystal causing a change in the energy of the crystal and a change in the states \( (n \rightarrow n') \)
(the same thing happens to the source), with the total energy now expressed as \(E = E_s + E_n\). This process will be repeated each time a molecule from the source interacts with the crystal. In statistical mechanics we are interested in the probability of finding the system at energy \(E_n\), at temperature \(T\). The probability is expressed as:

\[
P_n = K \exp(-\beta E_n), \quad \text{with } \beta = 1/kT
\]

(2.115)

where \(K\) is a prefactor, and \(k\) is the Boltzmann constant. At temperature \(T\), the crystal is in a mixture of states for which \(K\) can be expressed as \(K = 1/Z\) with the condition of \(\sum_n P_n = 1\). Using equation 2.115, the quantity \(Z\) is given by:

\[
Z = \frac{1}{K} = \sum_n \exp(-\beta E_n).
\]

(2.116)

With this expression, the probability then becomes as \(P_n = \frac{1}{Z} \exp(-\beta E_n)\). Now we can define the average value of any physical observable of the crystal. If \(A\) is an operator representing a physical quantity, then its expectation value can be expressed as \(\langle n \mid A \mid n \rangle\). The corresponding statistical average of this operator is then given by:

\[
\overline{A} = \sum_n P_n \langle n \mid A \mid n \rangle.
\]

(2.117)

These averages are the quantities that one may use when comparing with experimental data. The statistical average of the energy is then determined by using the equations 2.115 and 2.116, and is given by:
\[ \overline{E} = \sum_n P_n \langle n \mid H \mid n \rangle \]
\[ = \sum_n \frac{1}{Z} \exp(-\beta E_n) \times E_n . \]  (2.118)

Since the partition function is expressed as \( Z = \frac{1}{K} = \sum_n \exp(-\beta E_n) \) in equation 2.116, and then the average statistical energy is further expressed as:

\[ \overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} (\ln Z) . \]  (2.119)

The entropy is given by:

\[ S = -k \sum_n P_n \ln P_n . \]  (2.120)

Using the definitions provided in equations 2.115 and 2.116, entropy can be re-written as:

\[ S = k\beta \sum_n P_n E_n + k \ln Z \]  (2.121)

inserting equation 2.119 into 2.121 leads to its relation to the average statistical energy:

\[ S = (1/T) \overline{E} + k \ln Z . \]  (2.122)

The free energy can be obtained using equation 2.112 -- by replacing the internal energy with the potential energy \((\phi_o)\) and the average statistical energy, and using also entropy (equation 2.122) -- and is given by:

\[ F = \phi_o + \overline{E} - TS = \phi_o - kT \ln Z \]  (2.123)
2.4.1 Partition Function and Free Energy of Harmonic Crystal

The thermodynamical functions of a harmonic crystal are determined by means of the partition function [89]. In the treatment of the harmonic model, the energy levels of a crystal containing \( N \) atoms are the same as those of a set of independent harmonic oscillators with the frequency of the \( j^{th} \) oscillator being \( \omega(q_j) \). These energy levels corresponding to a frequency are given by the quantum theory of harmonic oscillator as:

\[
E(n(q_j)) = \hbar \omega(q_j)[n(q_j) + 1/2].
\]  

(2.124)

The total energy of such a crystal is the potential energy (when atoms are at the equilibrium configuration) plus the term for each of the \( 3N \) normal modes. The energy of the crystal when it is in a particular state is defined by the integers as:

\[
|n\rangle = |n_1\rangle|n_2\rangle|n_3\rangle\ldots|n_{3N}\rangle
\]

(2.125)

\[
|n\rangle = \prod_{q_j} n(q_j)
\]

(2.126)

The partition function describing the system is a sum over all the states and is given by:

\[
Z = \sum_{\{n\}} \exp\left\{ -\beta \sum_{q_j} \hbar \omega(q_j) [n(q_j) + 1/2] \right\}
\]

(2.127)

The sum is to be carried out over all the possible set of integers -- for all normal mode frequencies, the sum is performed over all integers from zero to infinity. Using the convenient exponential function property -- exponential of a sum is the product of the exponentials of the factors.

\[
Z = \sum_{\{n\}} \prod_{q_j} \exp\left\{ -\beta \hbar \omega(q_j) [n(q_j) + 1/2] \right\}
\]

(2.128)
\[ Z = \prod_{q_j} \sum_{n(q,j)=0} \exp\{ -\beta \hbar \omega(q_j) [n(q,j) + 1/2] \} \]  
(2.129)

for \( \sum_{n=1}^{\infty} \exp(-n\hbar\omega / kT) \) defining \( X = \exp(-\hbar \omega / kT) \) leads to:

\[ \sum_{n=1}^{\infty} \exp(-n\hbar\omega / kT) = \sum_{n=1}^{\infty} X^n = \frac{1}{1 - \exp(-\hbar \omega / kT)}. \]  
(2.130)

Applying this to equation 2.129, the partition function is then expressed as:

\[ Z = \prod_{q_j} \frac{\exp[-1/2 \beta \hbar \omega(q_j)]}{1 - \exp[-\beta \hbar \omega(q_j)]} \]  
(2.131)

and using here the property of \( 2 \sinh x = e^x - e^{-x} \), where \( x = -1/2 \beta \hbar \omega(q_j) \), then the partition function is derived as:

\[ Z = \prod_{q_j} \frac{1}{2 \sinh[1/2 \beta \hbar \omega(q_j)]} \]  
(2.132)

Using equation 2.119 for the average statistical energy and inserting the partition function for the harmonic solid and taking the derivative with respect to \( \beta \), we obtain:

\[ \overline{E} = -\frac{\partial}{\partial \beta} (\ln Z) = \sum_{q_j} \hbar \omega(q_j) \left[ \frac{1}{\exp[\beta \hbar \omega(q_j)] - 1} + \frac{1}{2} \right]. \]  
(2.133)

Since the energy levels are quantized, this equation can be written as:

\[ \overline{E} = \sum_{q_j} \hbar \omega(q_j) \left[ \frac{n(q,j) + 1}{2} \right], \]  
(2.134)
where \( \bar{n}(q,j) = \frac{1}{\exp[\beta \hbar \omega(q,j)] - 1} \) represents the mean number of phonon modes.

Referring back to equation 2.123 for the Helmholtz free energy and inserting the partition function, we obtain the following expression:

\[
F = \phi_0 - kT \ln Z = \phi_0 + kT \sum_{qj} \ln \left[ 2 \sinh \frac{1}{2} \beta \hbar \omega(q,j) \right]
\]

Specific heat and entropy are then derived the same way using the partition function in equation 2.131, and is given by:

\[
C_v = \frac{\partial E}{\partial T} = k \sum_{qj} \left[ \frac{\beta \hbar \omega(q,j)}{2} \right]^2 \frac{1}{\sinh^2 \left( \frac{1}{2} \beta \hbar \omega(q,j) \right)}
\]

\[
S = -\frac{\partial F}{\partial T} = k \sum_{qj} \left\{ \frac{1}{2} \beta \hbar \omega(q,j) \coth \left( \frac{1}{2} \beta \hbar \omega(q,j) \right) \ln 2 \sinh \left( \frac{1}{2} \beta \hbar \omega(q,j) \right) \right\}
\]

**2.4.2 Frequency Spectra**

The above mentioned equations involve summation over all the normal modes. The number of wave vectors \( q \) is usually very large within the first BZ and one may assume that they distributed uniformly and continuously inside the first BZ. With this assumption, the vibrational frequencies form a continuum represented by a density of states.

We will call \( G(\omega^2)d(\omega^2) \) as the fraction of the total number of frequencies squared lying between \( \omega^2 \) and \( \omega^2 + d\omega^2 \). Same way \( g(\omega)d(\omega) \) is the fraction of frequencies
lying between $\omega$ and $\omega + d\omega$. These two functions are related to each other by:

$$g(\omega) = 2\omega G(\omega^2)$$  \hfill (2.138)

If $\omega_k$ is the maximum frequency for the crystal, then the following conditions are imposed:

$$\int_{0}^{\omega_k} g(\omega) d(\omega) = 1 \hfill (2.139)$$

$$\int_{0}^{\omega_k} G(\omega^2) d(\omega^2) = 1. \hfill (2.140)$$

Using the vibrational densities of states $g(\omega)$, we can re-write the thermodynamical functions of interest as:

$$U_{vib} = N_d \int_{0}^{\omega_k} \frac{\hbar^2 \omega}{2} \left[ \frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right] g(\omega) d(\omega) \hfill (2.141)$$

$$F_{vib} = \frac{N_d}{\beta} \int_{0}^{\omega_k} \ln \left[ 2 \sinh \left( \frac{1}{2} \beta \hbar \omega \right) \right] g(\omega) d(\omega) \hfill (2.142)$$

$$S_{vib} = k_B \int_{0}^{\omega_k} \left( \frac{1}{2} \beta \hbar \omega(q \cdot j) \coth \left( \frac{1}{2} \beta \hbar \omega(q \cdot j) \right) - \ln \left( 2 \sinh \left( \frac{1}{2} \beta \hbar \omega(q \cdot j) \right) \right) \right) g(\omega) d(\omega) \hfill (2.143)$$

$$C_V = N_d k \int_{0}^{\omega_k} \left( \frac{\beta \hbar \omega}{2} \right)^2 \frac{g(\omega) d(\omega)}{\sinh^2 \left( \frac{1}{2} \beta \hbar \omega \right)} \hfill (2.144)$$

$$\left\langle u_i^2 \right\rangle = \frac{\hbar}{2M} \int_{0}^{\infty} \coth(\hbar \omega 2k_B T) \rho_i(\omega) d\omega \hfill (2.145)$$

$$\theta_i^2 = \frac{3\hbar^2 T}{M k_B \left\langle u_i^2 \right\rangle} \hfill (2.146)$$
where \( U_{\text{vib}}, F_{\text{vib}}, S_{\text{vib}}, C_V, \langle u_i^2 \rangle \) and \( \theta_i^2 \) are the internal energy, vibrational free energy, vibrational entropy, specific heat, mean square displacement of atom \( i \), and Debye temperature of atom \( i \), respectively. \( N_d \) is the total number of degrees of freedom of the system. Using some of the above thermodynamical functions, one can calculate the prefactor -- attempt to diffuse frequency -- for a given diffusion process. The prefactor is calculated as:

\[
D_0(T) = \frac{k_B T}{h} \frac{n d^2}{2 \alpha} \exp \left( \frac{\Delta S_{\text{vib}}}{k_B} \right) \exp \left( \frac{-\Delta U_{\text{vib}}}{k_B T} \right)
\]

(2.147)

where \( \Delta S_{\text{vib}} \) and \( \Delta U_{\text{vib}} \) represent the difference in the vibrational entropy and the internal energy of the system being at two configurations -- the minimum energy and the saddle point. Using the Arrhenius relation, one can determine the diffusion coefficients from the calculated prefactor as:

\[
D = D_0(T) \exp \left( \frac{-\Delta E}{k_B T} \right)
\]

(2.148)

where \( \Delta E \) is the diffusion activation energy -- the difference in the total energy of the system being at two configurations.

### 2.5 Molecular Static (MS) Simulations

Understanding such transition processes as chemical reactions and diffusion is an important problem in condensed matter physics and chemistry. At finite temperature, the motion of atoms around an equilibrium position causes the system to move along paths that correspond to the lowest free-energy maximum. The path that minimizes the contour
integral of total energy is designated as the minimum energy path (MEP). Any path for a transition process starts from a local minimum (initial state configuration, IS) and move towards the successive local minimum (final state configuration, FS). Although there are several possible reaction paths from an initial to a final state, the path that costs the lowest activation energy is the one we assume to be followed. The highest energy configuration along the path is called the transition-state or saddle point. Figure 2.3 shows a diffusion process for a single Cu atom on Cu(100) taking place along the chosen reaction path. As shown in the figure, the Cu atom moves from an initial position (#1) -- the minimum energy configuration -- to a final position (#2) via a transition-state (which is metastable). This transition leads to a progressive re-arrangement of atoms in the system that constantly increases the total energy along the transition path. The energy cost (the activation energy, $\Delta E_A$, in the figure) for such a diffusion event is 0.505 meV [90].
Figure 2.3 System total energy as a function of reaction path from an initial (IS) to a final (FS) state through a saddle point for Cu adatom diffusion on Cu(100). The gray balls represent the first layer atoms (top view of (100) surface). The crosses correspond to the second layer atoms. Initial (#1) and final positions (#2) of the adatom are shown as red balls.

For any transition process, it is necessary to determine the exact position of the saddle point in order to calculate such reaction parameters as rates and activation energies. The challenge in such a task is that one has no a priori knowledge of the paths. For some transition processes, simple methods are used in which one takes into account only the local environment around the saddle point and two end points of the path in predicting these parameters. More sophisticated methods, such as molecular approaches, have been shown to be appropriate for searching for transition states. MS, also known as
quasi-static method [53], is one of the most commonly used for transition-state searches. It is based on searching for the saddle point that provides minimum activation energy for the chosen reaction paths. The total energy can be minimized using such minimization schemes as Steepest Descent, Conjugate Gradient (CG) or Downhill Simplex methods [91]. Accurate determination of the saddle-point configuration requires thorough examination of how the potential energy behaves along the reaction paths. This is no trivial matter even when semi-empirical methods are used.

Once the saddle-point configuration is determined, one considers the energy gradients downhill both forwards and upwards in order to map out the MEP. This can be done in many ways, depending on the nature of the system and reactions under study. For instance, if one has a priori knowledge of the final state, the initial and final state configurations can be used as the boundary conditions for the search. The oldest and the simplest methods invoked for such purposes are the NEB [60] and the Drag. More recent and complicated methods are the Ridge [92] and the Conjugate Peak Refinement [93] methods. A quite recent refinement has been put forward by Dewar, Healy and Stewart [94]. If the knowledge of final state configuration is not available, the search for reaction path becomes more challenging still owing to the fact that in such cases, the search has to be performed as well for the transition path. What is known as Dimer method [95] has recently been proposed for studying such cases. An excellent review on transition-state search methods and MEP is that by Henkelman et al [96].

Throughout the thesis, we have carried out the MS simulations in order to determine the minimum energy configurations for surfaces and NPs with interactions derived from EAM and DFT. We have employed the CG scheme for total energy
minimization. In order to calculate diffusion activation barriers and diffusion coefficients for single atoms and clusters diffusion, we have in most cases used the Drag method for saddle-point search. For comparison purposes we have also employed the NEB method for more challenging diffusion processes -- those involving more than a single atom. In the following two sections, we will summarize these two saddle-point search methods.

### 2.5.1 Drag Method

The Drag method is the simples and the most commonly used. One chooses a drag coordinate (x, y or z) and constrains it while letting the remaining degrees of freedom of the system to relax. The system total energy is minimized in N-1 dimensional hyper plane. In the case of one-dimensional (1D) drag method -- constrain is applied in only one dimension -- the position of the drag coordinate along the reaction path is dragged in small increments (the choice of which is system- and process-dependent) from an initial to a final state. At each step along the reaction path, system total energy is minimized. The overall result provides the relation between the change in system’s total energy and the chosen reaction path. The maximum of the energy along the path is the saddle-point energy (Figure 2.3). This method is applicable when there is a priori knowledge of the final state. The drag coordinate is chosen through an educated guess (using symmetry arguments, etc.). When the starting guess is not transparent, an alternative is to choose the drag coordinate as the straight-line interpolation between the initial and the final states. Since the choice of reaction path involves an assumption, it leads to the shortcoming that if the path chosen is not the true reaction path for the process, the resulting transition-state configuration will be far from the actual saddle-
point. There are cases for which the method works accurately, as well examples where it fails [97].

### 2.5.2 Nudged Elastic Band (NEB) Method

The NEB method belongs to the chain-of-states methods [96], in which several images of a system are connected to trace the path for transition process. It is used not only to search for reaction paths but also to establish the MEP for a given transition process when both the initial and the final states are known *a priori*. In applying the method [60], one begins with a number of images (states) of the system that are connected by artificial springs. These images actually represent a particular configuration of the system along the path between the initial and the final states. The method works by means of linearly interpolating a set of images between the known initial and the final states, and by minimizing the energy of these images. During the minimization process the distance between the neighboring images is kept equal. Once the energy of each image is minimized, one can also determine the MEP. Hence the method can provide both the transition-state configuration and insights into the characteristics of the energy landscape.

Let the string of images to be described by \( R_0, R_1, R_2, R_3, \ldots, R_N \), each of which is a copy of the system in a particular configuration. The initial (\( R_0 = I \)) and the final points (\( R_N = F \)) along the reaction path are fixed, while all the images in between are free to relax. Such a process can be represented by an object function, which is expressed as:

\[
S(R_1, R_2, \ldots, R_N) = \sum_{i=1}^{N-1} E(R_i) + \sum_{i=1}^{N} \frac{k}{2} (R_i - R_{i-1})^2
\]  

(2.149)
where $E(R_i)$ is the potential energy of a particular image $i$, while $k$ is the artificial spring constant connecting these images. This object function is then minimized with respect to the images between the initial and the final points. This procedure brings with it two major problems, namely corner-cutting and down-sliding. The former occurs when the MEP is curved -- the elastic band cuts corners and pulls away from the MEP owing to the presence of spring forces. The latter occurs because the images slide down towards the fixed points that reduce the population of images around the saddle point. The corner-cutting problem originates from the presence of the spring force, which is perpendicular to the path, while the down-sliding problem occurs owing to the parallel component of the force (emerging from the interaction among the atoms). The solution to both problems is to introduce a force projection called “nudging”. This is done by introducing a unit tangent ($\tau$) to the path at each image, so that one considers only the parallel component of the spring force pointing towards the MEP, and the perpendicular component of the inter-atomic force normal to the MEP. This new force definition is given by:

$$F_i = -\nabla E(R_i) \perp + F_i^{spring} \cdot \tau \tau$$

(2.150)

where $\nabla E(R_i)$ is the gradient of the energy with respect to the atomic positions at image $i$, and $F_i^{spring}$ is the spring force acting on image $i$. The perpendicular component of the inter-atomic force and the parallel component of the spring forces are expressed, respectively, by:

$$\nabla E(R_i) \perp = \nabla E(R_i) - \nabla E(R_i) \cdot \tau \tau \cdot \tau \tau$$

(2.151)
\[ F_{i,\text{spring}} = k \left( |R_{i+1} - R_i| - |R_i - R_{i-1}| \right) \hat{\tau}_i \] (2.152)

Figure 2.4 Force components along a reaction path. \( F^{\text{NEB}} \) is the nudged elastic band force, \( F^{S}_i \) represents the spring force along tangent \( \hat{\tau}_i \), and \( F^{\perp}_i \) is the perpendicular force due the interaction (\( F_i \)). *Image courtesy of G. Henkelman et. al, [98].*

The tangent vector is estimated by bisecting the two unit vectors thus:

\[ \hat{\tau}_i = \frac{R_i - R_{i-1}}{|R_i - R_{i-1}|} + \frac{R_{i+1} - R_j}{|R_{i+1} - R_j|}. \] (2.153)

It is normalized as \( \hat{\tau} = \frac{\tau}{|\tau|} \) and the result rejects the corrective component of the forces.

This definition (equation 2.153) ensures the images are kept equidistant during the optimization. It has been shown that the description so far may still not lead to convergence to the MEP, especially when the total energy along the path changes rapidly.
In such a case, a further corrective function is introduced to increase slightly the perpendicular component of the spring force. In this new form, at an image \( i \), the tangent of the path is defined as the vector between the image and its neighboring image with higher energy, and is given by:

\[
\tau_i = \begin{cases} 
\tau_i^+ & \text{if } E_{i+1} > E_i > E_{i-1} \\
\tau_i^- & \text{if } E_{i+1} < E_i < E_{i-1}
\end{cases}
\]  

(2.154)

where \( \tau_i^+ = R_{i+1} - R_i \) and \( \tau_i^- = R_i - R_{i-1} \) and \( E_i = E(R_i) \). Yet another factor has to be taken into account is the possibility that neighboring images are lower or higher in energy than that for the image \( i \). To accommodate this possibility the tangent is finally specified as the weighted average of the vectors of the neighboring images. If image \( i \) is at minimum \( E_{i+1} > E_i < E_{i-1} \) or at maximum \( E_{i+1} < E_i > E_{i-1} \), the tangent is expressed as:

\[
\tau_i = \begin{cases} 
\tau_i^+ \Delta E_i^\text{max} + \tau_i^- \Delta E_i^\text{min} & \text{if } E_{i+1} > E_{i-1} \\
\tau_i^+ \Delta E_i^\text{min} + \tau_i^- \Delta E_i^\text{max} & \text{if } E_{i+1} < E_{i-1}
\end{cases}
\]  

(2.156)

where \( \Delta E_i^\text{max} = \max(|E_{i+1} - E_i|, |E_{i-1} - E_i|) \) and \( \Delta E_i^\text{min} = \min(|E_{i+1} - E_i|, |E_{i-1} - E_i|) \). This modified tangent ensures true convergence to the MEP provided that enough images are included.

These force projections are used to force the calculated paths to approach more closely to the true MEP. Once these projections are chosen, an optimization method is employed to move along a reaction path. The optimization process requires that the
magnitude of the force should satisfy criteria chosen as appropriate for the particular system and/or reaction under study. The force-based optimization routines commonly used include Steepest Descent (SD) [91], Quick-Min (QM) [99], Fast Integral Relaxation Engine [100], Conjugate Gradients (CG) [91] and limited memory Broyden-Fletcher-Goldfrab-Shanno (L-BFGS) routines. The NEB method has been extensively used for both chemical reactions and diffusion processes.

We have used the NEB method to determine diffusion paths and the corresponding activation energies for the diffusion of single metal atoms or a collection of atoms (clusters) on metal surfaces. Although one can use the method with the interactions derived from *ab-initio* methods, owing to the high computational cost, its usage is restricted for those cases in which only a small number of atoms is considered. When we use *ab-initio* methods, we have used the NEB method for some cases to compare with the results obtained using the Drag method. For cases in which the interactions are described by empirical potentials, we have used the NEB method.

### 2.6 Molecular Dynamic (MD) Simulations

MD is a powerful simulation technique whose results provide insights into the evolution of a set of interacting atoms (through some kind of an interaction potential) for a given time and temperature. The technique was introduced as early as the 50’s [54], providing bridge between the microscopic and macroscopic world. The first MD paper was written by Alder and Wainwright [101] in reporting the phase diagram of a hard sphere system. J.B. Gilson, *et al’s* investigation of the creation of defects induced by radiation damage [102] is the first MD simulation using a continuous potential and based
on finite time integration method. Finally, the famous paper by A. Rahman reported several properties of Argon [103] using the Lennard-Jones potential.

The idea behind the method is simple: the forces acting on atoms are calculated in an iterative manner and the evolution of the system in time and space is obtained. In MD simulation the classical mechanical laws -- particularly Newton’s law -- are employed. Each individual atom $i$ in a system consisting of $N$ atoms vibrate due to the thermal excitations and evolve according to Newton’s equations. The force acting on atom $i$ thus expressed as:

$$ F_i = m_i \ddot{q}_i = -\nabla_{q_i} V(q_i(t),\ldots,q_N(t)) \quad i = 1,N $$

where $F_i$ is the force acting on $i^{th}$ atom due to the interactions with its neighbors, $\nabla_{q_i}$ is the gradient with respect to atomic coordinates of the $i^{th}$ atom, $V$ is the inter-atomic potential describing the interactions, and $m_i$ and $\ddot{q}_i = d^2q_i / dt^2$ are the mass and the acceleration of the $i^{th}$ atom, respectively. The technique proceeds by means of integrating numerically the equations of motion. At the end of each time step, it provides a new arrangement of atoms in the system. In order to collect enough statistics to reveal the true thermodynamical properties, an averaging over successive configurations of the system is required (ensemble average). The assumption -- Ergodic Hypothesis -- here is that an ensemble average is the same as an average over time of one replica. This can be true provided that one spends long enough time for averaging. Long simulation time in general assures that the phase space can be completely sampled. Realistically, since all simulations are of finite length in time, complete sampling of the phase space is not easily reachable.
Figure 2.5 presents a simplified description of how a MD simulation is performed. Initialization is done by means of providing atomic positions (from a crystal structure) and velocities (generated from random numbers). The forces acting on the atoms in the system are calculated explicitly from the interaction potentials. The second step is to follow the Newton’s equations of motion using the initial parameters, at a small time interval to generate the new positions and velocities can be generated. The motion of atoms is obtained using a numerical integration method. These new positions are used to recalculate the forces. This cycle is repeated several times during the whole simulation (generally many thousands of time steps).

MD simulation starts out with a thermalization step that usually lasts a few thousands of time steps. The system is driven towards a desired thermodynamic state via
a temperature scaling technique. In order to control the temperature during the simulation, thermostat methods such as Nose-Hoover thermostat and Langevian dynamics are used to add or remove energy from the system.

\textbf{2.6.1 Periodic Boundary Conditions (PBC)}

For a realistic simulation of the properties of a system consisting of N number of atoms -- N here is negligible relative to the number of atoms contained in a macroscopic piece of matter -- a treatment of spurious surface effects is vital. In order to remove these surface effects one has to introduce periodic boundary conditions (PBC). In the PBC scheme, all the atoms of the system are closed in a box of certain size that in turn is considered as being replicated to infinity. Incorporation of the scheme allows the simulation of a few atoms to be treated as if it were infinite in size. This yields each atom to interact with its neighbors and its images.

Figure 2.6 illustrates the concept of PBC. The colored box represents the simulated system in question, while the surrounding boxes are exact copies of the simulated system. This scheme ensures that when an atom leaves the simulation cell, it is replaced by another one from the other side of the cell. This ensures that the number of atoms in the system remains constant that there are no surface effects.
2.6.2 Time Integration Algorithm

In MD simulation, one solves the Newton’s equation of motion by taking small steps in time using a time integration algorithm [104], which is required to integrate the equation of motion of the atoms in order to obtain new positions and velocities and later on for building the trajectories of the atomic motions. Integration algorithms used in MD simulations are based on finite difference methods, which rely on a Taylor expansion truncated at some term. Using the positions and their time derivatives at time $t$, the algorithm generates the new positions and velocities at a later time $(t + \Delta t)$. The most popular integration method used in MD simulations is the Verlet algorithm [104], in
which the third-order Taylor expansions for the positions $q(t)$ are written one for forward
and one for backwards in time, as expressed by:

$$q(t + \Delta t) = q(t) + v(t)\Delta t + (1/2)a(t)\Delta t^2 + (1/6)b(t)\Delta t^3 + O(\Delta t^4)$$ (2.158)

$$q(t - \Delta t) = q(t) - v(t)\Delta t + (1/2)a(t)\Delta t^2 - (1/6)b(t)\Delta t^3 + O(\Delta t^4)$$ (2.159)

$$a(t) = -(1/m)\nabla V(q(t))$$ (2.160)

where $v(t)$ and $a(t)$ are the velocity and acceleration, while $b(t)$ is the third derivative of
$q(t)$ with respect to $t$. Summation of these forward and backward equations hence results
in:

$$q(t + \Delta t) = 2q(t) - q(t - \Delta t) + a(t)\Delta t^2 + O(\Delta t^4).$$ (2.161)

In order to generate the velocities directly, the velocity Verlet scheme, using the same
algorithm, provides the positions and velocities at time $(t + \Delta t)$ from the knowledge
obtained for these quantities at an earlier time $t$. The positions and velocities at a forward
time are given by:

$$q(t + \Delta t) = q(t) + v(t)\Delta t + (1/2)a(t)\Delta t^2$$ (2.162)

$$v(t + \Delta t/2) = v(t) + (1/2)a(t)\Delta t$$ (2.163)

$$a(t + \Delta t) = -(1/m)\nabla V(q(t + \Delta t))$$ (2.164)

$$v(t + \Delta t) = v(t + \Delta t/2) + (1/2)a(t + \Delta t)\Delta t$$ (2.165)

There are other integration algorithms such as predictor-corrector and the Verlet
leap-frog algorithms [105]. These algorithms are approximate, introducing such
distortions as truncation errors originating from the accuracy of the finite difference
method with respect to the true solution. These errors can be reduced by decreasing the
step size $(\Delta t)$. 

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2.6.3 Time-Scale Problem

The purpose of a MD simulation is to reveal the dynamical evolution of a system of atoms by means of integrating the classical equations of motion. This provides system’s behavior forward in time and the trajectories of the motion of atoms. The accuracy of the method in describing the dynamical behavior of a system is based on the quality of the interaction potential in describing the forces realistically. The method does not rely on any assumptions or interpretations to obtain the true dynamical evolution of the system. With this advantage, it has become a widely used method and has provided valuable contributions into the understanding of the evolution in time and space of atomic events, especially for surface diffusion problems [106]. But despite its many positive features, it suffers from an important shortcoming (namely the time-scale problem). The time-scale problem emerges from the fact that revealing atomic vibrations in solids requires the time step of integrations to be set in the order of femtoseconds (10^{-15} seconds). Yet the most widely used simulation time is less than one microsecond (10^{-6} seconds). The processes/events of interest to the community (e.g., diffusion and chemical reactions) are rare, thus require much longer time-scales. Practically choosable time step, MD simulations can not reach long enough simulation times to reveal these rare events. Hence, the results of these simulations can not be compared one-to-one with those obtained from experimental observations.

The time-scale problem of MD simulation is addressed by KMC method [36]. It stresses that one does not need to follow the trajectory for every vibrational period owing to the fact that long-time dynamics involve jumps from one state to another. This
assumption enables KMC method to extend to much longer time scales -- long enough to enable one-to-one comparison with experimental observations. The method uses TST [55], in which only the crossings at the dividing surface are allowed to calculate rate constants for any given path.

There are continuous efforts in advancing the MD method such as accelerated versions of the method with performances higher by several orders of magnitude than those obtained with regular MD technique [54]. These techniques are namely Parallel-Replica (PR), Temperature-Accelerated Dynamics (TAD), and Hyperdynamics. A thorough review of the accelerated techniques has been provided by Voter [107].

In this study, we have employed MD simulation technique to study diffusion of single atoms and clusters (Chapter 4.5), and also to reveal the dynamics of extraction of atoms and manipulation of 2D/3D clusters on Cu(111) and Ag(111), see Chapter 7.

2.7 Transition State Theory (TST)

Transition State Theory provides a useful relation between the activation energy and the associated frequency of an infrequent event. It was first proposed by Marcelin in 1915 [55]. Given the knowledge of possible transition paths, the method provides a way to calculate the rate constants associated with each path. Along the reaction coordinate, there is a well-defined transition-state, which is termed as the saddle-point configuration. The method’s assumptions restrict its applicability to those cases in which the potential energy surface is smooth -- in which the activation energies are larger than the thermal energy, $k_B T$. With a priori knowledge of the transition-states, the rate constants are
computed by determining the flux going into the two sides of the dividing point. Even though it is based on several approximations, TST gives good approximation for the dynamics of rare-events, particularly for that of diffusion events on solids.

Chemical reactions and nucleation in condensed systems are examples of rare events, for which the dynamics are characterized by infrequent transitions between initial and final states. Such a system appears as largely be inactive, spending a long period of time before any transition occurs. Figure 2.7 represents a schematic view of an infrequent event. The right and left sides of the figure show single energy basins (A and C), each of which is connected to an energy basin (B) through saddle points (shown as dots in the figure). In order for a transition to happen from any basin to an adjacent one, the system has to pass through the saddle point by overcoming the associated energy barrier. This happens very rarely owing to the fact that the system stays for a very long time (relative to the timescale for one vibrational period) in a particular basin before any transition occurs. Transition is defined with a rate constant \( k_{BA} \) or \( k_{BC} \), which is the probability per unit time for that transition to take place. The rate constant mostly depends on the shape of the potential energy surface that constitutes to the basin and that of the saddle-point.
Figure 2.7 Schematic view of potential energy contour plot for an infrequent-event. Dots represent the saddle points (transition-states) to be passed to reach a new state (A or C) from the initial basin, (B)

In TST, the rate constant for a transition is described as the equilibrium flux passing through the dividing surface that separates the states (Figure 2.8). The system is seen to be an equilibrium ensemble consisting of many of these states (reduced in the diagram to three). Each state is allowed to perform many transition attempts between itself and the neighboring states. In order to obtain the rate constant $k_{BA}^{TST}$, the number of forward crossings (for example from B to A) is counted, and divided by the number of trajectories. Hence, the assumption of TST is that it restricts the transitions to take place in only one direction “forward crossings”. Each forward crossing of the dividing surface corresponds to an event that leads the system to move from state B to state A. Only crossing is allowed, re-crossing is not allowed. TST differs from MD, in which the
system can cross in each direction, and repeatedly. Realistically, there is always a
possibility for recrossing at the dividing surface. For such cases TST overestimates the
transition rates, which can be corrected using dynamical correction formalism [108].

Figure 2.8 Illustration of a jump with a rate constant of $k_{TST}^{Ba}$. The frequency of the jump
is proportional to $\exp(-E_{\text{static}}/k_B T)$. The solid line presents the dividing surface between
the states. The solid arrow shows the direction of the jump.

The rate of a transition from one state to another in TST is expressed in terms of
the probability density of particles to be located at the two sides of the dividing surface,
and the flux ($f(r)$) passing through that surface. By introducing a microscopic density
($n(r)$) -- the probability of finding a particle at position $r$ -- one can define the rate of
such a transition as:
\[
\kappa^{TST} = \frac{\int f(r) n(r) \, dS}{\int n(r) \, dV}
\]  \hspace{1cm} (2.166)

In order to derive the microscopic density, we assume a Canonical ensemble in which the density is expressed as:

\[
n(r) = \langle \delta(r - R_p) \rangle = \frac{\int d\{R\} \delta(r - R_p) \exp(-E(\{R\})/k_B T)}{\int d\{R\} \exp(-E(\{R\})/k_B T)}
\]  \hspace{1cm} (2.167)

where \( R_p \) is the coordinate of the particle. This is directly derivable from the potential of the mean force expressed in the equation given below:

\[
n(r) = \frac{\exp(-W(r)/k_B T)}{\int dr \exp(-W(r)/k_B T)}
\]  \hspace{1cm} (2.168)

taking the mean force acting on the particle to be \( F(r) = \langle -\nabla_r E(\{R\}) \rangle_r \) and the relation for the potential \( W(r) - W(r0) = \int_{r_0}^{r} F(r') dr' \). The flux in this ensemble is then derived using Maxwell distribution, and is given by:

\[
f(r) = \frac{1}{2} \langle |v| \rangle = \frac{\int_0^\infty dv \, v \exp(-mv^2/k_B T)}{\int_\infty^{-\infty} dv \, \exp(-mv^2/k_B T)} = \frac{k_B T}{2\pi m}
\]  \hspace{1cm} (2.169)

Referring to the equation 2.169 and incorporating the microscopic density and the flux into equation 2.166, one obtains the transition rate, and now expressed as:

\[
\kappa^{TST} = \frac{\int_0^\infty v \exp(-E_x/k_B T) \exp(-mv^2/2k_B T) \, dv}{\int_{-\infty}^{\infty} dx \exp(-V(x)/k_B T) \int_{-\infty}^{\infty} \exp(-mv^2/2k_B T) \, dv}
\]  \hspace{1cm} (2.170)
where $V$ is the potential and $V(\text{saddle}) = E_s$. The contribution to the denominator becomes the greatest when $x \approx 0$. Thus by replacing the potential with the harmonic approximation in which the potential is described as $V(x) \approx 1/2m\omega^2x^2$, we arrive at the following Arrhenius relation:

$$k_{\text{TST}} = \frac{\omega}{2\pi} \exp(-E_s / k_B T) = \nu_0 \exp(-E_s / k_B T)$$  \hspace{1cm} (2.171)

where $\nu_0$ is the prefactor.

A modified version of TST with an additional assumption -- known as Harmonic TST (HTST) or Vineyard theory [109] -- is often employed in KMC simulations. That assumption is that if one accurately defines the potential energy near the basin minimum, the vibrational modes may be treated as harmonic. Hence, for a system of $N$ atoms, there are $3N$ vibrational modes at the minimum energy configuration, and $3N-1$ modes at the saddle point owing to the fact that one degree of freedom is restricted (along reaction coordinate). If one calculates these modes, there should be a single imaginary frequency at the saddle-point configuration. The rate of a transition for a system of $N$ atoms is then expressed as:

$$k_{\text{HTST}} = \frac{\prod_{i=1}^{3N} \nu_i^{\text{min}}}{\prod_{i} \nu_i^{\text{saddle}}} \exp(-E_{\text{static}} / k_B T)$$  \hspace{1cm} (2.172)

where $E_{\text{static}}$ is the static barrier -- the total energy difference between the saddle point and the minimum energy configurations -- $\nu_i^{\text{min}}$ and $\nu_i^{\text{saddle}}$ are the $3N$ and $3N-1$ (non-imaginary) vibrational normal-mode frequencies at the minimum energy and the saddle-point configurations, respectively. For this version, the knowledge of only two
configurations -- minimum energy configuration and the saddle point -- is sufficient to obtain the rates. Even though based on many assumptions the TST method has been shown to describe very well the characteristics of the surface diffusion mechanism.
CHAPTER 3: SURFACE VIBRATIONAL THERMODYNAMICS FROM AB-INITIO CALCULATIONS FOR FCC(100)


We present vibrational dynamics and thermodynamics for the (1 0 0) surfaces of Cu, Ag, Pd, Pt and Au using a real space approach. The force field for these systems is described by DFT. The changes in the vibrational dynamics and thermodynamics from those in bulk are confined mostly to the first-layer. A substantial enhancement of the low-frequency end of the acoustic branch was found and is related to a loosening of the bond at the surface. The thermodynamics of the first-layer also show significant differences (higher heat capacity, lower free energy and higher mean vibrational square amplitudes) from what obtains in bulk. Comparing these results with those calculated using embedded-atom method potentials, we discovered that for Ag(1 0 0) and Cu(1 0 0), the two methods yield very similar results while for Pd(1 0 0), Pt(1 0 0) and Au(1 0 0) there are substantial differences. The chapter consists of the above article and the additional results for the Cu(100) and Ag(100).
3.1 Introduction

In considerations of relative stability of surfaces, nanostructures, as well as bulk phases of different crystallographic orientations, the quantity of interest is the free energy which includes contributions from the structural potential energy and the system’s vibrational and configurational entropy. While the latter is an important constituent for any system containing more than one type of element (alloys), vibrational entropy is the quantity to be evaluated for surfaces and nanostructures of single elements. This is the factor that controls the temperature dependence of surface free energy, mean square vibrational amplitudes of surface atoms, the surface Debye temperature, and the surface heat capacity. It is also the quantity that may determine the equilibrium shape of the crystal surface and its propensity to undergo structural transitions. Knowledge of surface free energy, together with that of the step and kink free energy is also essential for considerations of surface faceting, bunching, and roughening. The extraction of free energy from experimental data is, however, nontrivial [110]. The lattice contribution, which can be critical for determining structural transitions, is non zero, albeit a small fraction of the structural energy. It is thus encouraging to see the flurry of activity in analyzing the contribution of vibrational entropy [111]. Several recent theoretical studies have been devoted to determining the vibrational contribution to the thermodynamic functions for surface systems [21]. These calculations have already provided a qualitative measure of the effect of vibrational entropy on surface stability and structure. They have also set the stage for a systematic evaluation of the local vibrational contribution to the free energy. Since these calculations were based on usage of many body interaction
potentials [50], questions have been asked about their accuracy, particularly for 5d metals Pt, Ir and Au, for which these potentials are not expected to work as well as they do for Ag, Cu, and Ni.

With the availability of *ab-initio* electronic structure methods based on the density functional perturbation theory [112], surface phonon dispersion curves can be drawn with remarkable accuracy [113]. These dispersion curves further lend themselves to the calculation of vibrational density of states and thus of the vibrational contribution to surface free energy and entropy. Our interest in the present study is to analyze the thermodynamic properties of the (100) surface of several metals and to compare the findings with those obtained earlier using potentials from the EAM [50]. We first carry out an analysis of the interatomic surface force-constants obtained from the *ab-initio* methods to examine the range of the interaction, and for comparison with those obtained from EAM. As is known, EAM potentials are relatively short ranged and do not extend to interactions beyond the fourth neighbor. These potentials are well-suited for the six transition metals (Ag, Cu, Ni, Pd, Pt, and Au) and numerous efforts have been made to develop such potentials for a number of other metals and metallic alloys [61]. Out of these six metals, we restrict our study to the five nonmagnetic systems, with the awareness that Au(100) and Pt(100) undergo a hexagonal surface structural transition [114]. However, for the purpose of the present study we use the results available for the surface phonons of the unreconstructed surface [113].

In section 3.2 we will present the details of the calculations. In sections 3.3 and 3.4 we discuss the results. In section 3.5 we compare the vibrational dynamics,
thermodynamics and the force constants obtained from DFT with those from EAM. In section 3.6, we present overall conclusions.

3.2 Calculation of Vibrational Densities of States (VDOS) and Thermodynamic Functions

We have used the force-field results obtained from an early DFT study whose authors calculated the structure within the mixed basis (MB) pseudopotential representation [115]. A density perturbation theory [116], as adapted for the MB representation [117], was used to evaluate the force-constants. The complete description of the calculation of the structure and force constants can be found in Ref. 113. We have also performed calculations to obtain these force-constants using EAM. Using these force-constants, we have performed calculations to determine the vibrational and thermodynamical properties of these (100) surfaces.

The vibrational modes and the density of vibrational states can be obtained from lattice dynamics calculations [118] or molecular dynamics simulations [119]. Lattice dynamics methods can be further classified into those based on real space and those based on reciprocal space. Using a reciprocal-space based method; Heid and Bohnen have calculated the dispersions of different modes for the systems mentioned [113]. In the present study, we use a real-space based method, more suitable for calculating directly the local vibrational densities of states (LVDOS) hence the corresponding local thermodynamics quantities. The force constants used in the present DFT part of the study were extracted from the results of the calculations by Heid and Bohnen [113], while the
force constants used in the EAM part are evaluated through the direct calculation of the partial second derivatives of the potential.

The LVDOS can be calculated using the continued fraction method (CF) based on the real space. In this method, the surface matrix is treated as a perturbation to the bulk and the surface Green’s function is obtained by projecting the bulk Green’s function into the subspace defined by the perturbation matrix. If the interest lies in gaining insights into the local contributions to the dynamics and thermodynamics of systems possessing site specific environments, a local approach in the real space is perhaps more useful than one based on k-space. The real-space Green’s function (RSGF) method is one such method [52]. Instead of wave vectors and Brillouin zones, one can focus on any ‘local’ region and analyze the effect of the rest of the system on it, recursively. Since this method does not require the system to be periodic, it is particularly suitable for studying local vibrational density of states of the systems with defects and disorder. The only prerequisite is that the inter-atomic potential between the atoms in the system be of finite range, to enable writing the force constant matrix in a block-tridiagonal form. There is also no a priori truncation in the system size, as would be the case for the matrix diagonalization methods based on k-space. The real space Green’s function method also has an advantage over the familiar “continued fraction” method [52] in that it does not involve truncation schemes to determine the recursion coefficients, but applies a more general and simpler recursive scheme. The details of how RSGF method works are extensively discussed in Chapter 2.3 hence will not be repeated here. Also, the calculation of thermodynamical functions are extensively discussed, the reader is suggested to refer to (Chapter 2.4).
For the calculations performed using EAM, we have constructed a system of 10x10 atoms for each layer with total of 20 layers. The system total energy is optimized using CG method [91], and force constants are determined from the second derivative of the potential. The resulted force constants matrix (here as the Hamiltonian) is used as input to construct the Green’s function by following the steps discussed in Chapter 2.3. The method is employed in a layer-by-layer manner (Figure 3.1), viewing an infinite system with in-plane periodicity as two-dimensional atomic layers stacked one upon the other along the axis normal to the planes.

![Figure 3.1 A schematic view of layer-by-layer manner application of RSGF method](image-url)

Once the local vibrational density of states is calculated, the local thermodynamic functions of the systems namely the vibrational free energy, the lattice heat capacity, and
the vibrational mean-square atomic displacements can be determined (in the harmonic approximation, as discussed in Chapter 2.4).

### 3.3 Structure and Force Constants

The results of the relaxations for Ag, Cu, Pd, Pt and Au(100) surfaces using DFT and EAM are presented in Table 1, and compared with previous calculations and experimental data when available [120-130]. For both Cu(100) and Ag(100), the calculated contraction between the first and second layer is larger than the experimental observations, except for the case of Cu(100) using EAM, for which a remarkable agreement is achieved with data. For Cu(100), the corrected effective medium theory calculations [128] show a large deviation from the other DFT based values (Table 3.1). For Pd, Pt and Au(100), all DFT-based calculations show a modest contraction between the first and second layer, while EAM potentials predict rather larger values (by a factor of about four or larger). This is an indication that additional physical properties of these three surfaces as calculated using DFT will reveal differences from those calculated using EAM.
Table 3.1 The calculated surface relaxation ($\Delta d_{ij}$) from DFT and EAM, $\Delta d_{ij} = 100(d_{ij} - d_0)/d_0$. $d_{ij}$ is the interlayer spacing between the atomic layers $i$ and $j$. $d_0$ is the interlayer spacing in the unrelaxed surface.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>$\Delta d_{12}$ (%)</th>
<th>DFT (EAM) present study</th>
<th>$\Delta d_{12}$ others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(100)</td>
<td>-2.1 (-1.9)</td>
<td></td>
<td>-1.4[120] -1.9[121,127]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1.9[122] 0±0.03[123*]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2.9[124] -1.4[125]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-3.0[126] -3.5[122]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-6.0[128] -1.1±0.40[129*]</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>-3.0 (-1.4)</td>
<td></td>
<td>-1.4[124]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-2.9[125] -3.0[126]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-3.5[122] -6.0[128]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-1.1±0.40[129*]</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>-1.3 (-4.5)</td>
<td>-0.6[121]</td>
<td>-1.2[130]</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>-2.3 (-6.9)</td>
<td>-2.2[130]</td>
<td>-1.0[127]</td>
</tr>
<tr>
<td>Au(100)</td>
<td>-1.6 (-6.0)</td>
<td>-1.2[84]</td>
<td></td>
</tr>
</tbody>
</table>

*Experimental data

For the calculation of the vibrational dynamics, since we will be using a method that assumes a finite interaction range, a truncation on the number of neighbors is necessary. Because knowledge of the interaction range is not available a priori, one needs to investigate this effect for every element in order to achieve high accuracy. For this purpose, we introduced a simple quantity to identify the “strength” of the interaction between neighbors via force constants. This force constant strength (fcs) is evaluated in equation 3.1 as the maximum strength for a given level of neighbors (the maximum is chosen over the average in order not to exclude a possible case for which one particular $n^{th}$ neighbor has exceptionally large strength). The force constant strength also helps us
decide how extensive a neighborhood we need to consider for a particular system. The
force constant strength is calculated between the atoms (i, j) that are \( n \)th neighbors; where
\( n \) can be anything between the 1st and 20th neighbor. For the \( n \)th neighbor, we define the
force constant strength as:

\[
(fcs)_n = \text{Max} \left[ \sum_{\alpha, \beta} \left( K_{i,j}^{\alpha,\beta} \right)^2 \right]
\]

where \( \alpha \) and \( \beta \) are x, y or z. We normalize the force constant strength by that of the 1st
neighbors and designate the result as relative strength (Rfcs). The DFT calculations for
(100) surfaces presented in Ref. 113 are the basis of these analysis.

![Diagram](image.png)
Figure 3.2 Relative force constant strength versus neighbors calculated using DFT for (a) Ir(100), Rh(100), Pd(100) and Pt(100) (b) Au(100), Ag(100) and Cu(100).

The Rfcs for Rh, Ir, Pd, and Pt(100) are presented in Figure 3.2.a, and for Ag, Au and Cu(100) in Figure 3.2.b. As one may note from Figure 3.2, the Rfcs decreases very rapidly with neighbors; hence their values are presented in a log scale. In Figure 3.2.a, one notes that the second nearest neighbor contribution is less than 20%, while it is less than 10% for those represented in Figure 3.2.b. For all cases, the contribution of the 5th neighbors is of the order of 2%. Contribution of yet higher-order neighbors is less than 2% for all the cases with the exception of the 9th-neighbor contribution for Rh and Ir(100) for which the Rfcs is about 10%. If the contribution of the neighbors with Rfcs less than or equal to 2% is neglected, we can classify these systems into two categories: the first consists of Ag, Au, Cu, Pd and Pt(100) (up to 5th neighbors) and the second one including
Ir and Rh(100) (up to 5\(^{th}\) neighbors plus the 9\(^{th}\)). In this work, we will present a detailed study of the vibrational dynamics and thermodynamics of the elements in the first category.

3.4 Results and Discussions

We will first present the DFT results on the LVDOS (the locality here being an atom in a given layer) for each surface and analyze mainly the differences between the first- and the fourth-layer LVDOS, since the latter is bulk-like. Attention paid mainly to the low- and high-frequency ends of the vibrational spectra. We then turn to the corresponding thermodynamic functions, and discuss the differences between surface and bulk-like behaviors. Finally, the aim is to correlate these with an analysis of the differences between the force constants at the surface, and with bulk. In the figures, in addition to the results for Pd, Pt and Au(100), we also illustrate those for Cu and Ag (100) for comparison purposes. Note that the vibrational and thermodynamical properties of these two surfaces are studied earlier using EAM [131].

3.4.1 Local Vibrational Densities of States (LVDOS)

The layer resolved vibrational density of states for the first to fourth layers are presented in Figures 3.3.a-e for Cu, Ag, Pd, Pt and Au(100), respectively. Note from these figures that the LVDOS corresponding to the first layer is remarkably different from those corresponding to second, third and the fourth layers. Hence we focus on the analysis of the LVDOS only on the first layer. With creation of a (100) surface, a first
layer atom has coordination 8, resulting from a loss of 4 neighbors. The effect of this loss causes loosening of the bond, resulting in softening of the in-plane force constants in the first layer. The softening of the force constants yields a shift towards lower frequencies.

This feature is characteristic of all the five elements subject of this study and illustrated in Figures 3.3.a-e for Cu, Ag, Pd, Pt and Au(100). This is not a global shift of the density of states but rather a relatively important depletion of the high-frequency band accompanying an enhancement of the low-frequency band. As the figures make plain, these effects are marginal for the second-layer atoms and are absent for the third and fourth layers.
3.4.2 Thermodynamic Functions

As a consequence of the observed features in the LVDOS discussed in the previous sub-section, we expect deviations in the thermodynamics from the bulk values to be localized at the top layer atoms. This is in line with findings reported in earlier publications on the vibrational dynamics and thermodynamics of vicinal and kinked fcc metal surfaces using EAM potentials [131,132]. The quantities of interest here are the
lattice heat capacity (local and excess), the contribution of the vibrational dynamics to the free energy (local and excess) and the mean square displacement. We present in Figures 3.4, 3.5, 3.6, 3.7 and 3.8 the local and excess thermodynamical functions for Cu, Ag, Pd, Pt and Au(100), respectively. As shown in Figures 3.4.a, 3.5.a, 3.6.a, 3.7.a and 3.8.a, the local lattice heat capacity (C_v) of the first-layer atoms differs from that of the other atoms in the system and it is temperature dependent. These differences are better described by the local excess from the bulk as illustrated in Figures 3.4.b, 3.5.b, 3.6.b, 3.7.b, and 3.8.b. Indeed, for Pd and Pt(100), the maximum deviation was found to be 3.4 and 2.8 JK\(^{-1}\)mol\(^{-1}\), respectively, both occurring at a temperature of 50K. However, the first-layer atoms of Au(100) behave differently; with a maximum deviation of only 2.2 JK\(^{-1}\)mol\(^{-1}\) occurring at a lower temperature (30K).

Let us now turn the attention to the local and excess vibrational free energy. The results are presented in Figures 3.4.c-d, 3.5.c-d, 3.6.c-d, 3.7.c-d, and 3.8.c-d, for Cu, Ag, Pd, Pt and Au(100), respectively. Here again, only the first-layer atoms show differences from the atoms in the other layers. As shown in the figures, the local contributions to vibrational free energies for the layers beyond the second converge to the corresponding bulk values. For the atoms in the first layer, the local contribution to the vibrational free energy decreases with temperature and reaching -48, -64 and -79 meV/atom for Pd, Pt and Au(100), respectively at 300K. The excess vibrational free energies are significantly different for the first layer atoms as can be seen in Figures 3.6.d, 3.7.d, and 3.8.d, with the contribution amounting 19, 17 and 14 meV/atom at 300K. Our DFT calculations for Cu and Ag(100) show 15 meV/atom, which are in good agreement with the EAM results (about 18 meV/atom for both surfaces at 300K).
In the harmonic approximation, the vibrational mean square amplitude (VMSA) is expected to vary linearly with temperatures. Note that at 0K, the VMSA does not go to zero due to the zero point motion. In Figures 3.4.e, 3.5.e, 3.6.e, 3.7.e and 3.8.e, we present our DFT results for the VMSA of Cu, Ag, Pd, Pt and Au(100), respectively. The VMSA of the atoms in the third and fourth layers are bulk-like (0.008, 0.0075, and 0.0130 Å² at 300K for Pd, Pt and Au(100), respectively). Through VMSA of the second layer atoms is close to the bulk values, that corresponding to the first-layer atoms shows large deviations. The ratio between the first layer and the bulk VMSA is 2.06, 1.73, and 1.73 for Pd, Pt and Au(100), respectively. This deviation is due to the decrease of coordination at the surface as compared to the bulk. Note that the ratio is the same for Pt and Au(100) and the highest for Pd(100), reflecting the mass effect.
Figure 3.4 The thermodynamic functions for Cu(100): a) lattice heat capacity b) excess lattice heat capacity c) vibrational contribution to the free energy d) excess vibrational contribution to the free energy and e) vibrational mean square amplitude
Figure 3.5 The thermodynamic functions for Ag(100): a) lattice heat capacity b) excess lattice heat capacity c) vibrational contribution to the free energy d) excess vibrational contribution to the free energy and e) vibrational mean square amplitude
Figure 3.6 The thermodynamic functions for Pd(100): a) lattice heat capacity b) excess lattice heat capacity c) vibrational contribution to the free energy d) excess vibrational contribution to the free energy and e) vibrational mean square amplitude
Figure 3.7 The thermodynamic functions for Pt(100): a) lattice heat capacity b) excess lattice heat capacity c) vibrational contribution to the free energy d) excess vibrational contribution to the free energy and e) vibrational mean square amplitude
Figure 3.8 The thermodynamic functions for Au(100): a) lattice heat capacity b) excess lattice heat capacity c) vibrational contribution to the free energy d) excess vibrational contribution to the free energy and e) vibrational mean square amplitude
3.5 Comparison between the Results of DFT and EAM

The physical properties of interest in this study depend intimately on the local details of the interactions that describe the system at hand. Indeed, the vibrational dynamics, hence the corresponding thermodynamics, emerge from treatments of the partial second derivatives of the potential. Comparison between two potentials at this level is expected to reveal important differences inherent to the different classes of potentials (first principles versus semi-empirical). We start out with comparison by means of presenting the changes in some key force constants and correlate these changes with differences in the LVDOS and corresponding thermodynamics.

3.5.1 Force Constants

A complete analysis of the changes in the force constants for each system is possible but not necessary. We choose to present the changes (with respect to bulk) in the two most affected force constants (matrix elements), namely the ones connecting two neighbors that are in the first layer ($K_{11}$, corresponding to the matrix element $K_{\alpha\alpha}$ where $\alpha$ (x or y) can be chosen to host both surface atoms) and two neighbors in the first and the second layer ($K_{12}$, corresponding to the matrix element $K_{zz}$, where $z$ is the direction perpendicular to the surface). Note that a positive value reflects stiffening, while a negative reflects softening of the force constants.
Table 3.2 Percentage change in the force constants (in-plane and perpendicular to the plane) from DFT and EAM

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>$\Delta K_{11}$ DFT (EAM)</th>
<th>$\Delta K_{12}$ DFT (EAM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(100)</td>
<td>-10.8 (-17.9)</td>
<td>16.8 (21.2)</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>-11.0 (-14.5)</td>
<td>22.7 (13.5)</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>-30.5 (-33.0)</td>
<td>7.8 (34.0)</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>-39.3 (-48.8)</td>
<td>15.0 (54.9)</td>
</tr>
<tr>
<td>Au(100)</td>
<td>-25.7 (-42.6)</td>
<td>8.7 (59.5)</td>
</tr>
</tbody>
</table>

In Table 3.2, the changes in the force constants are summarized for the five surfaces studied. Let us first analyze the changes as calculated using DFT and highlighting the elemental effect. The softening in the in-plane force constants ($K_{11}$) is caused by the loss of four neighbors experienced by the first-layer atoms and, as one notes, it is very large for Pd, Pt and Au(100). For $K_{12}$, we note that the largest changes are found for Cu, Ag and Pt(100), owing to the relatively large contraction (shortening of the bond between atoms in the first and second layers) of $d_{12}$ (see Table 3.1). Let us now compare the changes in the force constants as calculated using DFT and EAM. As one may have already noted from Table 3.1, the interlayer contractions calculated using DFT differ notably from those calculated using EAM for Pd, Pt and Au(100). This in turn reflects the large discrepancies in $\Delta K_{12}$ for which the ratio between the EAM and DFT values is 4.5, 3.7, and 6.8 for Pd, Pt and Au(100), respectively. On the other hand, because the change in $K_{11}$ is due to the loss of neighbors (four), which is independent of the choice of the potential, we expect differences between DFT and EAM to be less dramatic than for $K_{12}$. Indeed, these differences stand at a ratio less than 2 (Table 3.2).
3.5.2 Local Vibrational Densities of States (LVDOS)

In Figures 3.9-3.13, we present the comparison of the LVDOS for Cu, Ag, Pd, Pt and Au(100), for the first, second and the fourth layers as calculated from DFT and EAM. As is discussed above, the LVDOS features for the layers above the second represent bulk-like behavior. We find the calculated LVDOS under DFT for Cu and Ag(100) to be very close to those produced by EAM. For these systems, the top of the bulk band is 0.5THz higher for DFT than for EAM. This shows that the vibrational dynamics for copper and silver can be well described using EAM.

However, for Pd, Pt and Au (100), as shown in Figures 3.11.c, 3.12.c, and 3.13.c, the top of the band for the fourth layer (hence for the bulk atoms) is substantially higher for the spectrum calculated using DFT than for that using EAM. For Pd(100) (Figure 3.11.c), the top of the DFT-band is higher (1.2 THz) than that of the EAM-band. We also note that the ratio (relative intensity) of the top of the high frequency band to the top of the low-frequency band is 1.08 and 1.29 from DFT and EAM, respectively. The same trend can be seen for both Pt and Au(100) in Figures 3.12.c and 3.13.c, respectively. The results calculated using DFT show that the top of the band are 1.2 and 1.0 THz higher than those derived from EAM for Pt and Au(100), respectively. We find the ratio between the top of the two frequency bands to be 1.09 and 1.07 (from DFT) and 1.52 and 1.31 (from EAM) for Pt and Au(100). Similar to the LVDOS features for the fourth layer, we find for the second layer that the top of the frequency band calculated using DFT is about 1THz higher than the EAM results, for each surface (Figures 3.11.b, 3.12.b, and 3.13.b). Interestingly, the comparison of the LVDOS results from DFT and EAM for the
first layer shows less pronounced deviations from each other as compared to the rest of the layers mentioned above.

Figure 3.9 Comparison of the LVDOS from EAM and DFT for Cu(100): a) Layer 1 b) Layer 2 and c) Layer 4
Figure 3.10 Comparison of the LVDOS from EAM and DFT for Ag(100): a) Layer 1 b) Layer 2 and c) Layer 4
Figure 3.11 Comparison of the LVDOS from EAM and DFT for Pd(100): a) Layer 1 b) Layer 2 and c) Layer 4
Figure 3.12 Comparison of the LVDOS from EAM and DFT for Pt(100): a) Layer 1 b) Layer 2 and c) Layer 4
Figure 3.13 Comparison of the LVDOS from EAM and DFT for Au(100): a) Layer 1 b) Layer 2 and c) Layer 4
3.5.3 Free Energies

In Table 3.3, comparison between the DFT and EAM results for the vibrational contribution to the free energy at 5, 100 and 300K for the first and the second layers is presented. From the table, it is clear that for both Cu and Ag(100), the calculated contribution to the free energies from DFT and EAM are in good agreement. We find at most 6 meV/atom deviation (for copper, for the first layer) between the EAM and DFT results at 300K. The agreement between the EAM and DFT results for the thermodynamical functions can be traced to the excellent agreement in the vibrational dynamics (both for bulk and at surfaces), as discussed above. However, the vibrational contribution to the free energy (first layer) at 300K for Pd, Pt and Au(100) is found to deviate by more than 15meV/atom for each surface, the highest being for Pt(100). The contribution is found to be larger for EAM than for DFT. The vibrational contribution to the free energy (at relatively low temperature) is controlled by the low-frequency end of the vibrational spectrum hence future analysis of this region may explain the large deviations between the EAM and DFT results. Figures 3.11.a, 3.12.a, and 3.13.a show a more pronounced enhancement of the low-frequency band for EAM than for DFT results. Of the three elements, the deviation between the EAM and DFT results (first layer) at the low frequency end of the spectrum is the largest for Pt(100).
Table 3.3 Vibrational contribution to the free energy (meV) for layer 1 and layer 2 at 5K, 100 K and 300 K.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>Temperature (K)</th>
<th>DFT (EAM) 1st Layer</th>
<th>DFT (EAM) 2nd Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(100)</td>
<td>5</td>
<td>0.018 (0.018)</td>
<td>0.022 (0.022)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.008 (0.008)</td>
<td>0.015 (0.015)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.066 (-0.067)</td>
<td>-0.050 (-0.048)</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>5</td>
<td>0.027 (0.025)</td>
<td>0.032 (0.031)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.022 (0.019)</td>
<td>0.029 (0.027)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.033 (-0.039)</td>
<td>-0.017 (-0.020)</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>5</td>
<td>0.022 (0.019)</td>
<td>0.029 (0.024)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.015 (0.010)</td>
<td>0.024 (0.018)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.048 (-0.062)</td>
<td>-0.027 (-0.043)</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>5</td>
<td>0.018 (0.015)</td>
<td>0.024 (0.018)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.009 (0.002)</td>
<td>0.017 (0.009)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.064 (-0.083)</td>
<td>-0.044 (-0.064)</td>
</tr>
<tr>
<td>Au(100)</td>
<td>5</td>
<td>0.015 (0.013)</td>
<td>0.018 (0.016)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.003 (0.002)</td>
<td>0.009 (0.004)</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>-0.079 (-0.095)</td>
<td>-0.065 (-0.077)</td>
</tr>
</tbody>
</table>

3.6 Conclusions

We have calculated the force constants between neighbors up to the 20th order using density functional perturbation theory. These force constants are then used to calculate the vibrational dynamics and thermodynamics of five surfaces Ag, Cu, Pd, Pt and Au(100). The changes, from the bulk, in the local properties of these surfaces were found to be confined mainly to the first-layer atoms. The vibrational dynamics of all these surfaces (Cu, Ag, Pd, Pt and Au(100)) show analogous qualitative behaviors with a substantial reshuffling of the densities of states. The low-frequency end of the spectrum is enhanced at the expense of the high frequency range, resulting in a lower contribution to the vibrational free energy as compared with that of the bulk. The vibrational mean
square amplitudes for atoms in the first layer were found to be as much as twice those in the bulk. When comparing results using density functional theory with those using embedded atom method potentials, we found that the two methods yield very close results for silver and copper. However, for palladium, platinum and gold, the embedded-atom method describes very poorly the interactions in these systems and thus delivers misleading picture of their vibrational dynamics and thermodynamics.
CHAPTER 4: MULTI-SCALE MODELLING OF HOMO- AND HETERO-EPITAXIAL DIFFUSION ON METAL SURFACES

4.1 Diffusion Barriers for Ag and Cu Adatoms on the Terraces and Step Edges on Cu(100) and Ag(100)

- Handan Yildirim and Talat S. Rahman, “Diffusion barriers for Ag and Cu adatoms on the terraces and step edges on Cu(100) and Ag(100): An ab initio study”, Phys. Rev. B 80, 235413 (2009)

We present the results of density functional theory based calculations for the activation energies for the diffusion of adatoms (Cu or Ag) on Cu(100) and Ag(100) with and without steps. We find that only for Cu on Ag(100), exchange is the dominant mechanism for the diffusion on terraces. On the other hand, for diffusion at step edges, exchange is the dominant mechanism except for Ag on Cu(100). This result also indicates that incorporation of Cu atoms into the step edges of Ag(100) costs only 330 meV, while the energy cost for Ag incorporation into Cu(100) step edge is much higher (about 700 meV). We find the hierarchy of Ehrlich-Schwoebel barriers to be: 170 meV for Ag on Cu(100); 60 meV for Cu on Cu(100); 20 meV for Ag on Ag(100), and $-30$ meV ($-270$meV) for Cu on Ag(100). These barriers point to a striking difference in the growth modes for Ag layers on Cu(100) and Cu layers on Ag(100).
4.1.1 Introduction

Understanding thin film growth (growth mode, morphology, etc.) on metal surfaces has been the goal of investigations by both experiment and theory [133] for more than a decade because of the potential applications in electronic devices, chemical reactions and catalysis [134]. This effort has intensified with the introduction of powerful experimental tools such as STM and AFM that are used to see surfaces and to manipulate atoms, clusters, and molecules so as to control diffusion, other reactions and microscopic events [135]. The morphology of thin films, and the size, density and shape of adatom islands on surfaces can be altered by controlling the external growth parameters, such as deposition rate of atoms, substrate temperature and coverage, and by the introduction of defects and surfactants (see [136] and references therein). Though it is a challenge to obtain a comprehensive picture of all parameters that govern growth of thin films, it is possible to proceed with a controlled study of the effect of each parameter on the growth mode and the end products. Towards this end, the last decade witnessed a great deal of effort in the determination of diffusion parameters on single crystal surfaces [137]. In particular there has been a focus on understanding self diffusion via hopping [27] in which an adatom diffuses on the surface from one equilibrium position to the next, or via exchange [27] in which an adatom replaces its position with a surface atom which then becomes an adatom at the next binding site. Research in the area still continues because the complexity of the phenomena has left several unresolved issues even for the simple case of diffusion by hopping (see [138, 139] and references therein). As is well known, steps and kinks play an important role in determining the energetics and the dominant
diffusion mechanism for adatoms on surfaces. Exchange, for example, may dominate at a step edge but not for diffusion on terraces [140]. At the step edge there is also the issue of an additional activation energy barrier, the E-S [25, 26], which corresponds to the extra energy needed for an adatom to diffuse from an upper terrace to the layer below at a step edge. The existence of this barrier prevents downward diffusion and has been shown to lead to a morphological instability [141] resulting in the formation of mounds. The presence of this barrier also presents a good rationale for three dimensional growth, while the lack of it is expected to lead to layer by layer growth [26].

Diffusion being a “rare” event leads to shortcomings in both theory and experiment in accurate determination of its parameters. Diffusion coefficients, which comprise of pre-exponential factors and activation energies, are case in point since their theoretical evaluation requires a detailed and accurate knowledge of surface energetics and vibrational dynamics [90, 138, 142]. While experimental techniques have to be sensitive to subtle changes in energetics (meV range) and dynamics over long time scale (millisecond), in theory and modeling the focus has been mostly on extraction of activation energy barriers, although recipes are available [143] for calculation of the prefactors. Understandably most of the work so far has concentrated on homo-epitaxial systems. Of the two surfaces of interest here, Ag(100) and Cu(100), numerous theoretical studies of self diffusion on the terraces exist. For diffusion via hopping of Ag adatoms on Ag(100), first principles calculations based on DFT [144, 145, 126] find the energy barrier to be between 0.45 eV and 0.60 eV, while various model potentials find it to lie in the range 0.46-0.48 eV [146-148] to be compared with experimental findings of 0.40 eV [149] and 0.35 eV [150]. For the exchange mechanism, barriers are found to be
somewhat higher (between 0.62 eV and 0.78 eV) in theoretical calculations [144,145,146-148], while experiments report it to be 0.46 eV [150]. Interestingly, theoretical results for the energy barriers for diffusion via hopping of Cu adatoms on Cu(100) also lie in the range of 0.48-0.69 eV [90, 138, 145, 146, 151-153], while the range of experimental values is between 0.28 eV and 0.40 eV [154-156]. The energy barrier for diffusion of Cu adatoms on Cu(100) via exchange is, on the other hand, found to be much larger, close to 1 eV, in first principles calculations [138,145,151], and between 0.69 eV and 0.80 eV in results based on model interaction potentials [152, 153, 157]. To our knowledge there is no experimental data on exchange mediated self diffusion on Cu(100). In short, the above theoretical results indicate a preference for adatom diffusion to proceed via hopping on terraces of Cu(100) and Ag(100).

Attention has also been paid to evaluations of the E-S barriers for these two surfaces in the presence of step edges. For Ag adatoms at the step edge of Ag(100) first principles calculations find the E-S barrier for exchange to be 0 meV, and that for hopping to be 100 meV [144], signifying the importance of the former. Semi-empirical methods find the barrier via hopping to lay in the range 110-220 meV [148, 158, 159], while the barrier via exchange is between 30 meV and 160 meV [148, 158, 159]. Experimental studies report homo-epitaxial growth on Ag(100) to proceed layer-by-layer and the E-S barrier to lie in the range 30-70 meV [160]. These results nicely illustrate the correlation between layer-by-layer growth and almost vanishing E-S barrier. The growth mode on Cu(100) is, however, more puzzling. Experimental observations [161, 162] report a 3D growth mode along with the presence of mounds. Model potentials find the E-S barrier via hopping to lie in the range 125-320 meV [90, 152, 157-159, 163], while
that via exchange is between 30 meV and 130 meV [152, 158, 159]. If the values of the exchange E-S barrier are correct, one would expect the growth mode to be layer-by-layer also for Cu(100), unless prefactors for the processes are significantly different from the normal (10⁻³ cm²/s). To our knowledge there is no reported first principles value of the E-S barrier for Cu adatoms on Cu(100). Although from the values of the energy barriers cited above, there appear to be no systematic difference between the results from ab-initio electronic structure calculations and those based on model interaction potentials, and that the latter may at times give better agreement with experiment than the former, it would still be interesting to find this barrier using DFT.

Attention has recently turned also to examination of the diffusion of adatoms and small clusters for hetero systems. For the hopping of Cu adatoms on Ag(100), Tight Binding (TB) [146] and DFT [164] calculations find the activation energy barrier to be about 0.60 eV. For Ag adatoms on Cu(100), model interaction potentials and TB studies reported the barrier to lie in the range 0.39-0.48 eV [146,165,166]. In a recent simulations using TB-SMA scheme [167] for the growth of silver shells on copper and palladium nanoclusters, the diffusion of Ag adatom on the (100) facets of the truncated octahedron Cu nanoparticle reported the diffusion via jump to be 0.28 eV. Another study [168] using Rosato–Guillopé–Legrand (RGL) potentials showed the diffusion barrier for Ag atoms on the (100) facets of polyhedral Ag clusters to be 0.43 eV. At the same time Reflection High Energy Electron Diffraction (RHEED) measurements of Cu deposition on Ag(100) showed that the growth mode is layer by layer [169]. For Cu on Ag(100), the simulations using Temperature Accelerated Dynamics (TAD) [164, 170] predicted downward diffusion at low temperatures (77K). For these hetero systems, there are no reported
experimental results for the E-S barriers. To the best of our knowledge, first principles calculations have not also been carried out for the diffusion of Ag adatoms on Cu(100) terraces, nor have they been performed for that of Cu adatom on Ag(100) via exchange.

In view of the above, we have carried out first-principles calculations of the activation energy barriers for the diffusion via hopping and exchange of Cu and Ag adatoms on Cu(100) and Ag(100), for both homo-and hetero-epitaxial systems, with and without steps. For comparison and completeness, we have included in our calculations also those processes for which calculated barriers already exist, as noted above. We have also tested the sensitivity of the results to the size of calculation supercell in order to extract as accurate a value for the diffusion barriers as feasible.

The chapter is organized as follows. In section 4.1.2 we describe the method and the calculation details. In section 4.1.3-4.1.5 we present the findings for the diffusion on the (100) terraces for homo-and hetero-epitaxial systems. We also discuss atomic relaxations and the bond lengths between the adatom and its neighbors at terraces and present the charge density distributions and differences for each system. In section 4.1.6-4.1.8 we will present the results for adatom diffusion near the step edges. Finally, in section 4.1.9 we present the conclusions.

4.1.2 Method and Details of the Calculations

We perform total energy electronic structure calculations using DFT [48] and the pseudopotential method as implemented in the computational code Vienna ab-initio simulation package (VASP) [171] for both homo-and hetero-epitaxial diffusion of an adatom on terraces and near step edges of Cu(100) and Ag(100). For the electron
exchange-correlation functional, we choose the two most popular functional of the
generalized gradient approximation (GGA), PW91 [78] and PBE [79]. We use plane
wave basis set providing kinetic energy up to 18 and 20 Ry for Ag and Cu, respectively.
According to our calculations, the bulk lattice constants are 4.17 Å (4.18 Å) and 3.64 Å
(3.66 Å) for Ag and Cu using PW91 (PBE), respectively.

For adatom diffusion on the (100) terraces, we construct the surface cell with five
atomic layers. In order to study the possible size effect on the diffusion barriers, we
choose the cell periodicities in the surface plane as 2x2, 3x3, 4x4 and 5x5. For each
calculation, a vacuum of 12-14 Å is used. All atoms in the top four layers are relaxed to
their equilibrium positions while keeping the last layer fixed (all forces having converged
to 0.01 eV/Å). We perform calculations using mainly PW91 and repeat some with PBE.
There is at most a 20 meV difference in the diffusion barriers calculated with these two
functional. In accord with earlier studies [138, 144], we also find that a basis with higher
(about 30%) energy cutoff changes the diffusion barrier by about 10-20 meV. As stated
in earlier investigations [138, 144, 172] increasing the number of k-points also introduces
a 20 meV maximum difference in the diffusion barriers, while changing the periodicity in
the surface plane from 2x2 to 5x5 introduces negligible deviations (10 meV) in the
diffusion barriers.

For the calculations of the diffusion barriers near the step edges via hopping, we
use a surface cell with four atomic layers and periodicities of 3x3, 4x3, 3x4 and 4x4 for
the stepped layer and that of 5x3, 6x3, 5x4 and 6x4 for that substrate below. The reason
for repeating the calculations for different step-substrate periodicities is to determine any
effect on the calculated barriers of spurious interactions introduced by periodic boundary
conditions. However, questions have been raised regarding the dependence of the calculated energy barriers (via exchange) on the size of the supercell. It is known that both diffusion mechanisms introduce some level of distortion of the lattice (both lateral and vertical), although much larger distortions are caused by exchange than by hopping. Not surprisingly calculated results depend on the robustness of the model systems. For example, for some metal surfaces [172], at least 25% decrease in the exchange diffusion barriers may be obtained by simply changing the number of layers or the number of active atoms on the surface [145, 147, 172]. To test the effect of the supercell size, we perform calculations for the diffusion (via exchange) near the step edges using 6x3-3x3 and 5x4-3x4 substrate-step periodicities. For the exchange process on (100) terraces, by taking the hint from previous calculations [145, 147, 172], we perform calculations using 5x5 cell.

To calculate the barriers for processes near step edges such as descent over the step and along the step (on a lower terrace), we introduce a close-packed \{111\}-faceted step (infinite stripe) running along \langle110\rangle direction as is sketched in Figure 4.1.a. For descent over the step, we determine the transition state configuration by placing the adatom first at position A (4-fold site) in Figure 4.1.a, and subsequently moving it perpendicular to the step by small increments along the diffusion direction with an applied constraint. We minimize the total energy of the system at each point (between 10 to 15 points) until the adatom reaches the next minimum energy configuration (position C in Figure 4.1.a). In accord with earlier studies [90, 144] we find the transition state to be slightly (~ 0.6 Å) beyond the exact bridge site (position B in Figure 4.1.a). One of the key diffusion processes for epitaxial growth is the diffusion along a step edge on a lower
terrace, since the height of this barrier determines how steps will evolve (the shape of steps) on the surface as atoms are deposited [144]. In order to simulate this process, we place the adatom on the lower terrace at the position C and move it towards the position D in Figure 4.1.a, with small increments along the direction of diffusion. Again, for each step between two equilibrium positions, we minimize the total energy of the system to determine the transition state configuration and hence the height of the corresponding diffusion barrier.

4.1.3 Adatom Diffusion on Terraces

Table 4.1 summarizes the results of calculations of adatom diffusion barriers via both hopping and exchange mechanisms. In Table 4.1 we also include the results for the bond lengths and binding energies. Table 4.1 shows an interesting trend in the barriers (via hopping) on the (100) terraces. It is the lowest for Ag on Cu(100) (0.37 eV) and the highest for Cu on Ag(100) (0.60 eV). The barriers for the homo systems are in good agreement with earlier theoretical calculations which were summarized above. In addition to the differences in the electronic interactions, the large difference in the barriers for Cu adatom on Ag(100) and Ag adatom on Cu(100) may be traced to the effect of compressive versus tensile strain on the diffusion. Here the case of Ag adatom on Cu(100) is an example of diffusion on a compressive-strained lattice: an adsorbate (with a larger atomic radius) diffusing on a substrate with a smaller lattice constant (3.64 Å), while that of the Cu adatom on Ag(100) provides the reverse case (diffusion on a tensile-strained lattice).
Table 4.1 Adatom bond lengths with the first nearest neighbors and atom below, adatom binding energies and diffusion barriers on terraces.

<table>
<thead>
<tr>
<th>Systems</th>
<th>Bond length (Å)</th>
<th>Bond length (Å)</th>
<th>E_{\text{bind}} (eV)</th>
<th>E_{\text{diff}} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4-fold (bridge)</td>
<td>atom below</td>
<td>4-fold (bridge)</td>
<td>hopping(exchange)</td>
</tr>
<tr>
<td>Ag/Ag(100)</td>
<td>2.79 (2.70)</td>
<td>3.88</td>
<td>2.18 (1.73)</td>
<td>0.45 (0.59)</td>
</tr>
<tr>
<td>Cu/Cu(100)</td>
<td>2.43 (2.33)</td>
<td>3.40</td>
<td>3.02 (2.49)</td>
<td>0.53 (0.79)</td>
</tr>
<tr>
<td>Cu/Ag(100)</td>
<td>2.59 (2.51)</td>
<td>3.48</td>
<td>3.45 (2.85)</td>
<td>0.60 (0.50)</td>
</tr>
<tr>
<td>Ag/Cu(100)</td>
<td>2.63 (2.52)</td>
<td>3.69</td>
<td>2.39 (2.02)</td>
<td>0.37 (1.02)</td>
</tr>
</tbody>
</table>

Note from Table 4.1 that the adatom binding energy in all cases is higher for the 4-fold site than for the bridge site. This is understandable since the former is the more stable configuration for an adsorbate. Also, the binding energy of a Cu adatom on Ag(100) is found to be higher than that on Cu(100) [173] as well as that of a Ag adatom on Cu(100). It is interesting that this trend on the surface is in agreement with that of the heat of solutions of Cu and Ag atoms in bulk material [64]. From Table 4.1 we find that, within first nearest neighbors, the binding energy (4-fold site) per bond (Cu-Ag) is 0.86 eV for Cu on Ag(100) and 0.60 eV for Ag on Cu(100), to be compared with 0.76 eV for (Cu-Cu) and 0.55 eV for the (Ag-Ag) bond. For the bridge site, the binding energy per (Cu-Ag) bond is 1.43 eV for Cu on Ag(100) to be compared with 1.01 eV for (Ag-Cu) bond, 1.25 eV (Cu-Cu) and 0.87 eV for (Ag-Ag) bond. The large difference in the binding energies per bond between that for Cu on Ag(100) and Ag on Cu(100) points the fact that adatom-substrate interaction is stronger for the former.

Since diffusion involves bond breaking between adsorbate and substrate atoms and the barrier is the cost for breaking these bonds, it is understandable that the trend in
the barriers (Table 4.1) correlates with that of binding energies. The recent study [30] of the diffusion of several types of adatoms on Cu(111) and Pd(111) show that the barriers near the step edges scale linearly with binding energy hence the knowledge of the binding energy near step edge is enough to determine E-S barriers. For our study in which the diffusion occurs on (100) surfaces, in contrast to the diffusion on (111) terraces, the barriers on the terraces compete with the barriers for descent over the step and hence the E-S barrier is governed via both barriers.

Figure 4.1 a) Top view of a mono-atomic terrace on fcc(100) surface with a closed-packed step running along <110> direction b) Top view of an adatom on fcc(100) at a 4-fold site (1), in a transition state for diffusion via hopping (2), and a transition state for diffusion via exchange (3).

In Figure 4.1.b, a top view of the transition state (position 3) of an exchange mechanism is shown. In accord with earlier prediction, as seen from the Table 4.1, for both homo systems diffusion via hopping is the dominant mechanism. The calculated barriers lie in the range of the earlier predictions [144-146, 148, 153]. The new result in
Table 4.1 regarding the diffusion via exchange for the hetero system is, however, interesting. For Cu on Ag(100) in which the diffusing atom is smaller than the substrate atom, we find the barrier via exchange to be about 100 meV smaller than that via hopping. Ag adatom diffusion on Cu(100) shows the opposite, i.e. exchange costs 650 meV more than hopping. These results indicate that deposited Cu adatom may incorporate into Ag(100) terrace, while the incorporation of Ag adatom into Cu(100) terrace is less likely.

4.1.4 Relaxations and Bond Lengths on Terraces

We have examined the relaxation trends and the bond lengths of the atoms in the systems for both 4-fold and bridge sites. Before discussing those, let us note that the top-layer relaxation ($\Delta d_{12}$) of Ag(100) and Cu(100) terraces are found to be -2.8% and -3.6%, respectively, in reasonable agreement with previous experimental and theoretical findings [126, 138, 144, 174]. In order to determine the change in the bonding upon adatom adsorption, we present in Figure 4.2.a schematic representation of the relaxation trends of the atoms in the first and second layers upon adatom adsorption on both 4-fold and bridge sites. Note that, for surfaces without an adatom, all atoms in a layer have the same vertical positions (equilibrium configuration). Not surprisingly, the first nearest neighbors and the atom underneath are affected most by the adatom’s presence. For all systems, the first nearest neighbors relax (upward) towards the adatom and occupying higher vertical positions than the rest of the atoms in the first layer. For both Ag and Cu adatoms on Cu(100), the atom below it relaxes (downward) away from it and sits at a lower vertical position with respect to the rest of the second layer atoms (Figure 4.2.a and Figure 4.2.d,
We find that for Ag and Cu adatoms on Ag(100) (Figure 4.2.b and Figure 4.2.c) the relaxation trend of the atom underneath is the opposite of that for the case on Cu(100). The atom underneath relaxes upward and gets closer to the adatom for Cu on Ag(100). For adatom adsorption on the bridge site, we find that for each system, the adatom’s neighbors in the first layer relax upwards while the neighbors in the second layer relax downward with respect to the neighbors far from the adatom. While these trends are interesting, the amount of relaxation is small, being no more than 1%.

Figure 4.2 Side views of a schematic representation of the relaxations upon adatom adsorption on 4-fold (on the left) and bridge (on the right) sites. Gray, black, and white circles represent the adatom, the first and the second layer atoms, respectively. The values reflect the vertical displacements of the atoms with respect to the rest of the atoms of the corresponding layer.
The optimized geometry of the systems shows that for the 4-fold site, the first nearest neighbors relax laterally and expand the 4-fold site further, while for the bridge site (position 2 in Figure 4.1.b), two nearest neighbors are pushed away to open the bridge. Upon adatom adsorption, we find that the expansion of the first nearest neighbor bond lengths is 3.4% for Cu adatom on Ag(100) and 1.6% for Ag adatom on Cu(100). We also find that the adatom vertical distances to the first nearest neighbors to differ up to 20% as we compare the systems with the same substrate while for the same adsorbate it differs up to 9%. Note that adatom vertical distance to the first nearest neighbors is the shortest for Cu on Ag(100) as compared to the others. This trend is in line with the bond length change (laterally) and also the differences in the adatom atomic size relative to that of the substrate atoms.

The bond length (for 4-fold site) between the Ag adatom and its first nearest neighbors on Ag(100) is found to be 2.79 Å (Table 4.1), which is 5.4% shorter than that of the inter-atomic distance (2.95 Å) in the bulk. When the adatom is at the bridge site for which the coordination is reduced to two from four, the bond length becomes shorter (2.70 Å) following the typical bond order-bond length trend. Similarly, for Cu on Cu(100), the bond length between the Cu adatom and its first nearest neighbor is 2.43 Å, which is 5.5% shorter than the inter-atomic distance (2.57 Å) in the bulk. At the bridge site, we find this bond length to be reduced to 2.33 Å (4.1% shorter than that of the 4-fold site). We find that the adatom bond length with the atom underneath (a second layer atom) is the shortest for Cu on Cu(100) and the largest for Ag on Ag(100) (Table 4.1).

For the hetero-epitaxial system, Ag on Cu(100), the bond length between the Ag adatom and the first nearest neighbor Cu atoms is 2.63 Å, while at the bridge site, the
bond length shortens 4.2% to 2.52 Å. Similarly, for Cu at the 4-fold site on Ag(100), the bond length with the first nearest neighbor Ag atoms is 2.59 Å, while at the bridge site, the bond length shortens 3.1% to 2.51 Å. Note that the adatom bond length (for 4-fold site) with it’s first nearest neighbors is shorter (1.5%) for Cu on Ag(100) than that of Ag on Cu(100), while at the bridge sites the bond lengths are the same. Note that for the former system, the adatom atomic radius being smaller than that of the substrate atoms causes the bond length within the first nearest neighbors to enlarge with it’s adsorption hence it’s (Cu adatom) vertical distance is closer (0.4 Å) to the surface atoms than that of the Ag on Cu(100). We also note that the bond length with the atom underneath is 6% shorter for Cu on Ag(100) as compared to the Ag on Cu(100). This is a result of the differences in the relaxation trends (see Figures 4.2.a. and 4.2.c) in which the atom below relaxes towards the adatom for Cu on Ag(100) while it relaxes away from the adatom for Ag on Cu(100).

In order to gain insight into the bonding strength, we present below the charge density distributions and differences (relative to the substrate) for each system.

4.1.5 Charge Density Distributions and Charge Density Differences on Terraces

The 2D contour plots of charge density distribution (for the plane perpendicular to the surface) between adatom and its first nearest neighbors are presented in Figures 4.3.a-d for the four systems of interest here. We find charge accumulation between the adatom and its nearest neighbors to be larger for Cu on Ag(100) than for Ag on Cu(100) (Figures 4.3.c-d). Note that the adatom bond length with its first nearest-neighbors (4-fold site) is shorter (1.5%) for the former as compared to that of the latter, (Table 4.1). The plots for
the homo-epitaxial systems, (Figures 4.3.a-b), show that there is stronger charge accumulation for Cu on Cu(100) as compared to that of Ag on Ag(100), revealing that the bond is more covalent in the former.

As a further measure of the adatom-substrate binding strength, we evaluate the charge re-distribution as determined by the charge density difference \( \Delta \rho(r) \) between that for the system with the adatom and that of the substrate and adatoms placed individually at the positions that they would otherwise occupy in the combination.

\[
\Delta \rho(r) = \rho_{\text{Cu on Ag(100)}}(r) - \rho_{\text{Ag on Cu(100)}}(r) - \rho_{\text{Cu}}(r)
\]  

We present the charge density re-distribution plots in Figure 4.4 for the plane perpendicular to the surface involving the adatom and its first nearest-neighbors along with the corresponding barriers via hopping. Once again we find charge accumulation to be larger for Cu on Ag(100) than that of Ag on Cu(100). The adatom binding strength relative to substrate (as is shown by charge re-distribution) is higher for the former and follows the same trend as the barriers.
Figure 4.3 2D charge density contour plots perpendicular to surface plane for a) Cu on Cu(100) b) Ag on Ag(100) c) Cu on Ag(100), and d) Ag on Cu(100)
Figure 4.4 Contour plots of the charge density re-distribution of the adatoms on Cu(100) and Ag(100) in the plane perpendicular to the surface. Red and blue contours correspond to accumulation and depletion of charge, respectively.

4.1.6 Adatom Diffusion Near Step Edges and the Ehrlich-Schwoebel Barriers

We now come to the ultimate goal of determining of the E-S barriers for each system. Since they are calculated by subtracting the diffusion barriers for descending over a step edge and from that on terraces, we need to now turn to the calculation of the former. As we have already noted, diffusion at a step edge can proceed via either hopping (Figure 4.5.a) or exchange mechanism (Figure 4.5.b). The earlier DFT study [144] for Ag
on Ag(100) and model potential results for Cu on Cu(100) [140, 148, 152, 158] reported that the diffusion by descent over the step proceeds via the exchange mechanism.

Figure 4.5 Schematic representation of diffusion by descent over the step edge a) via a hopping mechanism and b) via an exchange mechanism

In Table 4.2, we summarize the results of the barriers via both hopping and exchange for descending over the step ($E_{over}$), and for hopping along the step edge ($E_{along}$). The E-S barriers, the adatom bond lengths (with the first nearest neighbors and atom below) and the binding energies are also presented in the Table. For Ag on Ag(100), we find the adatom diffusion barrier (via hopping) along the step edge (on the
lower terrace) to be 0.24 eV, which is much lower than that on the terraces and in good agreement with the earlier theoretical predictions [144, 148, 158]. This low barrier may indicate that compact islands form on this surface [144]. For the descent of the Ag adatom over the step edge of Ag(100), we find the diffusion barriers to be very similar for the hopping (0.50 eV) and exchange (0.47 eV). Earlier studies have reported this barrier (via hopping) to lie in the range 0.55 eV to 0.59 eV [144, 148, 158], while the barrier via exchange lies in the range 0.45 eV to 0.64 eV [144, 148, 158]. Note here that, following the reports of an earlier study [172] in which it is shown that diffusion via exchange is strongly size dependent, we repeat the calculations of the exchange diffusion barriers near step edges for 5x4-3x4 in addition to 6x3-3x3 substrate-step configurations. We find that increase in the number of atoms in step chain (perpendicular to diffusion direction) decreases the diffusion barrier by 40 meV. The barrier values reported in Table 2 for the exchange are for the results of the calculation using the 5x4-3x4 unit cell. We also repeated the calculation for the diffusion via hopping for 5x3-3x3 and 6x4-4x4 periodicities and find that the effect on the diffusion barrier is utmost 20 meV.

For Cu on Cu(100), we find the barrier along the step edge to be 0.32 eV, which is in good agreement with the earlier reports (ranging from 0.25 eV to 0.40 eV) [90, 151, 152, 157, 158]. For Cu adatom descending over the step edge on the Cu(100) surface, we find the barriers for hopping and exchange to be 0.71 eV and 0.59 eV, respectively. The earlier studies using model potentials [90, 152, 157] reported these barriers to lie in the range 0.56 eV to 0.79 eV. Note that our results are in excellent agreement with those from a recent TB study [158]. From the barriers, we see that diffusion via exchange is energetically more favorable than that via hopping, near the step edge. In the calculations
of the barriers for the exchange process, we find that changing the number of atoms in the step chain from 3 to 4 affects (reduces) the diffusion barrier by 90 meV. The value reported in Table 4.2 is for the larger super cell.

For Cu on Ag(100), we find the barrier for diffusion along the step edge to be 0.36 eV, which is the largest for this process among the systems studied here. The barrier for the same process for Ag on Cu(100) is 0.20 eV, which is the smallest value for the rest of the studied systems. The barrier for Cu adatom descending over \(E_{\text{over}}\) the step edge on Ag(100) via hopping is 0.65 eV, while that for a Ag adatom at the step edge on Cu(100) is 0.54 eV. The barrier for Cu adatom’s descent over the Ag(100) step edge via exchange is about 300 meV lower than that via hopping, thereby pointing to the former as the energetically dominant mechanism. For Ag adatom diffusion at the Cu(100) step edge, the barrier for exchange is 150 meV higher than that for hopping. As on the terrace, at the step edge also, hopping is the dominant diffusion mechanism for this system.

Table 4.2 Adatom bond lengths (Å) with the first nearest neighbors and the atom under, binding energies, and adatom diffusion barriers at step edges and the E-S barriers

<table>
<thead>
<tr>
<th>Systems</th>
<th>Bond length 4-fold (Bridge)</th>
<th>Bond length 4-fold atom below</th>
<th>(E_{\text{bind}}) (eV) 4-fold (bridge)</th>
<th>(E_{\text{over}}) hopping (exchange)</th>
<th>(E_{\text{along}}) hopping</th>
<th>E-S (eV)</th>
<th>Relevant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag/Ag(100)</td>
<td>2.79 (2.70)</td>
<td>3.87</td>
<td>2.20 (1.70)</td>
<td>0.50 (0.47)</td>
<td>0.24</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Cu/Cu(100)</td>
<td>2.42 (2.34)</td>
<td>3.39</td>
<td>3.06 (2.35)</td>
<td>0.71 (0.59)</td>
<td>0.32</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Cu/Ag(100)</td>
<td>2.59 (2.51)</td>
<td>3.52</td>
<td>3.22 (2.57)</td>
<td>0.65 (0.33)</td>
<td>0.36</td>
<td>-30 (-270)</td>
<td></td>
</tr>
<tr>
<td>Ag/Cu(100)</td>
<td>2.62 (2.53)</td>
<td>3.68</td>
<td>2.44 (1.90)</td>
<td>0.54 (0.69)</td>
<td>0.20</td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>

From the calculated barriers on terraces and near step edges, which are summarized in Tables 4.1 and 4.2 for Ag on Ag(100), we find the E-S barrier via hopping
to be 50 meV. The calculated E-S barrier is smaller than that of the earlier studies which reported the barriers to be in the range of 100-127 meV \[144, 148, 158\]. However, note that, the dominant diffusion mechanism is hopping on terraces and exchange at the step edges hence the actual E-S barrier is 20 meV (Table 2), which is in good agreement with the result (0 meV) of an earlier DFT study \[144\]. Experimental observations report this barrier to be in the range of 30-70 meV \[160\]. The smallness (nearly zero) of the E-S barrier goes along with the observed \[144, 160\] layer-by-layer growth mode for Ag on Ag(100). For Cu on Cu(100), the E-S barrier for the hopping is 180 meV. For this surface, terrace diffusion via hopping costs less energy than exchange, while at the step edge the dominant diffusion mechanism is exchange (120 meV less than that of hopping). This actual E-S barrier is thus 60 meV (Table 4.2). The earlier predictions based on experimental observations of 3D growth mode \[144, 145\] suggested that the E-S barrier should be positive and non zero. The studies using model potentials \[90, 140, 152, 157-159, 163\] reported this barrier for hopping to be in the range of 125-320 meV, and that for exchange to be 30-130 meV. Our DFT results may help refine the theoretical predictions for these barriers.

From the calculations for the hetero-epitaxial systems, we find the E-S barrier via hopping to be 150 meV for Cu on Ag(100). For this surface, we find exchange to provide lower adatom diffusion barriers than hopping, both at terraces and at step edges (Table 4.1 and 4.2). Note that the difference between the diffusion barriers via hopping and exchange for Cu adatom on Ag(100) terraces is 100 meV, pointing to a possible competition between the mechanisms. If the Cu adatom reaches to the step edge via hopping then the E-S barrier is -270 meV. On the other hand if Cu adatom undergoes an
exchange process on Ag(100), a more likely possibility, the E-S barrier would be that for Ag on Ag(100). Of course, if the exchange takes place just near the step edge the E-S barrier for Cu on Ag(100) is -30 meV. The relevant E-S barrier for this surface is negative either -30 meV or -270 meV. These negative barriers might be the rationale for significant terrace diffusion observed in the TAD study [164, 170] and experimental observation [169] that at very low temperature (77K) the surface grows layer by layer and the produced film is smooth. For Ag on Cu(100), the dominant terrace diffusion mechanism is hopping since the cost for exchange is about 1 eV, providing 320 meV for E-S barrier via exchange. At the step edge, following the same trend as terrace, diffusion is preferred via hopping. This surface provides the relevant E-S barrier to be 170 meV. To our knowledge, there are no data available in the literature for the height of the E-S barrier for these studied hetero systems, except in an earlier study using TB method, on the growth of Ag shells on copper and palladium nanoclusters [167], the step edge barriers for Ag adatom crossing from the (100) to (111) facets is reported to be 0.67 eV via hopping, while the barriers via exchange are 0.48 eV and 0.67 eV. Given the heights of the E-S barriers for the two hetero-epitaxial systems, we expect that these systems behave differently both at terraces and the step edges hence growth mode should be expected to be different from each other.

4.1.7 Relaxations and Bond Lengths Near Step Edges

Once again to investigate possible correlation between strength of bonding and bond lengths, we have examined structural relaxation of both step and substrate atoms in the presence of the adatom. In Figures 4.6.a-d, we present a schematic representation of
the relaxation trends of the step atoms and the atoms in the first layer upon adatom adsorption on 4-fold site. From the figure, it is seen that for each system studied except Cu on Ag(100), the first nearest neighbor step atoms (SC1 and SC2) move upward. The upward relaxation is the highest for Cu on Cu(100). Note that for Cu on Ag(100), the SC2 atom relaxation (upward) is the lowest as compared to the rest of the systems. It is also worth noting that the closest neighbors (at the first layer) of the step atoms show enhanced downward relaxation as compared to that of the rest of the studied systems. We find that the vertical relaxation (downward) of the atom underneath is enhanced for Ag on Cu(100). Note that the in-plane relaxation of the atoms (SC1 and SC2) is the highest for Cu on Ag(100). The optimized structure of the bridge site for Cu on Cu(100) and Ag on Cu(100) show similar relaxation trends, in which we find the first nearest neighbor step atoms relax upward. For Cu on Ag(100) and Ag on Ag(100), we find the step atoms (SC1 and SC2) relax downward.

The analysis of the bond lengths at the step edges shows that the adatom’s presence at 4-fold site expands the first nearest neighbor bond length as in the case of terraces. The expansion ranges from 1.6% to 3.1% and the highest (lowest) expansion is for Cu on Ag(100) (Ag on Cu(100)). At the bridge site, these bond lengths get closer to that of the surface without adatom.

From Table 4.2, we find that for Cu on Ag(100), the adatom bond lengths for both 4-fold and bridge sites are shorter than that of Ag on Cu(100). The decrease in the adatom bond length (at bridge site) with the first nearest neighbor step atoms with respect to the 4-fold site is about 3% for Cu on Ag(100) and 4% for Ag on Cu(100). We find the change in the bond length to be about 8% as we compare the systems with same substrate
element, while the change is 6\% for the systems with same adsorbate element. Note that
the adatom bond length for 4-fold site (bridge site) is 1.5\% (~1\%) shorter for Cu on
Ag(100) than that of Ag on Cu(100). We also see that, following the same trend as for the
terraces, the bond length with the atom under is the shortest for Cu on Cu(100) and the
largest for Ag on Ag(100). As compared to the corresponding terraces, near the step
edges, the bond length with the atom underneath becomes larger (0.04 Å) for Cu on
Ag(100) and the shorter (0.01 Å) for the rest of the studied systems.

Figure 4.6 Side view of a schematic representation of the relaxation trends upon adatom
adsorption on 4-fold site. Black, white and gray circles represent the step atoms, the first layer
atoms and the adatoms, respectively.
4.1.8 Binding Energies Near Step Edges

The binding energies near the step edges (Table 4.2) show that, as for terraces, they are higher for the 4-fold site than the bridge site. Also, similar to the trends on the terraces, we find the adatom binding energy near the step edge to be the highest for Cu on Ag(100) and the lowest for Ag on Ag(100). The binding energy for Cu on Ag(100) is higher (0.78 eV) than that of Ag on Cu(100). The binding energy (at bridge site) decrease with respect to that of the terraces is in the range of 2%-10%, with the highest decrease for Cu on Ag(100). The decrease can be understood from the fact that at bridge site of a step edge, the adatom binds to fewer neighbors than that on the terraces. Comparison of the binding energies (at 4-fold site) near the step edges and on terraces (Tables 4.1 and 4.2) shows that except for Cu on Ag(100), the rest of the systems present an increase of about 2%. There is 7% decrease in the binding energy (4-fold site) near the step edge for Cu on Ag(100). For all the systems studied, the step geometry is the same and hence the observed trends in the binding energies emerge from the dissimilarity in the electronic interactions between the adsorbate and substrate atoms.

4.1.9 Conclusions

In this study, we have summarized the results of the first-principles total energy calculations for the energetics of several microscopic diffusion processes that play key roles in homo- and hetero-epitaxial growth on Ag(100) and Cu(100) surfaces. In agreement with earlier investigations for the diffusion on terraces, our calculations show that diffusion proceeds via hopping rather than by exchange for both studied homo
systems. For the hetero systems, we find exchange to be the dominant mechanism for Cu on Ag(100), while for Ag on Cu(100) hopping is the relevant mechanism on terraces. For these hetero systems, we find that the terrace diffusion barrier (via hopping) is 0.23 eV higher for Cu on Ag(100) than that of Ag on Cu(100) which we argue to originate mainly from the differences in the electronic interactions. As compared to diffusion on the homoepitaxial system, Ag on Ag(100), we find the diffusion barrier for Ag on Cu(100) to be reduced by 80 meV. For this system, a large adatom diffuses on the substrate with small lattice constant (Cu), similar to the diffusion on a compressively-strained lattice in which the diffusion barrier is expected to be lower than that of the unstrained surface. This can be understood from the change (decrease) in corrugation in the case of compressive strain. On the contrary, for Cu on Ag(100), for which the small adatom diffuses on the substrate with a large lattice constant, like the diffusion on a tensile-strained lattice, we find the diffusion barrier to increase by 70 meV from that of Cu on Cu(100). For the tensile strain case, the increase in the corrugation enhances the diffusion barrier. The binding energy analysis shows that there is a linear relationship between adatom binding energies and the corresponding diffusion barriers for the terraces. The charge density difference, which is a measure of adatom binding strength relative to the substrate, revealed that the system with higher charge accumulation (between adatom and the first nearest neighbors) has higher binding energy hence higher diffusion barrier than that of the others. We also note that for cases in which diffusion barriers had been previously calculated, our results either concur or provide validation or help narrow the range of predicted values.
In contrast to the diffusion on terraces, we find for diffusion near the step edges of Cu(100) and Ag(100) that the descent over the step is governed by exchange, confirming earlier predictions and providing more quantitative results. For Cu adatom diffusion at the Ag(100) step edge, we show that exchange costs less energy than hopping. It is only for a Ag adatom’s descent over the Cu(100) step edge that exchange is more costly than hopping. From the analysis of the diffusion mechanisms and the corresponding energy barriers, we find the relevant height of the E-S barriers for Ag on Ag(100) to be small (20 meV), implying a good interlayer mass transport hence confirming the theoretical and experimental observations of a smooth 2D growth. For Cu on Cu(100), the relevant E-S barrier is 60 meV. For the hetero-epitaxial systems, our analysis show the E-S barrier for Cu on Ag(100) is negative -30 meV or -270 meV hence implying high mass transport at the step edges leading to possible layer by layer growth. The E-S barrier for Ag on Cu(100) is however found to be much larger (170 meV), implying less mass transport from the step edge to a lower terrace and possible mound formation on the surface. These results point to the feasibility of alloying Cu atoms into Ag(100) especially at the step edges, while that for Ag atoms on Cu(100) is less likely. We await further experiments and dynamical calculation to verify our findings.
4.2 Effect of Lattice Strain on Diffusion Barriers on Terraces and Step Edges

While it is well known that lattice strain has an effect on adatom diffusion barriers, its material specificity has not yet been explored. In a comparative study based on density functional theory, we find that self diffusion barriers for Pd(100) terraces and step edges are not affected by strain (up to 5%) as much as their counterparts on Ag(100) and Cu(100) under tensile strain. We trace these differences to local geometric response and characteristics in the electronic structure.

4.2.1 Introduction

As a key factor in growth phenomena [133], surface diffusion has attracted much experimental and theoretical attention [175]. Most of the theoretical studies of metal-on-metal diffusion have focused on systems in which adsorbate and substrate are of the same element. These homo-epitaxial diffusion studies (see [146, 158] and references therein) have helped to pin down the parameters that influence the growth in such systems. The most commonly studied diffusion parameters are the diffusion barriers and their corresponding attempt frequencies. Deeper understanding of the role of these parameters in growth is crucial for learning how to manipulate their effects in such a way as to control growth on surfaces. Hetero-epitaxial systems, for their part, have also attracted much attention [32], mainly because of the vast number of their technological applications, such as in laser diodes, solar cells, optic and magnetic data storage devices [176]. For hetero systems at which the atoms of the growing layer are different from
those of the substrate, the combination of electronic coupling and presence of strain due to dissimilarity in atomic size is expected to affect film morphology [42, 177]. In particular, adatom diffusion and island morphology are closely related: the effect of strain on diffusion may in turn indirectly affect the formation of islands. Many efforts have thus been devoted to study of the relations between strain and island morphology [178]. For some industrial needs, the ultimate goal of the epitaxial growth studies is to discover ways to achieve controlled fabrication of thin films. As shown in earlier studies [42] strain can play a role in altering the growth parameters and hence help in controlling fabrication of thin films with desired features. It has also been shown that strain-induced self-assembly can be a promising method for achieving controlled nanostructures [179]. Moreover, strain is also shown to alter the catalytic behavior of surfaces [180]. The recent efforts [41] to understand self-assembled nanostructures and properties at the interfaces have revealed the importance of understanding role of strain for such systems. In this study, the goal is to examine strain role in altering the diffusion barriers on terraces and near step edges in order to determine its role in modifying nucleation and growth. In the following paragraph we will discuss some of the earlier experimental and theoretical studies which have helped to shed light on strain-related perturbations in diffusion parameters and hence upon growth.

The pioneering works for the role of strain on nucleation and growth are the STM experiments by Brune et. al [181, 182] and the DFT study by Ratsch et. al [52] for the diffusion of Ag adatom on Ag(111) and on Pt(111). The former study, combining STM experiments and calculations using effective-medium theory (EMT), reported that for
compressive-strained lattice ($\varepsilon = \frac{a_{\text{substrate}} - a_{\text{adatom}}}{a_{\text{substrate}}} < 0$), the diffusion barrier decreases, while it increases in the presence of tensile strain ($\varepsilon > 0$). It also reported that strain can strongly alter E-S barriers, which ultimately affect nucleation process [181, 182]. Ratsch and colleagues [52], using DFT for the same systems showed that deposition of 1ML of Ag on Pt(111) strongly lowers the Ag adatom barrier as compared to that of Ag adatom on Pt(111). This is attributed to the fact that the diffusion for the former is performed under a compressive strained (4.2%) substrate. In order to isolate strain effect from the electronic, they studied the self diffusion of Ag on strained Ag(111) substrate. They concluded that the barrier for Ag on 1ML Ag on Pt(111) converges to the barrier for Ag on compressive-strained Ag(111).

The recent studies [43] for self diffusion on strained transition metal (100) surfaces using Lennard Jones (LJ), Tight Binding (TB) and EAM have also reported strain dependence to be similar to that of the Ratsch’s study [52]. For instance, for Pt adatom diffusion on strained Pt(100) (un-reconstructed) using TB, the authors showed the barriers (via hopping) on terraces to decrease with compressive, and to increase with tensile strain, with a linear dependence up to 5% of strain. The same study also reported the E-S barriers (via hopping) to change with strain: opposite to the strain dependence on terraces. The studies using EAM for the diffusion of Pt on strained Pt(100) and Cu on strained Cu(100) have reported similar strain influence on the barriers. To the best of our knowledge, for self-diffusion on fcc(100), the only available DFT study [130] is for Ag diffusion (via hopping) on a stretched Ag(100) terrace. The authors reported that increase
in surface corrugation with strain increases the adsorption energy that causes an increase in the barrier.

In the present study, our main interest lies in determining the effect of strain on the self-diffusion barriers (via hopping) of Cu, Ag and Pd adatoms on compressive and tensile strained (100) terraces and near step edges. In addition to the diffusion barriers, it is also important to examine strain role in altering attempt frequencies as is shown in an earlier study [143], however, in this study, we only evaluate strain effect on the barriers via hopping mechanism.

4.2.2 Theoretical Details

We calculate the barriers by performing plane-wave DFT as implemented in VASP [171] using PW91-GGA [78] for the exchange-correlation functional. For diffusion on terraces, we use a 5x5 unit cell of a slab five layers thick with bottom layer fixed, and set the vacuum spacing to 14 Å. For diffusion near step edges, we compose a 6x3-3x3 (substrate-step) slab four layers thick with bottom layer fixed. The barriers near step edges are calculated for the close-packed {111}-faceted step edge running along the <110> direction. We perform the calculations using kinetic energy cut-offs of 249.8 eV, 273.2 eV and 250.9 eV for Ag, Cu and Pd, respectively. We use a 2×2 ×1 k-point mesh. In each energy minimization step, all unconstrained atoms are relaxed until the forces converge to 0.01 eV/Å. Our calculations revealed the bulk lattice constants for Cu, Ag and Pd to be 3.64 Å, 4.17 Å and 3.955 Å, respectively. We use drag method to search for the transition state. Possible size effects on the calculated barriers are examined by performing additional calculations using 6x6 and 7x7 unit cells consisting of 7 layers. In
order to ensure proper convergence, for some cases, we also repeat the calculations using 40% higher energy cut-offs than the default values. The convergence test is also performed for k-point mesh. For the calculations performed using EAM, we have constructed a supercell 10x10 atoms per layer with 20 layers. We have optimized the structure using CG method, and for the calculation of the diffusion barrier, we performed the Drag method.

In order to study diffusion on strained surfaces, we apply up to 5% compressive and tensile strain to the lattice. One way of inducing strain on a lattice is via misfit, which emerges from the presence of two or more dissimilar elements. For hetero systems, misfit strain and electronic coupling between the elements is coupled thus revealing strain effect solely becomes challenging. In order to isolate strain effect, we choose to study the diffusion on strained homo systems, and apply surface strain by modifying the lateral dimensions of the simulation cell [43]. The change in cell dimension exerts an external force thus strains the lattice. The decrease in the dimensions reduces the surface corrugation. At extreme conditions for which the corrugation is almost removed, an adsorbate responds to the surface as if it were flat. Conversely, increase in the dimensions enhances the corrugation. The change in surface corrugation plays role in altering diffusion barriers by way of modifying adsorption energies [43].

4.2.3 Change in Diffusion Barriers on Terraces

We summarize our results for strain dependence of the terrace diffusion barriers in Table 4.3. The table shows that strain can alter the diffusion barriers over 100 meV. As seen from the Table 4.3 the largest change is obtained for the 5% tensile Cu(100) surface
as compared the other surfaces. The change in the diffusion barriers is less pronounced for the compressive strain as compared to that for the tensile. This is not the case for Pd(100). In Figure 4.7.a, we plot the percentage change in the barriers (obtained using DFT) from that of the unstrained value. Before discussing the change in the barrier, we first summarize the self-diffusion barriers on unstrained Cu(100) [31], Ag(100) [31] and Pd(100) terraces. We find the self-diffusion barriers of Cu, Ag and Pd adatoms to be 0.53 eV, 0.45 eV and 0.72 eV on Cu(100), Ag(100) and Pd(100), respectively. The corresponding binding energies (fourfold site) are -3.02 eV, -2.18 eV and -3.23 eV, for Cu, Ag and Pd, respectively.

Table 4.3 Terrace diffusion barriers ($E_{\text{diff}}$) as a function of strain for adatom diffusion via a hopping mechanism. Compressive strain is represented with a negative sign.

<table>
<thead>
<tr>
<th>Strain %</th>
<th>$E_{\text{diff}}$ (meV) Cu on Cu(100)</th>
<th>$E_{\text{diff}}$ (meV) Ag on Ag(100)</th>
<th>$E_{\text{diff}}$ (meV) Pd on Pd(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.68</td>
<td>0.55</td>
<td>0.78</td>
</tr>
<tr>
<td>4</td>
<td>0.64</td>
<td>0.53</td>
<td>0.76</td>
</tr>
<tr>
<td>3</td>
<td>0.62</td>
<td>0.51</td>
<td>0.75</td>
</tr>
<tr>
<td>2</td>
<td>0.59</td>
<td>0.49</td>
<td>0.74</td>
</tr>
<tr>
<td>0</td>
<td>0.53</td>
<td>0.45</td>
<td>0.72</td>
</tr>
<tr>
<td>-2</td>
<td>0.50</td>
<td>0.42</td>
<td>0.69</td>
</tr>
<tr>
<td>-3</td>
<td>0.48</td>
<td>0.40</td>
<td>0.67</td>
</tr>
<tr>
<td>-4</td>
<td>0.47</td>
<td>0.39</td>
<td>0.64</td>
</tr>
<tr>
<td>-5</td>
<td>0.45</td>
<td>0.38</td>
<td>0.62</td>
</tr>
</tbody>
</table>
As shown in the figure, the barriers decrease with increasing compressive and increase with increasing tensile strain with nearly linear strain dependence. This trend is in agreement with the earlier reports [52, 51]. Although strain dependence is qualitatively similar for all the studied systems, there are quantitative differences. For instance, for the self-diffusion on 5% tensile-strained Cu(100) and Ag(100), the change in the barriers to be above 20%, enhanced for Cu(100). It is worth noticing that the increase in the barrier for Pd adatom is only 8%. For Cu and Ag, the change in the barriers in case of compressive strain is less pronounced than that of the tensile strain, however, Pd shows the opposite trend. In contrast to the observed difference for tensile strain, we find the change in the barriers for 5% compressive-strained terraces to be close to each other; 16%, 15% and 13% for Ag, Cu and Pd adatoms, respectively. We have also tested the results by performing additional calculations using 6x6 and 7x7 unit cells with 7 layers, and find no more than 20 meV deviation in the barriers. Figure 4.7.b presents the percentage change in the diffusion barriers for Cu, Ag, Ni, and Pt calculated using EAM. As shown in the figure, the diffusion barriers are altered with strain; increase with increasing tensile, while decrease with increasing compressive strain. Note that the change in diffusion barriers is enhanced for Cu as compared to the other surfaces in agreement with the results obtained using DFT. Notice from the figure that strain dependence of the diffusion barriers is linear.
The analysis of the adatom binding (at minimum energy site) energies for each surface shows that for the diffusion on tensile strained surfaces, the adatom binding energy increases up to 6% (for 5% tensile strain) as compared to that of the unstrained surface. Note that for the diffusion on compressive strained surface the change in the binding energies is much smaller and decreases slightly. The change in the binding energies is reflected in the change of diffusion barriers with strain. For tensile strain, the.

Figure 4.7 Change in the barriers with strain on terraces a) DFT results and b) EAM results
increase in the adatom binding energy causes more energy for breaking the bonds with its
neighbors in order to diffuse to the successive minimum energy configuration. The cost
for breaking the bonds is the corresponding diffusion barriers. Slight change in the
binding energy for the case of compressive strain leads to slow variation in the diffusion
barriers as shown in Figure 4.7. As we proceed further, one sees that the alteration in
adatom bond length and the vertical distance to surface is much more enhanced for
tensile strain than that for compressive strain. Thus this is expected to be revealed
explicitly as the change in the diffusion barriers with tensile strain.

Figures 4.8.a-4.8.f shows the charge density differences of the adatom with
respect to the substrate for 5% tensile-strained, unstrained and 5% compressive-strained
cases for both Cu(100) and Ag(100) surfaces, respectively. The charge density difference
is calculated using the equation 4.2. The first term in the equation is the total charge
density of the system, while the second and the third terms are the charge densities of the
substrate and the adsorbate, respectively. Note that in the calculation of the charge
densities for substrate and the adsorbate, we keep the exact same positions of the atoms
as they do in the total system. The charge density difference reflects the binding energy
of the adatom relative to the substrate. Notice from the figure that the change in surface
corrugation is noticeable in the figures -- high on the left (tensile strained case), while
low on the right (compressive strained case). The accumulation of the charge density (in
red) between the adatom and its first nearest neighbors is highest for the tensile-strained
case as compared to that for the unstrained case. High charge accumulation reflects
shortening of some of the bonds that may lead higher binding energy. Note that in the
case of compressive strain, it is hard to detect the charge accumulation/depletion relative
to the substrate owing to the fact that increase in the effective coordination compensates
the binding of the adatom to the substrate. The increase in the binding energy for tensile
strain case relative to the unstrained case is confirmed by the charge density differences.

\[ \Delta \rho (r) = \rho_{\text{ads} + \text{sub}}(r) - \rho_{\text{sub}}(r) - \rho_{\text{ads}}(r) \]  \hspace{1cm} (4.2)

Figure 4.8 Charge density differences (on terraces) for a) Ag on 5% tensile-strained Ag(100)
b) Ag on unstrained Ag(100) c) Ag on 5% compressive-strained Ag(100) d) Cu on 5%
tensile-strained Cu(100) e) Cu on unstrained Cu(100) and f) Cu on 5% compressive-strained
Cu(100). The red (blue) color represents the accumulation (depletion) of the charge
4.2.4 Change in Ehrlich-Schwoebel Barriers

In order to examine the change in the E-S barriers, we calculate adatom diffusion barriers (via hopping) near the step edges of strained Cu(100), Ag(100) and Pd(100). In Table 4.4, we summarize the diffusion barriers for descending over step edge process in the presence of strain along with that of the unstrained value. Table shows that the diffusion barriers do not change very sharply as one introduces strain progressively to the system as was the case for the barriers on terraces. Note the E-S barrier is the difference between the barrier for descending over the step and that of the terrace. As seen from the Table 4.4, the E-S barrier changes very sharply (up to 200 meV) with strain owing to slow variation in the descent over the step process and sharp variation of the terrace diffusion barrier. Note that it increases with increasing compressive and decreases with increasing tensile strain.
Table 4.4 The step descent barrier $E_{\text{step}}$ (eV) and E-S barriers (meV) for adatom diffusion via a hopping mechanism as a function of strain. Compressive strain is represented with a negative sign.

<table>
<thead>
<tr>
<th>Strain %</th>
<th>$E_{\text{step}}$ Cu/Cu(100)</th>
<th>$E_{\text{step}}$ Ag/Ag(100)</th>
<th>$E_{\text{step}}$ Pd/Pd(100)</th>
<th>E-S Cu/Cu(100)</th>
<th>E-S Ag/Ag(100)</th>
<th>E-S Pd/Pd(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.66</td>
<td>0.50</td>
<td>0.90</td>
<td>-20</td>
<td>-50</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>0.68</td>
<td>0.50</td>
<td>0.92</td>
<td>40</td>
<td>-30</td>
<td>162</td>
</tr>
<tr>
<td>3</td>
<td>0.69</td>
<td>0.49</td>
<td>0.92</td>
<td>70</td>
<td>-20</td>
<td>174</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>0.49</td>
<td>0.93</td>
<td>110</td>
<td>0</td>
<td>192</td>
</tr>
<tr>
<td>0</td>
<td>0.71</td>
<td>0.50</td>
<td>0.93</td>
<td>180</td>
<td>50</td>
<td>206</td>
</tr>
<tr>
<td>-2</td>
<td>0.73</td>
<td>0.52</td>
<td>0.91</td>
<td>220</td>
<td>100</td>
<td>223</td>
</tr>
<tr>
<td>-3</td>
<td>0.73</td>
<td>0.53</td>
<td>0.91</td>
<td>250</td>
<td>130</td>
<td>237</td>
</tr>
<tr>
<td>-4</td>
<td>0.74</td>
<td>0.54</td>
<td>0.90</td>
<td>270</td>
<td>140</td>
<td>260</td>
</tr>
<tr>
<td>-5</td>
<td>0.74</td>
<td>0.54</td>
<td>0.90</td>
<td>290</td>
<td>160</td>
<td>276</td>
</tr>
</tbody>
</table>

In Figure 4.9, we plot E-S barriers for each corresponding strain value as a function of strain. The calculations show that the barrier for descending over step edge varies slowly with strain. As seen from the figure strain dependence is the opposite to that of the terraces. This difference can be attributed to the dissimilar relaxations near a step edge as compared to a terrace. Near a step edge, atoms have freedom to relax in-plane (inward or outward) that relieves strain. Less pronounced strain dependence near a step edge causes the change in E-S barriers to be governed mostly by the change in terrace diffusion barriers. We find the largest deviation in the E-S barrier from the unstrained value for the highest tensile strain (5%) to be 200 meV for Cu(100), while Ag(100) and Pd(100) show smaller (~100 meV) deviation. On the other hand, for compressive strain, all three surfaces show similar deviation (about 100 meV). Note here that island
nucleation is an important step for growth. The results show the possibility of altering the diffusion barriers both at terraces and near a step edge that provide control on island nucleation.

![Figure 4.9 Change in the E-S barriers with strain](image)

The results illustrated in the Figures 4.7 and 4.9 suggest that there is considerable change in the barriers on terraces and near step edge. We will now discuss possible explanations for these variations and determine the underlying reasoning for the observed behavior. Particularly, we will examine strain-induced modification in both geometric and electronic structures. As a first step, we discuss the elastic response of each surface by examining the change in relaxations, bond lengths and adsorbate height relative to surface. We will then discuss strain effect in altering the position of the center of metal d band and its consequences on the barriers. Note that the interaction between the adsorbate d-states and that of the metal is an important aspect of adsorbate-metal interaction. The small change in environment can alter the d-states and expected to affect adsorbate-metal interaction. This interaction is the key factor for the binding strength hence the diffusion barrier.
In Figure 4.10.a, as part of the elastic response analysis, we report the change in the interlayer separation with strain. For unstrained surfaces, we find the interlayer separation between the first and the second layers (\(d_{12}\)) to contract about -3.8%, -2.85% and -1.33% for Cu(100), Ag(100) and Pd(100), respectively. Compressive strain causes an increase in the interlayer separation as the solid tends to preserve its volume. The increase for the 5% compressive strain is the largest (6.3%) for Pd(100), then (4.7%) for Ag(100) and the least (3.0%) for Cu(100). Tensile strain decreases the \(d_{12}\). We find for the 5% tensile strain that the decrease in the \(d_{12}\) is almost the same for all three surfaces; 11% for Cu(100) and Ag(100) and 10% for Pd(100). The change in \(d_{23}\) follows the same trend as \(d_{12}\) for both compressive and tensile strain. Note here that as opposed to Cu(100) and Ag(100), we find \(d_{23}\) for Pd(100) to contract, and the change in tensile strain region to be almost the same as \(d_{12}\). The percentage change in adatom’s vertical distance to the first nearest neighbors (1\(^{st}\) NN) shows that for all three surfaces, the adatom distance to the metal surface decreases with tensile strain and increases with compressive strain (Figure 4.10.b). As clear from the figure, the largest deviation for the highest tensile strain (5%) is for Cu and Ag adatoms, while the deviation is less enhanced for Pd adatom. The deviation is almost the same for compressive strained surfaces. In Figure 4.10.c, we plot the percentage change in the distance between the adatom’s 1\(^{st}\) NN. We find that for 5% tensile strain, the change is enhanced for Cu(100) and the least for Pd(100). For 5% compressive strain, the change is less enhanced for Cu(100) and the same for Ag(100) and Pd(100). As shown here the elastic response of the three systems differ from each other, and particularly for Pd(100); the effect of tensile strain on the barriers is less enhanced as compared to Cu(100) and Ag(100).
Figure 4.10 Change in a) interlayer separations $d_{12}$ and $d_{23}$ b) adatom distance to the metal surface and c) distance between the first nearest neighbor neighbors
In Figure 4.11.a, we plot the percentage change in the bond lengths between the adatom and the 1st NN when the adatom is placed on fourfold site on the terraces. For unstrained surfaces, the bond lengths are 2.43 Å, 2.79 Å and 2.65 Å for Cu, Ag and Pd, respectively. The bond lengths to the atom below are 3.40 Å, 3.88 Å, and 3.59 Å for Cu, Ag and Pd, respectively. For the strained surfaces, we find the bond length between the adatom and the 1st NN neighbors to stay the same, while the bond length with atom below is strongly altered. For instance, on 5% tensile-strained surface, the bond length decreases about 20% for Cu, 15% for Ag and 13% for Pd. On 5% compressive-strained surface, the bond length increases about 8%, and slightly higher for Pd. As a result of dissimilar elastic responses in case of tensile and compressive strain, the atomic relaxations and the bond lengths show differences. For tensile strain, the adatom relaxes downward towards the surface and the atom underneath upwards towards the adatom. Compressive strain exhibits the opposite trend in which the adatom is pushed upwards (away from the surface), while the atom underneath relaxes downward away from the adatom. The same bond length analysis is also conducted for the step edges. In Figure 4.11.b, we plot the percentage change in the bond lengths between the adatom and the 1st NN step atoms and atom below. As for terraces, the bond length with the 1st NN step atoms stays the same, while the bond length with the atom below decreases with tensile and increases with compressive strain. For 5% tensile strain, we find the bond length to decrease 12% for Cu and Ag, and 8% for Pd. Note that the change in the bond length is smaller at steps than on terraces (Figure 4.11.a) reflecting that at a step edge strain is relieved via in-plane relaxation that is not possible for atoms on terraces. This difference
reflects the reasoning for the slow variation of the barriers near a step edge, causing the change in terrace diffusion barriers to control the height of the E-S barriers.

Let us note that, Pd has unoccupied states above the Fermi level, while Cu and Ag are far below it. The relaxation response of the Pd adatom observed for the tensile region can be attributed to the existence of the unoccupied states above the Fermi level. These unoccupied states causes easily bond making for the Pd adatom thus the adatom relaxation towards surface is much less enhanced as compared to Cu and Ag cases.

Figure 4.11 Percentage change in the bond length (fourfold site) between the adatom and the 1st NN, and atom below a) on terraces and b) near step edges
We now turn the discussion into the change in electronic structure. As shown in earlier studies, change in environment can alter the position of d states that modifies the adsorption energies \[41\]. The measure of the position of d states is the d-band center. We have examined the change in d-band center for the strained surfaces. Note that, when the surface (tensile strain) is stretched in-plane, the overlap between the d electrons of the metal atoms on the surface is reduced. The band width as compared to the unstrained case is expected to decrease with an increase in the intensity to keep the fixed occupancy for the d states. By plotting the total d states of the 1st NN, we find that for tensile strain, there is a slight narrowing of the d-band for each surface, while for compressive strain, the band gets slightly wider. This trend reflects the decrease (increase) in the effective coordination number in the presence of tensile (compressive) strain. In order to gain further insight, in Figure 4.12.a, we plot the change in the d-band center of the surface atoms for both clean surface and the surface with adsorbate. The largest deviation in the d-band center for both tensile and compressive strain is found to be for Pd(100), then Cu(100) and the least for Ag(100). It shows that strength of deviation depends on the position of the d states of the metal relative to Fermi level. For tensile strain, we find that d-band center shift towards Fermi level, while for compressive strain, the opposite is observed. The shift in the d-band center is expected to induce changes in the barriers. Analysis of the binding energies of the adatom for each strained surface and that of the unstrained value shows that the binding energies increases with increasing tensile strain that is in agreement with the d-band center shift observed towards Fermi for this case. The increase in the binding energy of the adatom is the largest for Cu adatom (for 5% tensile strain, the increase is 170 meV), for Ag the increase is about 150 meV, while for Pd
adamatom the increase is 100 meV. We also find that the binding energies decrease with compressive strain following the shift observed in the center of the d-band away from Fermi. For the largest compressive strain, we find the decrease to be slightly less than 100 meV. In order derive possible correlation in the shift observed in the d-band center and the binding energies with the change in the diffusion barriers, in Figure 4.12.b we plot the d-band center versus the diffusion barriers for unstrained, 5% tensile and 5% compressive strained cases. The figure reflects the correlation between the changes in the barriers as d-band center shifts with strain. The diffusion barrier increases as the d-band center shift towards Fermi level (tensile strain), while it decreases as it shifts away from it. Note further that, the quantitative differences observed for the deviation in the barriers between the three systems reflects the role of elastic response dissimilarities.
4.2.5 Conclusions

In summary, the calculations show that strain can alter the adatom diffusion barriers by means of altering the binding energies. The analysis of the d-band center shows that in the presence of strain, one can shift the center of the d-band towards either higher or lower binding energies; hence the change in the d-band center plays role in the change in the diffusion barriers. The diffusion barrier increases with increasing tensile strain, while it decreases with increasing compressive strain. This can be attributed to the fact that in the case of tensile strain, the d-band center of the metal atoms (substrate) is
shifted towards lower binding energy. This increases the adsorption energy of an adsorbate, hence increases the diffusion barrier. The compressive strain provides the opposite trends -- d-band center of the substrate atoms shifts towards higher binding energy causing a decrease in the adsorbate adsorption energy. The change in the d-band center is the most for Pd(100), and the least for Ag(100). This originates from the fact that the position of the d-states of Pd relative to Fermi level is closer than that for the Ag; hence any perturbation will appear strongly for Pd case. Note there is a quantitative difference in the strain dependence of the barriers between the surfaces. For Pd(100), the calculations revealed that for 5% tensile strain, the change in the diffusion barriers is much lower than that for Cu(100) and Ag(100) originating from the dissimilar elastic responses. The analysis of the elastic response for each surface has shown that the response is the highest for Cu(100), while the lowest for Pd(100). Combining the elastic and electronic perturbations induced by strain, we see that the effect of elastic response controls the changes introduced to the diffusion barriers.

The calculations also showed that the E-S barriers can be altered strongly with strain. The largest modification is induced for Cu(100), while the smallest for Pd(100). The change in the E-S barriers is governed by the change in the terrace diffusion barriers, and that the diffusion near step edges is much less affected by strain. This is attributed to the fact that strain near step edges is compensated by in-plane relaxation. Strong modification of the E-S barriers brings about a possibility of controlling growth via strain. One obtains thin films with smooth surfaces by applying tensile strain (decreases the E-S barrier), while compressive strain (increases the E-S barrier) causes the growth of rough films.
Our results show that strain can be used as a manipulative tool to alter diffusion barriers. It also reveals that strength of strain dependence is not universal but element dependent as the E-S barriers. To derive a conclusive argument how strain modifies the diffusion barriers and growth, one has to study the relevant diffusion mechanisms both at terraces and step edges owing to the fact that for each system, the relevant diffusion mechanism differ at terraces and near step edges. We should also note that the evaluation of the prefactors is highly necessary for deriving a complete picture of strain dependence. The earlier studies showed that strain can influence the prefactors only about factor two. Its transferability to a corrugated surface as (100) needs careful analysis. If the prefactors stay the same, then for a 5% tensile strained lattice, the change in the diffusion barrier can influence the diffusivity about two orders of magnitude that can change the early stages of nucleation and ultimately growth.

The results can be applied to several surface science problems for which the properties are expected to be controlled by strain. One example is the self-assembly of nanostructures in which strain role on the phenomena is still an open question. It is also important to understand strain role at the interface of hetero systems and finds its application for nano-scale devices. Catalytic activity of thin metal over layers can also be altered with strain.
4.3 Diffusion Barriers and Prefactors for Adatom Diffusion on Terraces and Step Edges of Cu(100) and Cu(110)

- Handan Yildirim, Abdelkader Kara, Sondan Durukanoglu and Talat S. Rahman,

“Calculated pre-exponential factors and energetics for adatom hopping on terraces and steps of Cu(1 0 0) and Cu(1 1 0)”, Surf. Sci. 600, 484 (2006)

We have calculated the vibrational dynamics and thermodynamics for Cu adatom hopping on terraces and near step edges on Cu(1 0 0) and Cu(1 1 0), using the embedded atom method for the interatomic potential. The local vibrational densities of states were calculated using real space Green’s function formalism and the thermodynamical functions were evaluated in the harmonic approximation. The calculated diffusion energy barriers for six specific local environments on Cu(1 0 0) agree well with experimental and previous theoretical results. Contribution of vibrational entropy to the change in the free energy of the system as the adatom moves from the equilibrium configuration (hollow site) to the saddle point, is found to be as much as 55 meV (144 meV) at 300 K (600 K). The prefactors for all 13 cases are found to be of the order of $10^{-3} \text{ cm}^2/\text{s}$, almost independent of temperature, and the respective activation energy barriers.

4.3.1 Introduction

Understanding atomistic diffusion processes is of vital importance to studies of surface related phenomena such as crystal growth, thin film growth, surface chemical
reactions and catalysis. However, in spite of the conceptual simplicity, the phenomenon of diffusion of adatoms or small clusters on clean, infinite, defect-free surfaces stays a challenging problem. The first surface diffusion study using Field Ion Microscopy (FIM) was reported by Muller [184], and since then, surface diffusion of a single atom on various metals has been observed [184], as FIM is capable of resolving individual atoms, although observations have been limited to a few metals: tungsten [185], rhodium [186], platinum [187], nickel [188], and iridium [184, 187, 189]. From the usually observed Arrhenius form of the diffusion coefficient \( D \), the diffusion pre-exponential factor \( D_0 \), also called the prefactor, and the activation energy barrier \( \Delta E \) are generally obtained using an Arrhenius equation:

\[
D = D_0(T) \exp\left(-\frac{\Delta E}{k_BT}\right)
\]  

(4.3)

Even after several instrumental advances, reliable diffusion data are available only for the simplest processes on a small number of surfaces [27]. Because diffusion is an activated process, small errors in energy barriers translate into large uncertainties in the diffusion coefficients [153]. In order to determine the prefactor from observed Arrhenius behavior, several measurements are needed in a reasonable range of temperature. Since such measurements are difficult, quite often the prefactor is simply assumed to be close to a so-called “usual value” of about \( 10^{-3} \) cm\(^2\)/s, although experimental results have quoted “abnormal” values for the prefactor [190]. While most theoretical studies of surface diffusion also ignore explicit calculations of diffusion prefactors, some attempts have
already been made to recognize the significance of vibrational entropy contributions [191] in calculations of diffusion prefactors. Of particular relevance to the study here there are series of papers in which diffusion prefactors have been calculated with explicit inclusion of the vibrational dynamics of the system with the moving entity at both the equilibrium position and at the saddle point. In one set of calculations such prefactors are calculated using Vineyard’s formula [109]:

\[
D_0 \propto \frac{\prod_{i=1}^{3N} \nu_i^{\text{hollow}}}{\prod_{j=1}^{3N-1} \nu_j^{\text{saddle}}} \quad (4.4)
\]

where the \( \nu_i \) and \( \nu_j \) are the set of vibrational frequencies of the system for the equilibrium and saddle point configurations, respectively. In the other set of calculations, Kurpick et al. [148, 192] have developed a recipe for the calculations of the prefactors through evaluations of the changes in the vibrational contributions to the free energy of the system within the limits of validity of the transition state theory [193].

The goal of this study is to examine the influence of the local environment on the prefactor for the diffusion of a single atom on metal surfaces. For this purpose, using the calculational scheme developed by Kurpick et al. [148, 192], we have carried out a systematic study of the activation energy barriers and the corresponding prefactors for the diffusion of a Cu adatom on the terraces and near the step edges of Cu(100) and Cu(110). An interesting feature of prefactors was introduced by Meyer–Neldel [194] who suggested that the processes in which the activation energy is larger than both the energies of the activation and thermal energy (\( k_B T \)), there is a compensation by which the prefactor
increases exponentially if the activation energy increases [195]. The rule has been tested by means of molecular-dynamics simulations for adatom diffusion on and near Cu(100) surface, and shown to remain valid [196]. On the other hand similar studies for Cu and Ni surfaces using semi-empirical potentials show that the compensation rule is not always upheld [143]. With the set of activation energy barriers and prefactors that we calculate, we also intend to check the applicability of the Meyer–Neldel rule. It should be pointed out that a few of the results are present here, for example a Cu adatom diffusion on Cu(100) is already available in the literature. Wherever possible we refer to the available results and include our results for completeness and comparison. Note also that in this study our interest of the diffusion mechanism is confined to the diffusion via hopping. While exchange mechanism is also possible, preliminary investigations and previous study show the barrier for exchange (for several of the cases presented here) to be larger than that for hopping. For example, for adatom diffusion via hopping on Cu(100) the barrier is found to be 0.53 eV, while the barrier for the exchange is 0.79 eV [159]. The adatom diffusion barriers in case of Cu(110) along the open channel are 0.24 eV for hopping and 0.87 eV for the exchange processes [152]. On the other hand the activation energy barrier for adatom exchange at a step edge (diffusion over the step) on Cu(100) is found to be 0.51 eV, while that for hopping is 0.77 eV [159]. In this case exchange mechanism is more likely. Nevertheless for purposes of comparison of the prefactor for a set of adatom hopping processes, the role of exchange mechanism in diffusion has been set aside for future consideration.

The chapter is organized as follows: In Section 4.3.2, we will present the systems
and the process of interest. In Sections 4.3.3-4.3.6 the theoretical and calculational details will be presented. The results are summarized and discussed in the sections 4.3.7-4.3.10. Finally the conclusions are presented in Section 4.3.11.

4.3.2 Processes of Interest

Figures 4.13-14 present several diffusion processes involving hopping of an adatom from an fcc hollow site to a neighboring hollow site on the terraces and near step edges of fcc(100) and (110) surfaces. Figure 4.13 shows minimum-energy configuration in which an adatom is adsorbed on a hollow (fourfold site) near or at a step edge or far from it on (100) surface. The arrows show the direction along which the adatom would perform the process labeled in the figure (P1-P6). The process labeled as P1 in Figure 4.13 corresponds to a hop on the (100) terrace, while processes P2, P3, P4 are associated with an adatom originally on the upper terrace and at the step edge, and correspond to a jump away from the step edge, descent from the step and along the step, respectively. Finally, the processes P5 and P6 correspond to diffusion on the lower terrace away from the step and along the step edge, as shown in the figure. In Figure 4.14, we summarize the processes studied for an adatom hopping on an fcc(110) terrace and at near a step edge on this surface. The fcc(110) surface may be envisioned as an arrangement of dense chains running parallel to each other and separated by a distance equal to the lattice constant of the element. An atom adsorbed on the fourfold site may then diffuse parallel to the open channels (shown in Figure 4.14 as the process P7) or perpendicular to the open channels, labeled as the process P8. When the adatom is placed on the upper terrace and at the step
edge, it may diffuse along the step edge (P11), away from it (P10), or jumps to the lower terrace (P9). The processes labeled P12 and P13 represent diffusion of an adatom away from the step and along the step edge on the lower terrace.
Figure 4.13 Diffusion of an adatom via hopping on fcc(100) on the terrace and at the step. The processes (P1-P6) are described in the text.

Figure 4.14 Diffusion of an adatom via hopping on fcc(110) on the terrace and at the step. The processes (P7-P13) are described in the text.
4.3.3 Theoretical Details

In this section, we will discuss some details of the theoretical techniques which are used to calculate the structure, energetics, VDOS, thermodynamics, prefactors and diffusion coefficients. These are presented in three sub-sections summarizing the calculational details for: (i) activation energy barriers, (ii) local vibrational densities of states (LVDOS) and (iii) thermodynamic functions, prefactors and diffusion coefficients. These details have already been presented in several publications [143, 192] and in the theoretical models chapter, and are included here only for completeness.

4.3.4 Calculation of Diffusion Barriers

In order to determine the static energy barriers, a series of energy-minimization namely molecular statics (MS) simulations are performed. In order to obtain the optimized (relaxed) configurations, standard CG method is used for minimizing the total energy of the system [91]. For these calculations, the important ingredient is the interaction potential between the atoms. In this study we have used semi-empirical many body potentials as obtained from the EAM [50]. When the position of the adatom at the saddle point is known (by symmetry means for example), one can perform only two calculations in which the adatom is at the minimum energy site and at the saddle point. When adatom diffusion occurs near a complex geometry (involving a step), the atomic configuration of the system at the saddle point is not known “a priori”. Depending on the complexity of the system, one may use sophisticated methods like the NEB [60], the drag or grid methods to calculate the activation energy barriers. Here we perform a 1D scan of
the energy landscape between positions of two consecutive minima of the adatom. We constraint the chosen drag coordinate and dragged along the chosen path until the next minimum energy configuration is established.

4.3.5 Calculation of Local Vibrational Densities of States (LVDOS)

There are several techniques for calculating the VDOS. The most widely used one is the slab method in which one needs to diagonalize the dynamical matrix portraying the force-constants between the particles in N layers of the slab [84]. The continued fraction (CF) method using real space Green function is another way to calculate the vibrational dynamics of surfaces [119]. Since, our interest lies in obtaining the local contributions to the dynamics and thermodynamics of systems with site specific environments, a local approach in real space is more appropriate than the one based on k-space. The real RSGF method with an efficient iterative scheme is one such method [52] in which one focuses on any local region and analyzes the effect of the rest of the system on it. The first step in applying the method is to set up the force constant matrix obtained from the analytical expressions of the partial second derivatives of the potential, in a layer-by-layer manner. Because of the finite range of the atomic interactions, this matrix takes a block-tridiagonal form allowing the Green’s function matrix corresponding to the local region of interest to be constructed following the procedure described in Ref. [52]. In this method of resolvent matrix, the calculation of the Green functions is reduced to a series of inversions and multiplications of matrices whose dimensions are usually smaller than the total number of degrees of freedom in the system. Another feature of the method is
that one can focus on any specific locality of the system and calculate the corresponding properties. From the calculated Green function, normalized LVDOS are obtained using:

\[ g(\nu^2) = \frac{-1}{3n\pi} \lim_{\varepsilon \to 0} \text{Im} \text{Tr}[G(\nu^2 + i\varepsilon)] \]  

(4.5)

where \( n \) is the number of atoms in the chosen locality. The frequency dependent VDOS \( N(\nu) \) is related to \( g(\nu^2) \) through the equation:

\[ N(\nu) = 2\nu g(\nu^2) \]  

(4.6)

### 4.3.6 Calculation of Thermodynamic Functions, Prefactors and Diffusion Coefficients

Once the local vibrational density of states is calculated, one can obtain all thermodynamic quantities for systems of interest from the partition function calculated within the harmonic approximation of lattice dynamics. The main quantity for the purposes here is the vibrational contribution to the free energy that is given by the standard definition \( F = U - TS \), where \( U \) is internal energy, \( S \) is entropy and \( T \) is temperature. Both \( U \) and \( S \) have contributions from the atomic configurations and the vibrations such that \( F = F^{\text{conf}} - F^{\text{vib}} \). That is, for each atomic configuration of the system there is a specific vibrational contribution that can be further written as:

\[ F^{\text{vib}} = U^{\text{vib}} - TS^{\text{vib}} \]  

(4.7)

In the harmonic approximation, the vibrational part of the free energy is further given by:

\[ F^{\text{vib}} = k_B T \int_0^\infty N(\nu) \ln(2 \sinh(\frac{\nu}{2})) d\nu \]  

(4.8)

while those contributions to the internal energy and entropy is obtained as:
\[
U_{vib} = k_B T \int_0^\infty N(\nu) \left( \frac{1}{2} x + \frac{x}{e^x - 1} \right) d\nu
\quad (4.9)
\]

\[
S_{vib} = k_B \int_0^\infty N(\nu) \left( -\ln(1 - e^{-x}) + \frac{x}{e^x - 1} \right) d\nu
\quad (4.10)
\]

where \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( x = h \nu / k_B T \) (\( h \) is the Planck constant) and \( N(\nu) \) is the VDOS (as a function of frequency \( \nu \)) that can be expanded as \( N(\nu) = \sum_n n_l(\nu) \), where \( n_l(\nu) \) is the LVDOS of the atoms in the first layer.

For an isolated atom migrating on a surface, the diffusion coefficient \( D \) may be obtained from the Einstein relation for a random walk, \( D = \langle \Delta r^2 \rangle / 2 \alpha t \), where \( \langle \Delta r^2 \rangle = nd^2 \) is the mean-square displacement of the diffusing particle during the time period \( t \), \( \alpha \) is the dimensionality of the motion, and \( d \) is the jump distance. The number of jumps (\( n \)) is the product of the time period and a hopping rate \( \Gamma \), which for thermally activated diffusion may be expressed according to TST [55] as:

\[
\Gamma = \frac{k_B T}{h} \exp\left(\frac{-\Delta F}{k_B T}\right)
\quad (4.11)
\]

where \( \Delta F \) is the difference in the Helmholtz free energy between the two states in which the system is at the minimum energy and at the saddle point configurations. In this formula \( F = E + U^{vib} - TS^{vib} \), where \( E \), \( U^{vib} \) and \( S^{vib} \) are the potential energy, the internal vibrational energy and the vibrational entropy of the system, respectively. The essential feature of this equation is the dependence of \( \Gamma \) on the free energy. Using the thermodynamic quantities in equation (4.7)–(4.9), re-writing the diffusion coefficient \( D \) provides the equations:
The values of $n$ (the number of equivalent jumps), $d$ and $\alpha$ for each process (P1–P13) are previously defined in the literature [192]. Note that one can retrieve the Vineyard’s formula (equation 4.4) starting from the equation 4.13 at high temperature and replacing the integral in equation 4.7 by a finite sum as shown in Appendix A: SUB-CHAPTER 4.3. In order to compare the results of the approaches used in calculating the prefactors (equation 4.13) with those obtained using the Vineyard equation (equation 4.4), we have studied the diffusion of Cu adatom on Cu(100) and on Cu(110) (open channel) for which only the adatom dynamics are taken into account (keeping the substrate rigid). This scenario will allow a one to one correspondence between the two methods. For the case of Cu adatom diffusion on Cu(100), the resultant vibrational frequencies are 3.28 THz, 3.28 THz and 4.71 THz for the fourfold site and 2.95 THz and 5.30 THz for the saddle point. For the diffusion of Cu adatom on Cu(110), the frequencies are found to be 2.68 THz, 4.20 THz and 4.49 THz for the fourfold site, and 5.16 THz and 4.31 THz for the saddle point. The corresponding prefactors for different temperatures using equation 4.13 will be presented in the section 4.3.10. The result obtained using from the Vineyard equation will be also included in the table.

4.3.7 Results and Discussion

In this section, we present the results of the activation barriers, VDOS and
prefactors and diffusion coefficients and compare with the existing experimental data and other theoretical values whenever available. The calculated diffusion activation energies for the processes P1–P13 (shown in Figures 4.13-14) are presented first that is followed by the specifics of VDOS for selected cases, and the contribution of vibrational dynamics to the diffusion prefactors. Note that the activation energy barriers for several processes and the diffusion prefactors for some processes have already been reported in the literature. The need to present them here is for comparison and completeness necessary to make the point.

4.3.8 Diffusion Barriers

The calculated activation barriers for Cu adatom diffusion on Cu(100) via hopping mechanism for the processes (P1 to P6 displaced in Figure 4.13) are presented in Table 4.5 in which the available experimental and theoretical values are also summarized. Notice that the activation energy associated with the process P1 (0.51 eV) is in quite good agreement with results of previous theoretical studies using ab initio methods and EAM potentials (with different parameterizations Voter and Chen (VC) [65], Adams, Foiles and Wolfer (AFW) [197] and Foiles, Baskes and Daw (FBD) [50]). Note that the comparison to the experimental observation, the theoretical studies overestimates the energy barrier. While helium beam scattering measurements find an activation barrier of 0.28 ± 0.06 eV [154], the low energy ion scattering (LEIS) experiments report them to be 0.39 ± 0.06 eV [198] and 0.36 ± 0.06 eV [155].

The activation energy barriers for the adatom to diffuse away from the step (P2)
and along the step edge (P4) are found to be 0.48 eV and 0.50 eV, respectively. Note that these values are only slightly different from that for the adatom diffusion on the Cu(100) terrace (P1). This reflects that the presence of a step does not noticeably perturb the energy landscape associated with these two processes. On the other hand, in agreement with previous theoretical results [152,199] the calculated diffusion barriers for adatom hop to a lower terrace (P3) from a step edge and away from a step edge (P5) are 0.79 eV and 0.85 eV, respectively. Note that these barriers are considerably higher owing to the fact the processes involve many bonds breaking. The results also indicate the tendency of the adatom to stay close to the step edges. The calculated barriers are in agreement with previous findings [152,199]. Diffusion barrier for adatom diffusion along the step edge at the lower terrace (P6) is found to be relatively small (0.27 eV). These results point that an adatom would prefer to diffuse along the step to the lower terrace rather than to diffuse away from it. The issue, of course, is whether the prefactors are dramatically different. This point will be addressed in Section 4.3.10.

Turning now to the activation energy barriers for Cu adatom hopping on Cu(110), note that geometric anisotropy of this surface leads to interesting variety in the processes. The diffusion activation energy along the open channel (P7) is found to be 0.23 eV, which is similar to that of earlier reported values [152, 159]. As expected, the activation energy barrier for the diffusion perpendicular to the open channel (P8) is much larger (1.15 eV). The dense chains of atoms on Cu(110) are separated by a length larger than the nearest neighbor distance making the diffusion parallel to these chains (open channel) more facile than the direction perpendicular to this channel.
Now turn to the case of adatom diffusion near a step edge and consider its diffusion via hopping mechanism (P9–P13). Note that for these processes there is no value reported in the literature. When the adatom is on the upper terrace, the diffusion activation barriers corresponding to jump over the step (P9), away from the step (P10) and along the step (P11) are 0.64 eV, 0.22 eV and 1.13 eV, respectively. In this cases too, the presence of the step does not influence the energy landscape along and away from it since the barrier energy for P10 is very close to those of P7, P18 and P11. When the adatom is at the lower terrace, the activation barriers are found to be 0.48 eV for P12, and 0.86 eV for P13 signifying decreased mobility along the step edge as compared to that away from it. This is also not surprising since the step edge atoms on this surface have coordination 6 and provide a kinked edge that offers the adatom opportunity for bonding as compared to the smoother edge on the Cu(100) step discussed earlier.
Table 4.5 Diffusion activation barriers via hopping for P1-P13 processes (displayed in Figures 4.13-14)

<table>
<thead>
<tr>
<th>Systems and Processes</th>
<th>Activation Barriers (eV) Present study</th>
<th>Activation Barriers (eV) Available data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu on Cu(100)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1 terrace hop</td>
<td>0.51</td>
<td>0.48 [192]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.40 [156]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.28±0.06 [154]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39±0.06 [198]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.36±0.06 [155]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.44 [192]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.52±0.05 [122]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.48 [152]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.44 [192]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.38 [200]- AFW</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.53 [200]- VC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.51 [192]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.43 [201]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.49 [199]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.53 [159]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.79 [159] - exch.</td>
</tr>
<tr>
<td>P2 away from step</td>
<td>0.48</td>
<td>-</td>
</tr>
<tr>
<td>P3 over step</td>
<td>0.79</td>
<td>0.77 [159, 152]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.51 [159] - exch.</td>
</tr>
<tr>
<td>P4 along step</td>
<td>0.50</td>
<td>-</td>
</tr>
<tr>
<td>P5 away from step</td>
<td>0.85</td>
<td>0.84 [152]</td>
</tr>
<tr>
<td>(lower terrace)</td>
<td></td>
<td>0.83 [199]</td>
</tr>
<tr>
<td>P6 along step</td>
<td>0.27</td>
<td>0.25 [152]</td>
</tr>
<tr>
<td>(lower terrace)</td>
<td></td>
<td>0.26 [199]</td>
</tr>
<tr>
<td>Cu on Cu(110)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P7 along open channel</td>
<td>0.23</td>
<td>0.24 [152]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25 [192]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.23 [200]- AFW</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.28 [200]- VC</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.23 [159]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.87 [152] - exch.</td>
</tr>
<tr>
<td>P8 perpendicular to open channel</td>
<td>1.15</td>
<td>1.15 [152]</td>
</tr>
<tr>
<td>P9 over step</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td>P10 away from step</td>
<td>0.22</td>
<td>-</td>
</tr>
<tr>
<td>P11 along step</td>
<td>1.14</td>
<td>-</td>
</tr>
<tr>
<td>P12 away from step</td>
<td>0.48</td>
<td>-</td>
</tr>
<tr>
<td>(lower terrace)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P13 along step</td>
<td>0.86</td>
<td>-</td>
</tr>
<tr>
<td>(lower terrace)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.3.9 Local Vibrational Densities of States (LVDOS)

The VDOS of the adatom is presented only for the two processes namely P7 and P8 that belong to the diffusion on Cu(110). It is aimed at illustrating important characteristics of vibrational dynamics of the adatom both at equilibrium and saddle point configurations. In Figure 4.15, we have plotted x, y and z-resolved local vibrational density of states for the adatom at the hollow site on Cu(110). The densities of states for the adatom at the saddle point corresponding to the processes P7 and P8 are also shown in Figures 4.16 and 4.17, respectively. Notice from Figure 4.15, the contribution from the x component of the density of states presents a dramatic softening of the low frequency end of the spectrum resulting from a substantial reduction of the force field along the x-direction (open channel). When the adatom is placed in the saddle point configuration, it is actually constrained along the diffusion direction and hence has only two degrees of freedom.

Figure 4.15 LVDOS for Cu adatom on Cu(110) in its minimum energy position for the process P7
From Figures 4.16 and 4.17 one can note a common feature for these two cases -- the appearance of high frequency peaks. In Fig. 4.16, the adatom is constrained in x-direction (P7), and high frequency mode is found for the y-component of the LVDOS.
reflecting the fact that the adatom is in the open channel making a strong bond (stiffening along y) with the atoms on the two surrounding chains. In the case of the process P8, the adatom is constrained in y-direction and high frequency peak is detected in the z-component of the LVDOS. In this case the bond with the atoms just below the adatom at the saddle point is stiffened along the z-direction. These observed features are consistent with what has been reported in earlier study using EAM [192, 202].

4.3.10 Prefactors and Diffusion Coefficients

In this section the calculated prefactors and diffusion coefficients for the two temperatures (300 K and 600 K) are presented and compared with the available experimental and theoretical observations. The results for the prefactors and diffusion coefficients corresponding to the displaced diffusion processes are summarized in Table 4.6. For self-diffusion of Cu adatom on Cu(100) (process P1), the calculated prefactor is found to be $7.29 \times 10^{-4} \text{cm}^2/\text{s}$ at 300 K. This value is similar to those reported from previous theoretical studies and experimental data. For self-diffusion of Cu adatom on Cu(110) terrace, the prefactors are $6.29 \times 10^{-4} \text{cm}^2/\text{s}$ for P7 and $9.97 \times 10^{-4} \text{cm}^2/\text{s}$ for P8. An earlier study [200] for the process P7 reported the prefactor to be $8 \times 10^{-4} \text{cm}^2/\text{s}$ and $4 \times 10^{-4} \text{cm}^2/\text{s}$ using two types of EAM potentials. The same study reported the prefactors to be $3.2 \times 10^{-3} \text{cm}^2/\text{s}$ and $2.7 \times 10^{-4} \text{cm}^2/\text{s}$ for the diffusion perpendicular to the open channel (P8). Notice from Table 4.6 that the calculated prefactors for all the process is of the order of $10^{-3} \text{cm}^2/\text{s}$. Note that this value is the widely assumed prefactor that is frequently
used in the literature. The results point that even though many of the processes studied here involves steps, hence low-coordinated atoms whose vibrational characteristics are different than those for the highly-coordinated atoms. The results show that the contribution from the vibrational characteristics somehow washed out hence leading to constant prefactor value for each process. This point will be addressed in the following Section 4.4.
Table 4.6 Diffusion prefactors and coefficients for P1-P13 processes displaced in Figures 4.13-14

<table>
<thead>
<tr>
<th>Systems and Processes</th>
<th>n, d, α</th>
<th>$D_0(T)$ (cm$^2$/s)</th>
<th>$D_0(T)$ (cm$^2$/s)</th>
<th>$D(T)$ (cm$^2$/s)</th>
<th>$D(T)$ (cm$^2$/s)</th>
<th>$\Delta F_{\text{vib}}$ (meV)</th>
<th>$\Delta F_{\text{vib}}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cu on Cu(100)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>4, 2.56, 2</td>
<td>7.29x10^{-4}</td>
<td>7.43x10^{-4}</td>
<td>2.39x10^{-12}</td>
<td>4.26x10^{-8}</td>
<td>44.4</td>
<td>123.4</td>
</tr>
<tr>
<td>P2</td>
<td>1, 2.56, 1</td>
<td>5.53x10^{-4}</td>
<td>5.64x10^{-4}</td>
<td>2.54x10^{-17}</td>
<td>1.20x10^{-10}</td>
<td>33.6</td>
<td>102.1</td>
</tr>
<tr>
<td>P3</td>
<td>1, 2.56, 1</td>
<td>8.00x10^{-4}</td>
<td>7.97x10^{-4}</td>
<td>5.70x10^{-12}</td>
<td>6.72x10^{-8}</td>
<td>24.1</td>
<td>84.2</td>
</tr>
<tr>
<td>P4</td>
<td>4, 2.56, 2</td>
<td>1.63x10^{-3}</td>
<td>1.62x10^{-3}</td>
<td>6.30x10^{-12}</td>
<td>1.00x10^{-7}</td>
<td>23.5</td>
<td>83.1</td>
</tr>
<tr>
<td>P5</td>
<td>1, 2.56, 1</td>
<td>5.63x10^{-4}</td>
<td>5.73x10^{-4}</td>
<td>3.32x10^{-18}</td>
<td>4.40x10^{-11}</td>
<td>33.2</td>
<td>101.3</td>
</tr>
<tr>
<td>P6</td>
<td>4, 2.56, 2</td>
<td>2.89x10^{-3}</td>
<td>2.81x10^{-3}</td>
<td>1.02x10^{-7}</td>
<td>1.67x10^{-5}</td>
<td>8.78</td>
<td>54.9</td>
</tr>
<tr>
<td><strong>Cu on Cu(110)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P7</td>
<td>2, 2.56, 1</td>
<td>6.29x10^{-4}</td>
<td>6.39x10^{-4}</td>
<td>8.61x10^{-8}</td>
<td>7.48x10^{-6}</td>
<td>48.2</td>
<td>131.5</td>
</tr>
<tr>
<td>P8</td>
<td>2, 3.615,1</td>
<td>9.97x10^{-4}</td>
<td>1.10x10^{-3}</td>
<td>5.57x10^{-23}</td>
<td>2.40x10^{-13}</td>
<td>54.4</td>
<td>144.1</td>
</tr>
<tr>
<td>P9</td>
<td>1, 2.56, 1</td>
<td>2.18x10^{-3}</td>
<td>2.12x10^{-3}</td>
<td>3.31x10^{-14}</td>
<td>8.25x10^{-9}</td>
<td>0.00</td>
<td>33.7</td>
</tr>
<tr>
<td>P10</td>
<td>1, 2.56, 1</td>
<td>1.32x10^{-3}</td>
<td>1.33x10^{-3}</td>
<td>2.46x10^{-7}</td>
<td>1.81x10^{-5}</td>
<td>11.1</td>
<td>58.0</td>
</tr>
<tr>
<td>P11</td>
<td>2, 3.615,1</td>
<td>8.6010^{-3}</td>
<td>8.4010^{-3}</td>
<td>8.55x10^{-22}</td>
<td>2.65x10^{-12}</td>
<td>0.00</td>
<td>34.6</td>
</tr>
<tr>
<td>P12</td>
<td>1, 2.56, 1</td>
<td>1.09x10^{-3}</td>
<td>1.10x10^{-3}</td>
<td>1.15x10^{-11}</td>
<td>1.12x10^{-7}</td>
<td>15.9</td>
<td>67.6</td>
</tr>
<tr>
<td>P13</td>
<td>2, 3.615,1</td>
<td>5.74x10^{-3}</td>
<td>5.72x10^{-3}</td>
<td>1.75x10^{-16}</td>
<td>3.20x10^{-10}</td>
<td>9.09</td>
<td>54.2</td>
</tr>
</tbody>
</table>
In Table 4.7, the prefactors calculated using both the Arrhenius equation (for different temperature) and the Vineyard equations are presented. It is aimed at revealing the fact that at relatively high temperature, the prefactors obtained using the Arrhenius equation is similar to those obtained using the Vineyard’s equation (explicit derivation is presented in the Appendix A: SUB-CHAPTER 4.3). The prefactors using the Vineyards equations (equation 4.4) are obtained by means calculating the vibrational frequencies of the diffusing atom at both equilibrium and the saddle point configurations.

Table 4.7 Variation of the prefactors calculated for different temperatures, and from the Vineyard’s equation

<table>
<thead>
<tr>
<th>Arrhenius Equation</th>
<th>Cu(100) Prefactors (cm$^2$/s)</th>
<th>Cu(110) Prefactors (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>2.263</td>
<td>1.479</td>
</tr>
<tr>
<td>200</td>
<td>2.143</td>
<td>1.475</td>
</tr>
<tr>
<td>300</td>
<td>2.123</td>
<td>1.475</td>
</tr>
<tr>
<td>400</td>
<td>2.120</td>
<td>1.475</td>
</tr>
<tr>
<td>500</td>
<td>2.113</td>
<td>1.475</td>
</tr>
<tr>
<td>600</td>
<td>2.111</td>
<td>1.475</td>
</tr>
<tr>
<td>700</td>
<td>2.110</td>
<td>1.475</td>
</tr>
<tr>
<td>Vineyard’s Equation</td>
<td>2.107</td>
<td>1.475</td>
</tr>
</tbody>
</table>

In order to find out whether the Meyer Neldel compensation rule [196] holds for these systems, we have plotted in Figure 4.18 the log of the prefactors for each process and their corresponding activation energy barriers. Notice form the figure that only few processes (P7, P12, P9, P13, and P11) on Cu(110) seem to follow the compensation rule. For these processes, the activation energy barriers vary between 0.23 eV to 1.13 eV, and the prefactors range from $6.29 \times 10^{-4}$ cm$^2$/s to $8.6 \times 10^{-3}$ cm$^2$/s. However, in general, this rule
is not obeyed especially for the processes on Cu(100). This conclusion is in qualitative agreement with that reported by an experimental study [203], while it contradicts the earlier theoretical findings.

Figure 4.18 Logarithm of the prefactors versus the activation barriers for the processes P1-P13 on Cu(100) and Cu(110).

4.3.11 Conclusions

In this study we have investigated the role of vibrational entropy on several adatom diffusion processes on Cu(100) and Cu(110) terraces and near step edges. We have calculated diffusion barriers, prefactors, and diffusion coefficients for each diffusion process for adatom hopping. The prefactors and the diffusion coefficients are obtained using the harmonic approximation of lattice dynamics. For Cu(100) the prefactors are found to be in the range from $5.53 \times 10^{-4}$ to $2.89 \times 10^{-3}$ cm$^2$/s at 300 K, in good agreement
with available experimental data and previous calculations. For adatom hopping on Cu(110) terraces and step edges, the prefactors range from $6.29 \times 10^{-4}$ to $8.6 \times 10^{-3}$ cm$^2$/s. Temperature has very little effect on these values when rising it to 600 K. The prefactors for each process are found to be the usual value ($10^{-3}$ cm$^2$/s). Though the Meyer–Neldel compensation rule is not found to be obeyed in general for the processes studied for each surface, most of the processes on Cu(110) show a certain tendency of compensation.
4.4 Origin of Quasi-constant Pre-exponential Factors for Adatom Diffusion on Cu(100) and Ag(100)


Many-body interaction potentials from the embedded atom method with two functionals and electronic structure calculations based on density functional theory and the plane-wave pseudopotential method are used to calculate the pre-exponential factors for self-diffusion of adatoms via hopping on Cu(100) and Ag(100) surfaces with and without steps. The pre-exponential factors are found to be in the range of $10^{-3}$ cm$^2$/s for all investigated processes regardless of whether substrate vibrational dynamics are included or omitted. When substrate dynamics are ignored, compensation effects between stiffening and softening of the vibrational frequencies of the diffusing atom are responsible for this quasi-constant pre-exponential. When these dynamics are included, subtle cancellations in the vibrational free energy make the local contribution of the diffusing atom the dominant one.

4.4.1 Introduction

Thermally activated processes often control the end product in technologically important processes such as thin film growth and heterogeneous catalysis. Detailed and
accurate knowledge of relevant energetics and dynamics of such processes is thus essential if simulation of spatio-temporal evolution of materials is to have predictive power. One of the major computational techniques used to study such evolution of materials is KMC calculating diffusion coefficients estimated from HTST [109, 204]. These coefficients depend on two main ingredients, namely, the activation energy barrier and the pre-exponential factor (or prefactor). Much attention has been given to the calculation of the activation energies, while the prefactor is often assumed to take the “standard value” of $10^{-3}$ cm$^2$/s [27, 42, 203]. It is also customary to note that uncertainties in the activation energies would generate fluctuations in the diffusion coefficient that are much larger than those generated by deviations in the prefactors from the standard value. Since accurate determination of the activation energies (for example, using DFT) is becoming more and more feasible, focus has been turning toward a more realistic determination of the prefactors. Such knowledge is certainly important for cases in which accurately determined energy barriers for competing processes lie very close in value to one another.

In previous publications [90, 148, 192], a detailed description of a quantum mechanical approach to calculate these prefactors within the harmonic/quasiharmonic approximation has been presented and recently applied to the case of adatoms hopping on terraces and steps of Cu(100) and Cu(110) [90]. Indeed, the prefactor was found to be of the order of $10^{-3}$ cm$^2$/s with a variation of about less than 1 order of magnitude. Note here that a full quantum mechanical treatment of the prefactor is not a trivial matter even when the inter-atomic interaction potential is of a semi-empirical nature [90, 148, 192]. In such calculations, force constant matrices (evaluated from the partial second derivatives of the
potential) for the whole system (diffusing entity plus substrate) in the minimum energy and saddle point configurations need to be calculated. Consequently, if the system has N atoms, it presents $3N$ modes at the minimum energy configuration and $3N-1$ for the saddle point configuration. With these frequencies, or their densities of states, one calculates the prefactors using the recipe presented in previous publications [148, 192].

While this procedure is feasible when the interaction potentials are of empirical or semi-empirical nature, it becomes quickly formidable with increasing system size when the interaction is described using DFT. Understandably, calculations of the prefactors based on DFT have been carried out by totally or partially neglecting the dynamics of the substrate [143, 205]. As a matter of fact, for the studied fcc metals, these approximations do not appear to be drastic as shown by Ratsch and Scheffler for the case of Ag adatom diffusion on Ag(111) for which the prefactor changes only by a factor of 2 when the dynamics of the substrate are partially included [143]. There was thus an informal consensus that for most fcc metals the prefactor for adatom hopping was close to the “standard” value and that the dynamics of the substrate played a minor role in its determination.

In a recent publication, Kong and Lewis [206], however, claim that the role of the substrate dynamics is crucial for the determination of the prefactor for self-diffusion on the same set of metal surfaces as above. Note that while previous DFT calculations have included the substrate dynamics partially, in one previous study [90] and see references therein, calculations based on semi-empirical potentials have incorporated the full vibrational dynamics of the substrate in calculating all contributions to the system vibrational entropy. Note also that in previous publications [148, 192] while only local
contribution to the system vibrational entropy was emphasized, calculations nevertheless included full substrate dynamics. We would like to mention that in a recent study [207] of both adatom and dimer diffusion on the (100) and (110) surfaces of Ag and Cu, using interaction potentials based on the EAM [50], we also find the prefactor to be “normal.” As we shall see, noticeable cancellations and compensations account for the insensitivity of the prefactor to the extended dynamics of the system, for the cases in question.

Two issues now arise. The first is the apparent contradiction between the conclusions reached by Kong and Lewis, and others about the role of the substrate dynamics in determining prefactors for adatom hopping on Cu and Ag surfaces. There is much confusion in the literature on when and how local approximations are invoked and when extended dynamics play a role. In this work, we isolate the different dynamical contributions and calculate the role of local and extended system geometry in determining the prefactor. The second, and perhaps the more important, is the lack of understanding of the factors that may contribute to a quasi-constant value for the prefactor. To make transparent such contributions, we present a systematic study using both semi-empirical and ab-initio approaches.

4.4.2 Theoretical Details

As prototype systems, we consider the case of adatom diffusion via hopping on Cu(100) and Ag(100) surfaces in order to demonstrate how local coordination dictates subtle cancellations in contributing to the vibrational free energy that makes the prefactor independent, to a good approximation, of substrate dynamics. Moreover, we will show that unless the diffusing entity experiences a dramatic softening and/or stiffening of one
or several of its modes, the prefactors lie in the range of $10^{-3}$ cm$^2$/s as a result of a compensation resulting from softening of some modes accompanied with stiffening of others. These two effects are general and can be expected to hold for all systems in which coordination is the main player in dictating the variations in vibrational energies and frequencies. To our knowledge, these two microscopic effects have not been reported before. Below, we will first present the results for prefactors calculated using the dynamics of the entire system under consideration. Since we use a local approach to determine vibrational dynamics, a detailed analysis of the contribution of every atom in the system to the dynamics and thermodynamics is possible. We thus separate out the local and the extended contributions and evaluate their relative importance. The local contributions to the prefactor are obtained independently through calculations of vibrational frequencies of the diffusing atom while the substrate is held fixed, as these can be used in the Vineyard equation [109, 204].

In Figure 4.19, we describe the diffusion processes involving hopping of an adatom from one fcc hollow site to the next on a terrace and near a step edge of a fcc(100) surface. Arrows are used to show the direction along which the adatom performs the diffusion process with the corresponding label. The process labeled P1 corresponds to a hop on a (100) terrace, while processes P2, P3, and P4 are associated, respectively, with an adatom originally on the upper terrace and at the step edge performing (i) a jump away from the step edge, (ii) a descent from the step, and (iii) diffusion along the step. Finally, processes P5 and P6 correspond, respectively, to diffusion on the lower terrace away from and along the step edge, as shown in the figure.
Figure 4.19 Investigated adatom diffusion processes via hopping on fcc(100). The red rectangular represents the locatility chosen to derive local contributions.

In the semi-empirical approach, the energetics and dynamics of the system (Cu or Ag) are calculated using EAM potentials [50] based on two functionals: one provided by Foiles, Baskes, and Daw (FBD) [64] and the other by Voter and Chen (VC) [65]. Total energy electronic structure calculations are performed using DFT [48], as implemented in the computational code Vienna ab initio simulation package (VASP) [171]. The generalized gradient approximation (GGA-PW91) is used to describe the exchange correlation functional [78]. For calculations using semi-empirical potentials, the system consists of a slab consisting of 14 layers, each containing 64 atoms (8x8) on top of which a 24 atom stripe (3x8) is added for the calculations involving a step. The whole system is relaxed except the last two layers and a few atoms in the stripe are fixed to prevent it from sliding during the saddle point search. To obtain relaxed configurations, a standard
CG method is used for minimizing the total energy of the system [91].

For DFT calculations of bulk systems, energy cut offs of 234 eV (for Cu) and 181 eV (for Ag) for the plane waves and a10x10x10 Monkhorst-Pack k-point sampling of the BZ are used that yields lattice constants of 3.645 Å and 4.168 Å for Cu and Ag, respectively. For the calculations involvin terraces, a 7x7x1 k-point mesh is used with a unit cell consisting of 5 layers with four (2x2) atoms per layer. For stepped surfaces, a unit cell consisting of 4 layers with 15 (5x3) atoms per layer, and a stripe consisting of 9 (3x3) atoms are used. The k-point mesh used in the calculations is 2x3x1. In all surface calculations, a vacuum of 12–14 Å is used to separate the slabs. The atoms in the bottom layer of the slab are held fixed during relaxations to prevent a global shift of the slab during the saddle point search.

For complete inclusion of the dynamics of the system, we perform calculations using a real space Green’s function method [52], which has been described extensively in previous publications [90, 192] and in Chapter 2.3. In this method, the VDOSs for any atom in the system are explicitly evaluated. With these VDOSs in hand, one can calculate all vibrational thermodynamics, and consequently prefactors, within the TST [109, 204] and the harmonic approximation of the lattice dynamics using the equation below:

\[
D_0(T) = \frac{k_B T}{h} \frac{n d^2}{2 \alpha} \exp \left( -\frac{\Delta F_{\text{vib}}}{k_B} \right)
\]  

(4.14)

where \(n\) is the number of equivalent jumps, \(d\) and \(\alpha\) are jump distance and dimensionality of the motion, respectively. Note that the TST is an approximation based on the assumption that a recrossing at the dividing surface is forbidden (for a detailed discussion on TST, see Ref. 208).
The critical factor in the determination of prefactors is the change in the vibrational free energy $\Delta F_{vib}$, which consists of contributions from all localities of the system. For the discussion here, we divide the system into three parts: the adatom, the atoms labeled 1–8 (Figure 4.19) (hereafter, we will drop the word “labeled”), and the rest (atoms 9–N, with N+1 being the total number of atoms in the system). Note that by symmetry, atoms 1 and 2, 3 and 4, and 5 and 6 are equivalent, and hence are grouped in equivalent, and hence are grouped in Table 4.8. The total vibrational free energy of the system can hence be written as:

$$F_{vib} = F_{vib}^{adatom} + \sum_{i=1}^{8} F_{vib}^{i} + \sum_{j=9}^{N} F_{vib}^{j}$$  (4.15)

### 4.4.3 Results and Discussions

In Table 4.8, the calculated values of $F_{vib}^{adatom}$ and $F_{vib}^{i}$ where $i \in [1,8]$ for the two configurations of Cu adatom (hollow site and saddle point) on Cu(100) for temperatures of 300 K and 600 K, using EAM-FBD potential are presented in Table 4.8. Analysis of the local vibrational free energy shows that $F_{vib}^{j}$ for all other atoms where $j$ between 9 and $N$ is independent of whether the adatom is at the hollow site or at the saddle point just as for atom 8 in Table 4.8. Consequently, these atoms do not contribute to $\Delta F_{vib}$ and to the prefactor. This observation leads to the conclusion that the presence of the adatom affects only locally the vibrational dynamics of the system. The same conclusion has been drawn for vicinal surfaces for which the vibrational dynamics of atoms away from the step were found to be unaffected by the presence of the step [209]. It can thus safely to be
concluded that only the neighbors of the diffusing atom contribute to the evaluation of the prefactor, in the systems under consideration.

Table 4.8 Vibrational free energy contributions per Cu atom at two different configurations of the system (hollow site and the saddle point).

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$F_{vib}$ (meV) Hollow site 300K</th>
<th>$F_{vib}$ (meV) Saddle point 300K</th>
<th>$F_{vib}$ (meV) Hollow site 600K</th>
<th>$F_{vib}$ (meV) Saddle point 600K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adatom</td>
<td>-52</td>
<td>-18</td>
<td>-214</td>
<td>-111</td>
</tr>
<tr>
<td>Atoms #1 and #2</td>
<td>-35</td>
<td>-40</td>
<td>-180</td>
<td>-189</td>
</tr>
<tr>
<td>Atoms #3 and #4</td>
<td>-35</td>
<td>-26</td>
<td>-180</td>
<td>-163</td>
</tr>
<tr>
<td>Atoms #5 and #6</td>
<td>-40</td>
<td>-40</td>
<td>-189</td>
<td>-189</td>
</tr>
<tr>
<td>Atom #7</td>
<td>-23</td>
<td>-20</td>
<td>-156</td>
<td>-150</td>
</tr>
<tr>
<td>Atom #8</td>
<td>-20</td>
<td>-20</td>
<td>-150</td>
<td>-150</td>
</tr>
</tbody>
</table>

We now proceed to a detailed analysis of the vibrational free energy of the adatom and its neighbors labeled 1–8 (Table 4.8) for the case of Cu adatom hopping on Cu(100). Notice from the table that the adatom itself has the largest contribution to the vibrational free energy difference: +34 meV and +103 meV at 300 K and 600 K, respectively. This is followed by atoms 3 and 4 with changes (for each atom) of +9 meV and +17 meV at 300 K and 600 K, respectively. For atoms 1 and 2, these changes are $-5$ meV and $-9$ meV for the two temperatures (note the negative sign for these two atoms). The second layer atom (7) is less affected with changes of +3 meV and +6 meV for the two temperatures. Finally, the change in the vibrational free energy for atoms 5, 6, and 8 is less than 1 meV. The net change in the vibrational free energy is 45 meV when calculated globally (using the whole system) and 34 meV when using the dynamics of only the adatom at 300 K. These values are 125 meV and 103 meV at 600 K for global
and local calculations, respectively. Note that the 103 meV found in this case is very close to that found by Kurpick, Kara, and Rahman (120 meV) who used only the local contribution of the adatom [192]. It is hence obvious from these values that the adatom is the main contributor to the change in the vibrational free energy and hence the prefactor. This is mainly due to the fact that the contribution of atoms 1 and 2 (−10 meV at 300 K) counters that of atoms 3 and 4 (+18 meV at 300 K), resulting in a net change that is marginally dependent on the substrate dynamics. To compare our results with those reported by Kong and Lewis, note that at 600 K, the contribution of the substrate to the change in the vibrational free energy is only 17% in the present study as opposed to −200% found by Kong and Lewis [206] (21.00 meV global as opposed to 61.17 meV local). Note that in the present case, the contribution of the substrate dynamics to the change of the vibrational free energy is positive, while that reported by Kong and Laurent [206] is negative. Consequently, in our calculations when the dynamics of the substrate are included, the prefactor decreases slightly in agreement with the findings of Ratch and Scheffler [143] whereas in the case of prefactors reported by Kong and Lewis, the prefactor always increases when full dynamics of the system are included in the calculations [206].

Since the compensation effect found above involves mainly atoms 1–4, we will present here a physical explanation of the possible origin of these contributions. First, let us analyze the case of atoms 1 and 2 in the two configurations of the adatom. When the adatom is at the hollow site (on top of atom 7), atoms 1 and 2 are neighbors of the adatom. Since these two atoms are originally from the (100) surface with coordination 8, the presence of the adatom increases their coordination to 9, and their contribution to the
vibrational free energy is $-35$ meV (each) at 300 K, in good agreement with the earlier published value of $-33$ meV for Cu(111) on which surface atoms have coordination 9 [131]. When the adatom is placed at the saddle point (on the bridge site between atoms 3 and 4), the coordination of atoms 1 and 2 is back to its surface value (8), and for this configuration, from Table 4.8, their contribution is $-40$ meV (each), again in agreement with previously published value of $-39$ meV for atoms on Cu(100) at 300 K [131]. The change of coordination from 9 to 8 is responsible for a negative contribution to the vibrational free energy. Now let us turn to the case of atoms 3 and 4 for which the coordination is 9 when the adatom is at the hollow site, with a contribution of $-35$ meV (each) at 300 K. When the adatom is placed at the bridge site, its coordination now is only two which forces its distance to atoms 3 and 4 to shrink (the bond length drops from 2.417 Å to 2.309 Å) causing an increase in the vibrational free energy of atoms 3 and 4 that reaches the value of $-26$ meV. This behavior is consistent with the previous published results on the behavior of the local vibrational free energy versus coordination and bond lengths [132].

Having demonstrated that the substrate dynamics may be neglected for evaluating prefactors for Cu adatom diffusion via hopping on Cu(100), the approach can be simplified in order to obtain further insights into adatom diffusion by focusing only on its vibrational frequencies. In other words, we will use the frozen phonon method in which we calculate the frequencies of the normal modes of the adatom: three modes at the minimum energy configuration and two modes at the saddle point. To determine the frequencies of these modes from EAM-FBD and EAM-VC, local force-constants are obtained from the calculated total energy of the system. For example, for the adatom
diffusion along the x direction, we start with the adatom in the fcc hollow site configuration and perform three sets of calculations corresponding to the adatom being placed between −0.2 Å and +0.2 Å around the equilibrium position and along the x, y, or z direction, with an increment of 0.02 Å. At the saddle point (taking the diffusion path to be along the x axis), only two sets of calculations are performed along the y and z directions with the same increment. Each set of calculations provides the energy of the system versus position around the equilibrium and/or saddle which was then fitted by a quadratic function yielding the force-constant associated with the normal mode along that direction. The same procedure has been adopted when using DFT calculations except that here the number of points along a given direction is reduced to 5 (a check using seven points did not introduce any change in the frequencies). To introduce substrate vibrational contribution (in the case of DFT calculations), we added the frequencies of the nearest neighbors of the adatom. Note that in a previous Chapter (4.3), we have already presented the results for prefactors for the above mechanisms on Cu(100) and Cu(110) using EAM-FBD potentials and with the inclusion of the vibrational dynamics of the whole system [90].
A comparison of the frequencies of the normal modes of the adatoms (Cu or Ag) on Cu(100) and Ag(100) obtained from either of the EAM functional and DFT shows interesting trends as may be noted from the plots in Figure 4.20, in which differences in the calculated frequencies are noted by their deviation from the diagonal. From Figure 4.20.a (the case of Cu), one notes that the force field around the adatom as described by VC functional is stiffer than that described by FBD functional. However, this is not true...
for Ag (see Figure 4.20.b) for which no systematic trend is found for either functional to yield stiffer force field. The same observation holds when comparing DFT-GGA and FBD (Figure 4.20.c) for which there is a tendency for FBD to yield a softer force field than DFT-GGA (with the exception of the case of saddle point for process P6). For Ag (Figure 4.20.d), the tendency for DFT-GGA to yield a stiffer force field is less pronounced than the case of Cu. One general observation is that differences in the calculated frequencies using the different potentials do not exceed 0.7 THz, for all cases studied here. Since the exact values of the calculated frequencies may be of the interest to the reader, we have summarized them in Table B.1 in Appendix B: SUB-CHAPTER 4.4.

When substrate dynamics are neglected, the calculations of the prefactor follow trivially from the Equation 4.14, using the adatom normal mode frequencies to calculate the difference in the vibrational entropy. Such prefactors for several diffusion processes of Cu adatom on Cu(100) and Ag adatom on Ag(100) using EAM-FBD, EAM-VC, and DFT-GGA are presented in Tables B.2 and B.3 in Appendix B: SUB-CHAPTER 4.4, respectively.

The prefactors obtained from DFT (when dynamics of neighboring substrate atoms are included) are also presented in these tables. Notice from the tables that the prefactors do not deviate by more than a factor of 2 from the so-called normal value of “10^{-3} \text{ cm}^2/\text{s},” in agreement with previous results. Since the temperatures chosen here are close to or higher than the Debye temperature of the solid, as expected [90, 148, 192] temperature has almost no effect on prefactors. It is interesting to point out that even when the full substrate dynamics are included as in our previous publication [90] for Cu adatom diffusion on Cu(100) and Cu(110), the prefactors also lie within a factor of 2 as
compared to those presented here, with the exception of the case of process P1 for which the factor is 2.9.

Another observation that can be deduced from the tables is that, even if the frequencies of the modes calculated from different potentials showed differences, these are washed out in the thermodynamic functions because of a subtle but systematic compensation effect. Indeed, in general, modes with polarization parallel to the surface have their frequencies soften when moving from the hollow site to the saddle point, while the frequencies of modes with polarization perpendicular to the surface experience stiffening. This again can be rationalized in terms of coordination of the adatom. Indeed, at equilibrium (let us say on fcc(100) surface), the adatom coordination is 4 and it drops to 2 when the atom is at the bridge (saddle) point. The loss of (in-plane) neighbors causes the softening of the in-plane (parallel) mode. On the other hand, at the saddle point, the coordination being very low and due to the bond-length/bond-order correlation, the relaxation is such that the adatom bond to the two surface atoms shortens drastically (the shortening involves mostly the component perpendicular to the surface) resulting in a stiffening of the perpendicular mode. This is a general argument that can be transferred to other surface geometries and the validity of these arguments are tested for (110) and (111) surfaces [90]. To quantify this observation, let us use the Vineyard equation [109, 204] to calculate the prefactor:

\[ D_0 \propto \frac{v_1^h v_2^h v_3^h}{v_2^s v_2^s} \]  \hspace{1cm} (4.16)

where \( v_1^h, v_2^h \) and \( v_2^s \) are the frequencies of the three normal modes when the adatom is in the
hollow site and $v_2^s$ and $v_3^s$ are those corresponding to the saddle point (here assume that the diffusion path is along direction “1”). Note that in the classical limit, Equation (4.14) reduces to Equation (4.16). We introduce the ratio $r \parallel = \frac{v_2^h}{v_2^s}$, $r \perp = \frac{v_3^h}{v_3^s}$, assuming that direction “2” is parallel to the surface (either $x$ or $y$, depending on the process) and direction “3” is perpendicular to the surface ($z$). In Table 4.9, these ratios of the frequencies are presented for the adatom on Cu and Ag surfaces for each diffusion process. We find that while these ratios never exceed 1.4 nor go below 0.7, in general, $r \parallel$ is larger than 1 (the mode parallel to the surface goes soft) while $r \perp$ is less than 1 (the mode goes stiff). Since the prefactor is proportional to the product of these two ratios, the net effect of the coupled softening and stiffening of the modes is to keep the prefactor almost constant. We expect this compensation effect to be general, at least for hopping processes, and present it as the rationale for the general tendency of the prefactor to stay close to the “normal” value of $10^{-3}$ cm$^2$/s.
Table 4.9 Ratios of the frequencies of the adatom parallel and perpendicular to the surface for each process (values in the parenthesis are for Ag)

<table>
<thead>
<tr>
<th>Processes</th>
<th>EAM-FBD</th>
<th>EAM-VC</th>
<th>DFT-GGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1 hopping on flat</td>
<td>1.11</td>
<td>1.08</td>
<td>1.06</td>
</tr>
<tr>
<td></td>
<td>(1.14)</td>
<td>(1.07)</td>
<td>(1.10)</td>
</tr>
<tr>
<td>P2 diffusion away from step on the upper terrace</td>
<td>1.04</td>
<td>1.06</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>(1.12)</td>
<td>(1.04)</td>
<td>(1.08)</td>
</tr>
<tr>
<td>P3 diffusion rolling over step</td>
<td>1.10</td>
<td>1.11</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>(1.18)</td>
<td>(1.13)</td>
<td>(1.03)</td>
</tr>
<tr>
<td>P4 diffusion along the step on the upper terrace</td>
<td>1.06</td>
<td>1.08</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>(1.16)</td>
<td>(1.08)</td>
<td>(1.02)</td>
</tr>
<tr>
<td>P5 diffusion away from step on the lower terrace</td>
<td>0.92</td>
<td>1.07</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>(1.02)</td>
<td>(0.94)</td>
<td>(0.94)</td>
</tr>
<tr>
<td>P6 diffusion along step on the lower terrace</td>
<td>0.98</td>
<td>1.06</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>(1.03)</td>
<td>(1.05)</td>
<td>(1.33)</td>
</tr>
</tbody>
</table>

4.4.4 Conclusions

In conclusion, we have calculated the pre-exponential factors of several processes for adatom diffusion via hopping on Ag(100) and Cu (100) including and excluding the full dynamics of the substrate. Two types of semi-empirical potentials and a first principles approach are used. We find that including the substrate dynamics in the determination of pre-exponential factors does not introduce pronounced effects (a factor less than 2 is, in general, observed) for adatom diffusion via hopping on flat and stepped surfaces of Cu(100) and Ag(100) regardless of the method used for describing the inter-atomic interaction. Compensation effects in the vibrational frequencies of the diffusing entity and cancellations in the change of the vibrational free energy are responsible for the quasi-constant value around $10^{-3}$ cm$^2$/s reported frequently in the literature.
The arguments used here to rationalize the quasi-constant value of the prefactor are based on coordination and one would need to test its validity neither for more complex situations at which the diffusion is not single atom nor via hopping, like in the case of an exchange mechanism. The validity of this approach is tested for the diffusion of single atoms and clusters on (111) surface. These results will be discussed in the following chapter.
4.5 Multi Approach to the Simulation of 7-atom Cluster Diffusion on Fcc(111)

We present results of comparative study using multi-scale simulation methods to derive diffusion activation barriers and dynamics for compact hexagonal Cu heptamers on Cu(111) and on Ag(111) using EAM and DFT. Analysis of the relaxations obtained for homo and hetero systems revealed that intra-cluster interaction is more enhanced for the hetero system as compared to that for the homo as a result of the large misfit between the cluster atoms and those of the substrate. The electronic DOS of the middle cluster atom for Cu$_7$ on Ag(111) presents discrete states originating from the strong interaction among the cluster atoms as compared to between cluster and substrate. Analysis of the cluster binding energies revealed that for Cu$_7$ cluster on Ag(111), the binding energy per cluster atom is lower than that for the single atom originating from the strong intra-cluster interaction which reduces the binding energy relative to the substrate. We find for the hetero system that the strong intra-cluster interaction increases the population at the low frequency end of the spectrum that governs the vibrational free energy. This then leads to smaller prefactor as compared to the homo system. Prefactors obtained from static calculations revealed small deviation of the prefactors for heptamer diffusion from those for single atoms. Short time MD simulations showed that the cluster diffuses via concerted motion for 400K and 550K. We observed that the cluster encounters shape change frequently during its diffusion for 700K. For the hetero case, we also find that cluster tends to become 3D. Effective diffusion parameters obtained from long time MD simulations revealed that the diffusion of the cluster governed by the motion of single atoms and dimers. For the homo case, we find the prefactor for the cluster diffusion to be
much larger than that for the single atom, while the hetero case does not show the same trend. Our results point that for multi-atom diffusion, the inclusion of full substrate dynamics are important revealing the limits of using static simulations.

4.5.1 Introduction

The mechanism and the energetics by which clusters diffuse on crystal terraces are important phenomena for understanding growth of thin films, since the kinetics of diffusion and stability of clusters determine the size and shape of nucleating islands [210]. As compared to the diffusion of single atoms, cluster diffusion involves additional information emerging from interactions of atoms within the cluster. Because the energetics and the mechanisms can be affected by these interactions, they are important for better understanding growth kinetics [211]. Cluster diffusion can be detected using such experimental techniques as FIM and STM. In such experiments, imaging of clusters is taken at intervals so that change in the position or the shape can be detected. However, it is challenging to image transition states, which are generally short-lived. Hence, many experimental observations have benefited from such theoretical studies as MD, which allow short-lived transitions to be determined in a more direct way. A good example is the studies combining FIM experiments (at about 450 K) and MD simulations to reveal the dominant mechanisms and the diffusion dynamics for the diffusion of hexagonal (compact) Ir clusters on Ir(111) [212]. In these experiments for the diffusion of several sizes of Ir clusters on Ir(111), the authors have shown that for non-compact clusters, diffusion takes place via migration of atoms along the cluster edges, changing the shape of the cluster [213]. They showed that the prefactor for the non-compact Ir_{18} cluster is
about $10^{-3}$ cm$^2$/s, which is comparable to that for a single atom [213-215]. On the other hand, for compact clusters, diffusion was found to be possible even without any change in cluster shape. They also showed that diffusion of Ir$_7$ and Ir$_{19}$ clusters (both compact) occurs via the entire cluster’s gliding over the Ir(111) surface [213]. They noted that the prefactors are three orders of magnitude higher than that for the non-compact Ir$_{18}$ cluster. They proposed that the high diffusivity observed for these compact clusters might be tied to the characteristics of some special mechanism by which the clusters diffuse. A subsequent MD study [216] for the diffusion of an Ir$_7$ cluster revealed that cluster gliding is the dominant mechanism. Experimental observations (FIM) [217] for the diffusion of Pt clusters have also shown that the prefactor for Pt$_7$ cluster is two orders of magnitude larger than that for single Pt atom diffusion [215, 218].

These experimental observations motivated many theoretical studies including both static and dynamic simulations [219]. A DFT [220] study for the diffusion of Ir$_7$ and Ir$_{19}$ clusters on Ir(111) showed that the bridge-glide is the favored mechanism for these compact clusters. They also performed calculations using EAM and effective medium theory (EMT) to calculate the prefactors for the studied mechanism. They reported prefactors to be higher than that of a single atom. In contrast to the reported high prefactors in this study, Kurpick et. al, using MD and MS simulations [221] found the prefactor for Ir$_7$ to be in the same range of that for single atom. Kurpick et. al have concluded that the observed high prefactor in the experiments is the result of a large number of non-equivalent processes [222] with similar activation barriers. The prefactors in the Kurpick et. al study are calculated using LVDOS for the mechanisms revealed by the MD simulation. This MD study also showed that although during most of the
simulation time, the cluster preserves its compact shape, nevertheless, for short times, shape distortions do arise. In accordance with these results, MD simulations for Pd clusters also reported similar behavior [223].

A recent MD study [224] for the diffusion of Cu clusters (from one to eight atoms) on Cu(111) using the modified embedded atom method (MAEAM) [225] reported that for compact clusters, intermediate distorted states are short–lived and suggested that this might be the reason why they are not seen in experiments. In agreement with the experimental observations for compact Ir and Pt clusters [213, 214, 218, 218], the authors also found that the prefactor for the diffusion of Cu$_7$ cluster on Cu(111) is three orders of magnitude larger than that for a single atom. However, the latter MD study by Yang et. al for the same system reported the prefactor to be only a couple of factors higher than that for single atom diffusion [226]. The difference in the prefactors reported in the former MD study may originate from lack of sufficient statistics. The latter study had also reported that dissimilarity in the prefactor results between the experiments for Ir$_7$ cluster and that of their MD simulation for Cu$_7$ cluster originates from differences in the interactions within the respective clusters.

The question thus arises from these observations as to whether the divergences over the scale of the prefactors lie in misinterpretation of the experiments or in shortcomings in the MD simulations. A MD simulation after all confronts an inherent obstacle in time scale that can be encompassed in a simulation. Even with today’s modern computers and using empirical potentials, the largest time scale that can be embraced is in the micro-second range. Such a time scale is obviously far short of any experimental one, which can run from minutes to days or even months. In addition to
that, realistic description of interactions between the atoms, is an issue especially for hetero-epitaxial systems, but even for homo-epitaxial systems as well. If one relies on semi-empirical potentials, the knowledge is confined to information about atomic charges, without equally crucial information about electronic interactions. The alternative is to derive the interactions from DFT. But if one does so, the simulations will be confined to relatively few number of atoms, and across a relatively minuscule span of time-even less than what can be attempted with semi-empirical potentials.

In order to address some of the issues set forth above, we take a multi-tool approach to the two outstanding questions concerning 7-atom Cu compact-cluster, namely, the scale of the prefactors in comparison with that governing single-atom diffusion and whether the dominant mechanism of the diffusion is concerted motion or some pattern of successive distortion of the cluster. For the calculation of energetics we use both EAM and DFT in order to see to what extent the two methods agree in their results. Moreover, we study the cluster’s diffusion in both a homoepitaxial (Cu$_7$ on Cu(111)) and a hetero-epitaxial system (Cu$_7$ on Ag(111)). We choose Ag for the hetero-epitaxial case because it affords a relatively large mismatch with the cluster atoms in order to investigate how an increase in binding energy within the cluster and decrease in binding energy between these and those of the substrate affects the diffusion barriers and prefactors (via phonons). Comparing the effect of inter-atomic interactions in these two systems on the prefactors also enables us to test the suggestion by Yang et. al [226] that the observed unusual prefactors for Ir, Pt in comparison to that of Cu emerges from the dissimilarity of the interactions.
We first perform MD simulations using EAM to reveal the dominant mechanisms for the diffusion of 7-atom cluster. These simulations can also help us to determine the energetics and dynamics. Note that these simulations provide effective values for both energetics and dynamics since they involve many possible diffusion mechanisms for the given time and temperature. Following the MD simulations, we also perform MS simulations for the diffusion of 7-atom cluster considering only the concerted motion diffusion mechanism. The information obtained from MD simulations combined with the calculated effective diffusion barriers from MD study is expected to reveal the dominant diffusion mechanisms from the energetics point of view.

For the calculation of the diffusion dynamics, we again use both DFT and EAM. We approach the problem in several steps. At the first step, we calculate the vibrational frequencies allowing only the adsorbate vibrations. We then examine the effect of the vibrational contributions of the substrate atoms to the attempt frequencies. These calculations are performed using RSGF method [52] with the interactions derived from EAM. For calculations using DFT, we calculate the vibrational frequencies by allowing additional degrees of freedom. We also examine these dynamical parameters via MD simulations for which the vibrational contribution of the whole system is embedded in the calculations.

The chapter is organized as follows. In section 4.5.2 we present the details of the methods used to calculate diffusion energetics and dynamics. This is followed by section 4.5.3 which contains our results and discussions. This section is divided in to four subsections focusing respectively on the structural and electronic properties, energetics and dynamics of the systems under study. In section 4.5.8, we will present the conclusions.
4.5.2 Details of the Calculations

Using MS simulations, we first calculate diffusion energetics and dynamics for the diffusion of a Cu adatom and a Cu$_7$ cluster (via concerted motion) on Cu(111) and Ag(111). For the calculation of diffusion barriers, we use the interactions derived from EAM [50] and DFT [48] to carry out MS simulations. For our EAM calculations, we use the lattice constants of 3.615 Å and 4.09 Å for Cu and Ag, respectively. A simulation box containing of 24 layers with 100 atoms per layer arranged in an fcc lattice is used.

For the total energy electronic structure calculations, we use DFT as implemented in the computational code Vienna ab-initio simulation package (VASP) [171]. For the electron exchange-correlation functional, we choose PW91 [78] functional of the GGA. We set the plane wave basis providing kinetic energy up to 20 Ry and 18 Ry for Cu and Ag, respectively. The calculations provide the bulk lattice constants of 3.64 Å and 4.167 Å for Cu and Ag, respectively. We use a 2x2x1 k-point mesh and repeat for larger k-mesh in order to ensure proper convergence. A supercell consisting of 6x6 atoms in the surface plane with 5 layers is constructed. We set the convergence criterion for the forces to be 0.01 eV/ Å. For transition-state search, we perform one-dimensional Drag method with 15 to 20 points depending on the system. The optimization of the system total energy is obtained using CG method [91].

For the calculations of diffusion dynamics, we use the RSGF method [52] with the interactions derived from EAM. The first step in this method is to construct the force-constant matrix from the analytical expressions of the partial second derivatives of the potential. From the force-constant matrix, to be used in a resolvent matrix method, we
construct sub-matrices corresponding to the local regions of choice. We then use the calculated Green’s function to determine the normalized LVDOS, as given by:

\[ g(\nu^2) = \frac{-1}{3n\pi} \lim_{\varepsilon \to 0} \text{Im} \text{Tr}[G(\nu^2 + i\varepsilon)] \] (4.17)

where \( n \) is the number of atoms in the locality, and \( \varepsilon \) is the width of the Gaussian. Frequency-dependent VDOS \( (N(\nu)) \) is related to the normalized local VDOS \( (g(\nu^2)) \) through the equation:

\[ N(\nu) = 2\nu g(\nu^2) \] (4.18)

These frequency-dependent VDOS are used as inputs for deriving the thermodynamic quantities within the harmonic approximation of lattice dynamics. The thermodynamic quantities of interest here are the vibrational free energy, the vibrational internal energy, and the vibrational entropy that are expressed in the harmonic approximation by:

\[ F_{\text{vib}} = k_B T \int_0^\infty N(\nu) \ln(\frac{\nu}{2}) d\nu \] (4.19)

\[ U_{\text{vib}} = k_B T \int_0^\infty N(\nu) \left( \frac{1}{2} \nu + \frac{\nu}{e^{\nu} - 1} \right) d\nu \] (4.20)

\[ S_{\text{vib}} = k_B \int_0^\infty N(\nu) \left( -\ln(1 - e^{-\nu}) + \frac{\nu}{e^{\nu} - 1} \right) d\nu \] (4.21)

where \( k_B \) is the Boltzman constant, \( T \) is the temperature, \( \nu = h\nu/k_BT \) and \( h \) is the Planck constant. Using these thermodynamic quantities, the diffusion prefactors \((D_0(T))\) and diffusion constants \((D(T))\) are obtained from the equations:
\[ D_0(T) = \frac{k_B T}{h} \frac{md^2}{2\alpha} \exp\left(\frac{-\Delta S_{\text{vib.}}}{k_B}\right) \exp\left(\frac{-\Delta U_{\text{vib.}}}{k_B T}\right) \]  
\[ D(T) = D_0(T) \exp\left(\frac{-\Delta E}{k_B T}\right) \]  

(4.22)  
(4.23)

where \(\alpha\) is the dimensionality of the motion, \(d\) is the jump distance, \(m\) is the possible number of equivalent jumps and \(\Delta E\) is the barrier for diffusion.

Knowledge of vibrational spectrum provides access to the attempt frequency \((\nu_0)\) of diffusion prefactor. We have calculated the vibrational frequencies for both single-atom and the cluster diffusion using both EAM and DFT by diagonalizing the force-constant matrix. We determine the force-constant matrix by displacing each individual atom in the unit cell and calculating the restoring forces. TST within the harmonic approximation is employed to calculate the attempt frequency using the Vineyard’s product formula [109]. In earlier calculations [90], we have demonstrated that at the limit of high temperature, equation 4.22 converges to equation 4.24. The Vineyard’s product formula is given by:

\[ \nu_0 = \prod_{j=1}^{3N} \nu_j^{\text{fcc}} / \prod_{j=1}^{3N-1} \nu_j^{\text{ts}} \]  

(4.24)

where \(3N\) is the number of degrees of freedom of the system, and \(\nu_j^{\text{fcc}}\) and \(\nu_j^{\text{ts}}\) are the normal mode frequencies of the system with the adatom at an fcc site and the transition state. The prefactors are also calculated using the equation below from the calculated attempt frequencies:

\[ D_0 = \frac{3d^2}{2\alpha} \nu_0 \]  

(4.25)
where \( d \) is the jump distance, and \( \alpha \) is the dimensionality of the problem. Calculation of the vibrational frequencies for the *whole* system is still not feasible using first-principles owing to the computational cost of such calculations. For instance in our study, the number of degrees of freedom of the whole system is too large (\( 3N=561 \)) to embrace. We therefore resort to an approximation in which *only* the diffusing entity is allowed to vibrate by freezing completely the substrate [143]. In order to assess the contribution of the substrate vibrations to the attempt frequencies; several additional calculations are performed at which we include *only* local contributions from the closest neighbors or from that of the whole first-layer atoms. This step helps us to determine the deviations in the attempt frequencies resulting from the additional degrees of freedom. The results show that for the diffusion of a Cu adatom on Cu(111), the attempt frequency obtained considering *only* the adatom vibrations (\( 3N=3 \)) is about a factor of two as compared to the contributions from the whole first-layer atoms (\( 3N=111 \)). Note that the deviation in the attempt frequency with the additional degrees of freedom (from \( 3N=57 \) to \( 3N=111 \)) is no more than a factor of \(~1\). Hence, when one allows *only* the adatom to vibrate for the calculation of the attempt frequencies, the resulting frequencies should be expected to differ a factor of two. This trend was reported in our earlier publication for the diffusion of a Cu and a Ag adatoms on Cu(100) and Ag(100) [227]. For the (111) surface, an earlier DFT study for the diffusion of a Ag adatom on Ag(111) reported similar trend [143]. Repeating the same analysis for the diffusion of a Cu adatom on Ag(111), we find that the addition of the substrate vibrational contribution introduces large deviation. We have analyzed carefully by increasing the number of degrees of freedom systematically, our conclusions did not change. We infer that the implementation of the method does not
involve the corrected masses (correction with mass ratio reduces the deviation) or better convergence is needed. When the resulting frequencies are multiplied by the mass ratio of the species simply corrects the calculated frequencies hence the attempt frequencies. Same analysis for the attempt frequencies is repeated for both Cu$_7$ cluster diffusion on Cu(111) and on Ag(111). The results for the former show that deviation in the attempt frequencies considering only the vibrations of cluster atoms (3N=21) is about a factor of two as compared to the contributions including the first-layer vibrational contributions (3N=129). For the latter, we infer that further analysis is needed to resolve this deviation. These calculations are computationally very expensive (for a system of about 43 atoms, the calculation of 129 modes takes about 15-20 days); hence if one can determine how much deviation is encountered by adding more degrees of freedom is important. For Cu$_7$ cluster diffusion on Ag(111) case, for the calculation of diffusion dynamics (using DFT), we will report the results obtained considering only the adsorbate vibrations.

The second step in the study -- to determine the diffusion energetics and dynamics -- involves MD simulations (with the interactions derived from EAM) for the temperatures ranging from 300 K to 700 K. As opposed to MS simulations, MD simulations reveal (within a given simulation time) what diffusion mechanisms that are in play for multi-atom diffusion. We use a simulation box of 12 atomic layers with 100 atoms in each layer. The adsorbate (the single atom or the 2D compact 7-atom cluster) is placed on the surface layer. In order to test the validity of the potential used in describing the hetero-system properties, we first perform MD simulations for the diffusion of a single Cu atom on Cu(111) for which there is ample precedent in the literature [228] and, for comparison, on Ag(111) for which the present study is the first instance. As the initial
step in these MD simulations, we carry out constant-volume, constant-temperature (NVT) simulations for 20ps in order to bring the system to the desired temperature. Following the thermalization, we perform constant-volume and constant-energy (NVE) simulations for 1ns (for single-atom diffusion) and 200ns (for cluster diffusion). The time step used in all calculations is 1 fs, which is sufficient to obtain reliable statistics for determination of diffusion dynamics. For the diffusion of the single atom, we perform simulations for 1ns for each of twelve different initial configurations at each temperature to ensure for collection of sufficient statistics. Repeating the simulations for over 10 ns, we find results similar to those obtained using 1ns. Hence we conclude that 1ns is long enough to derive single-atom diffusion energetics and dynamics from MD simulations.

We now turn to the calculation of diffusion constants from the slope of mean-square-displacement versus time for each temperature. From the temperature-dependent diffusion coefficients we construct an Arrhenius plot to determine the diffusion barrier from the slope and the prefactors from the intercept. Note here that since MD simulations bring to light the various diffusion mechanisms, the extracted diffusion parameters are effective values. By comparing the results of the diffusion parameters obtained using MS (for a single diffusion mechanism) and MD (for a collection of mechanisms), we aim at answering the question regarding the dominant mechanism for the diffusion of a 7-atom cluster. It is worth noting that in order to reveal all possible diffusion mechanism in play for a given temperature and time, one has to select carefully the write out time for the simulations. For instance, for a simulation of 200 ns, if one chooses the write out time as 5 ns or even much shorter time (100 ps), one looses the information about the diffusion mechanisms, which occur rarely (short-lived). This is especially the key importance to
our study to be able to reveal all the possible mechanisms that are in play since one of the main interests is to determine whether a 7-atom cluster diffuses only via concerted motion. Hence we performed several additional calculations with different write out time to accomplish the concern raised above. We use 0.5ps write out timing for all the simulations and reveal all possible mechanisms for the diffusion of a 7-atom cluster.

4.5.3 Results and Discussion

In the following sections, we present diffusion energetics and dynamics as calculated as discussed above. Before presenting the results concerning the central question our study addresses, we will first discuss how structural relaxation and the bond lengths between the middle atom and the periphery atoms of the cluster differ between the homo- and hetero-systems in question. We then discuss the differences in the electronic densities of states of the individual cluster atoms in each studied systems in order to gain further insight into the strength of intra-cluster interactions. Following these analyses, we present the diffusion energetics for both the single atom and the 7-atom cluster. By examining the binding energies of the adsorbates with respect to the substrates, we determine the role of electronic interactions in controlling the height of the barriers. We then discuss the results of diffusion dynamics as calculated using both static and dynamic simulations. We conclude by comparing the results of the different methodologies for both energetics and dynamics.
4.5.4 Relaxations, Bond Lengths, and Electronic Densities of States (EDOS)

System properties including vibrations and thermodynamics can be understood by examining the relaxations and bond lengths within the cluster atoms and between the cluster atoms and the substrate. In Figure 4.21.a, the model system used in the calculations is presented. In the figure a cluster made of seven atoms occupies an fcc site on the (111) surface. We have numbered the cluster atoms from 1 to 7; designating the middle atom of the cluster as #1. The stars, triangles and circles represent the atoms of the first, second and the third layers, respectively. In Figure 4.21.b and 4.21.c, we present the in-plane relaxations of cluster atoms. It is notable that the relaxation trends are virtually the same when we use EAM as when we use DFT.

The optimized structures show that the periphery atoms of the cluster (2-7) relax towards the middle atom (1). In-plane displacement (contraction) is enhanced for Cu\textsubscript{7} on Ag(111) as compared to Cu\textsubscript{7} on Cu(111). The reason is the lattice misfit in the hetero case between the cluster and substrate atom species and (as we shall see) the corresponding relative bond strengths. For Cu\textsubscript{7} on Ag(111), the competition between Cu-Cu (within the cluster) and Cu-Ag (cluster-surface) interactions resolves in favor of the intra-cluster interactions. The relaxation trend for Cu\textsubscript{7} on Ag(111) reveals the interactions within the cluster to be stronger than those of the cluster-substrate. The results for the perpendicular relaxation obtained using DFT and EAM are likewise similar. In both cases the cluster atoms relax inward towards the substrate but the contraction is enhanced for Cu\textsubscript{7} on Ag(111). For Cu\textsubscript{7} on Cu(111), the DFT results predict a contraction for the periphery atoms above 0.1 Å larger than for the middle atom. However, for Cu\textsubscript{7} on
Ag(111), the difference in the contraction is less than 0.1 Å. The EAM results follow the same trends as DFT with quantitative differences. However, in contrast to DFT; for the hetero case, EAM indicates enhanced perpendicular relaxation for the middle atom as compared to the periphery atoms.

Figure 4.21 **a)** Model systems for the diffusion of 7-atom cluster **b)** In-plane relaxations of the cluster atoms for Cu\textsubscript{7} on Cu(111) and **b)** In-plane relaxations of the cluster atoms for Cu\textsubscript{7} on Ag(111). Stars, triangles, and circles represent the first, the second and the third layer atoms, respectively. Crosses correspond to the positions of the cluster atoms (both initial and those after optimization). The arrows reflect the in-plane relaxation trends. Both EAM and DFT yield the same trend.
We turn now to an analysis of the bond lengths. For both systems, the bond lengths between the middle atom and the periphery atoms (at the fcc site) are shorter than those of bulk-terminated. The change in the bond lengths between the middle atom and the periphery atoms clearly reveals the cluster symmetry. For Cu$_7$ on Cu(111), the bond length between the periphery atoms and the middle atom according to DFT is 2.5 Å, which is 2.8% less than that of the bulk, according to EAM that bond length is 2.51 Å, 2.0% shorter than the bulk. For Cu$_7$ on Ag(111), the bond length between the periphery atoms and the central atom according to DFT is 2.50 Å, a contraction of 3%; according to EAM, that bond is 2.53 Å, a contraction of 1%. This difference can be attributed to the dissimilarity in the relaxations both in-plane (Figure 4.21.b and 4.21.c) and perpendicular to the plane.

We also analyzed the electronic densities of states of the cluster atoms in order to reveal possible differences in the electronic structures between the two systems emerging from the dissimilar interaction. In Figures 4.22.a-b, the total d-states of the cluster atoms (1-7) is plotted for both systems. Notice from the figures that for both systems as compared to a bulk atom, the densities of states of the cluster atoms exhibit band narrowing. Moreover, the narrowing is more enhanced for the periphery atoms than for the middle atom reflecting the difference in the coordination (a bulk atom has coordination 12, the middle cluster atom coordination 9 and a periphery atom coordination 6).

For Cu$_7$ on Ag(111), on the basis of strong intra-cluster interaction induced by the substrate with the larger atoms, we suspected that both middle and periphery atoms would exhibit discrete states. This shows forth most starkly when we plot the density of
states of the middle atom (Figure 4.23.a) and the periphery atoms (Figure 4.23.b) for a Cu$_7$ cluster when adsorbed on Cu(111) and on Ag(111). In order to reveal origin of these states, we have calculated the densities of states of the atoms of an isolated cluster and compared them (Figure 4.23.c) with the densities of states of the cluster atoms when the cluster is adsorbed on the Ag(111) surface. As seen in Figure 4.23.c, in the case of an isolated cluster, the middle atom exhibits discrete states. Note that, for Cu$_7$ on Cu(111), the interaction within the cluster and that of cluster-substrate is similar. However, for Cu$_7$ on Ag(111), the stronger interaction among the cluster atoms as compared to between cluster and substrate results in confinement of electrons, which appears as discrete states in the electronic densities of states for the atoms within the cluster.
Figure 4.22 Electronic densities of states of the cluster atoms for a) Cu$_7$ on Cu(111) and b) Cu$_7$ on Ag(111)
Figure 4.23 Electronic densities of states of Cu\(_7\) cluster atoms:

a) middle atom on Cu(111) and on Ag(111)

b) periphery atoms on Cu(111) and on Ag(111)

c) middle atom of an isolated cluster and that adsorbed on Ag(111)
4.5.5 Diffusion Barriers Using MS Simulations

In Table 4.10, we summarize the results obtained using DFT and EAM for the diffusion barriers and the binding energies for 7-atom cluster diffusion via concerted motion from an fcc to an hcp sites and vice versa. The DFT results show that the barrier for hopping from an fcc to an hcp site is higher than that for hopping from an hcp to fcc site. This trend may originate from the fact that when the cluster occupies an fcc site, it can penetrate more towards the substrate owing to the absence of an atom underneath. This explanation gains support when the binding energies at fcc and hcp sites are compared. The difference in the barriers for the cluster to diffuse from an fcc to an hcp site (Figure 4.24) and vice versa is 63 meV and 38 meV for Cu$_7$ on Cu(111) and on Ag(111), respectively. Of the two systems, the highest diffusion barrier is found to be for Cu$_7$ on Cu(111) and the lowest for Cu$_7$ on Ag(111) with a difference of 78 meV.

Figure 4.24 Schematic representation of concerted motion diffusion process
Since any diffusion mechanism involves bond breaking and making, examining the strength of the bonds, in other words adsorbate binding energies, is important for further understanding of the role of interactions in controlling the height of diffusion barriers. We calculate cluster binding energies from the formation energy -- the energy needed to form the adsorbed cluster from the vapor phase of single atoms.

The binding energy for Cu$_7$ on Cu(111) at fcc site is higher than that at hcp site explains why the barrier for the diffusion from an fcc to an hcp sites is higher than for vice versa. The binding energy per cluster atom at fcc site is 3.335 eV. The difference in the binding energies per cluster atom between the fcc and hcp sites is 10 meV/atom. In order to reveal the effect of coordination and the strength of interaction within the cluster atoms on the binding energies, we also calculate the barriers and the binding energies for single atom diffusion. The barriers for Cu adatom diffusion via hopping from an fcc to an hcp site and vice versa are found to be 53 meV and 44 meV, respectively. The corresponding binding energies are 2.89 eV at fcc site and 2.88 eV at hcp site. Note here that the single Cu atom on the (111) surface has coordination three, while the cluster atoms have an average coordination of 6.4 (nine for the middle atom and six for the periphery atoms). Hence, the stronger binding energy per cluster atom is understandable on the basis of the differences in their coordination.
Table 4.10 Diffusion barriers ($E_{\text{diff}}$) for concerted motion and the corresponding binding energies ($E_{\text{bind}}$) for 7-atom cluster diffusion

<table>
<thead>
<tr>
<th>Methods</th>
<th>Energetics</th>
<th>DFT</th>
<th>EAM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Processes</td>
<td>$E_{\text{diff}}$ (eV)</td>
<td>$E_{\text{bind}}$ (eV)</td>
</tr>
<tr>
<td></td>
<td>fcc-hcp</td>
<td>hep-fcc</td>
<td>fcc-hcp</td>
</tr>
<tr>
<td>Cu$_7$ on Cu(111)</td>
<td>fcc-hcp 0.452</td>
<td>hep-fcc 0.389</td>
<td>fcc-hcp -23.347</td>
</tr>
<tr>
<td>Cu$_7$ on Ag(111)</td>
<td>fcc-hcp 0.374</td>
<td>hep-fcc 0.336</td>
<td>fcc-hcp -22.318</td>
</tr>
</tbody>
</table>

For Cu$_7$ on Ag(111), we find that the difference between the cluster binding energies at fcc and hcp sites is 37 meV with the highest binding energy corresponding to the former. The diffusion barrier also follows the same trend as the binding energy: the highest barrier is for the diffusion from an fcc to hcp site. The binding energies per cluster atom at fcc and hcp sites are 3.188 eV and 3.183 eV, respectively. The barriers for Cu adatom diffusion from an fcc to an hcp site and vice versa on Ag(111) are 77 meV and 67 meV, respectively. It is worth noting that at an fcc site the binding energy is 3.41 eV, which is 222 meV higher than the energy per cluster atom. The binding energy at an hcp site is 10 meV smaller than that for an fcc site. As noted above, the binding energy per cluster atom is lower than that for single atom for this system. It is clear that the coordination factor is not sufficient to account this reverse trend. It can be explained rather by a detailed analysis of the loss or gain of bond strength during bond-making with an alien atom. Note that a single Cu atom has three Ag nearest neighbors and the bond length between it and these neighbors is different from that of the atoms of the cluster to their substrate nearest neighbors. For the Cu atoms in the cluster, the competition between Cu-Cu interactions within the cluster reduces the binding strength with the
substrate atoms, yielding a lower binding energy than that for single atom and those between the cluster and substrate atoms.

Let us now turn the discussion to the barriers calculated using EAM (also summarized in Table 4.10). The barrier for the diffusion from an fcc to an hcp site is found to be higher than that for an hcp to an fcc site for Cu$_7$ on Cu(111), while it is lower (by 19 meV) for Cu$_7$ on Ag(111). In contrast to the DFT results, we find that the highest barrier is for Cu$_7$ on Ag(111). The barrier for Cu$_7$ on Cu(111) obtained from DFT is 130 meV higher than that from EAM. For further understanding of the differences in the energetics, we look more closely to the cluster-binding energies summarized in Table 4.10. The calculations show that the binding energies per cluster atom are 3.20 eV and 2.99 eV for Cu$_7$ on Cu(111) and on Ag(111), respectively. On the other hand, we find the barrier for the diffusion of a single Cu atom from an fcc to an hcp site and vice versa on Cu(111) to be 30 meV and 28 meV, respectively. The barriers for a single Cu atom diffusion from an fcc to an hcp site and vice versa on Ag(111) are 68 meV and 67 meV, respectively. The binding energies at fcc site are 2.59 eV and 2.39 eV for Cu adatom on Cu(111) and on Ag(111), respectively. It is worth noting that as compared to single-atom binding energies, the binding energy per cluster atom is larger for both systems. This is in good agreement with our DFT results for Cu$_7$ on Cu(111). For Cu$_7$ on Ag(111), however, the DFT results disagree with those obtained using EAM. This trend may originate from the difference in the relaxation trends for the cluster atoms.
4.5.6 Prefactors and Diffusion Coefficients From Molecular Static Simulations

In this section we will report the MS simulation results of the attempt frequencies, prefactors and diffusion coefficients for 7-atom cluster diffusion via concerted motion using both EAM and DFT. For the purpose of comparison we begin by calculating the prefactors and diffusion coefficients for the diffusion of a single atom. As the first step, we calculate the attempt frequencies considering only the adsorbate vibrational frequencies (equation 4.24). The EAM results for the attempt frequencies of a single atom diffusion are found to be 2.873 THz and 3.637 THz for a Cu adatom on Cu(111) and on Ag(111), respectively. In Table 4.11, we summarize the attempt frequencies for both single atom and 7-atom cluster diffusion obtained using DFT taking into account different degrees of freedom of the system. For both adatom and cluster diffusion we first allow only the adsorbate vibrations to contribute to the calculation of the attempt frequencies. Thus the number of degrees of freedom contributing in the calculations are \(3N=3\) for single atom and \(3N=21\) for a 7-atom cluster at an fcc site. We then introduce the contributions from some neighbors and then from all the first-layer atoms (\(3N=111\) for a single atom and \(3N=129\) for the cluster). Notice from Table 4.11 that for Cu atom diffusion on Cu(111), the attempt frequency obtained using EAM is in good agreement (about 0.1 THz higher) with that of the DFT result. However, for the diffusion of a Cu adatom on Ag(111), the attempt frequency determined using EAM is 1.1 THz higher than that of the DFT. In our earlier publication [227] for the diffusion of a Cu adatom on Cu(100) and a Ag adatom on Ag(100), we have reported that the vibrational frequencies
obtained using DFT and EAM are in good agreement. To our knowledge, there are no available results for the hetero system.

Table 4.11 Attempt frequency for single-atom and 7-atom cluster diffusion obtained using DFT considering different degrees of freedom of the system

<table>
<thead>
<tr>
<th>Systems</th>
<th>$\nu_0$ (THz)</th>
<th>$\nu_0$ (THz)</th>
<th>$\nu_0$ (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 (21)</td>
<td>57 (93)</td>
<td>111 (129)</td>
</tr>
<tr>
<td>Cu on Cu(111)</td>
<td>2.806 (4.311)</td>
<td>1.538 (2.374)</td>
<td>1.221 (2.347)</td>
</tr>
<tr>
<td>Cu on Ag(111)</td>
<td>2.544 (1.135)</td>
<td>- (-)</td>
<td>- (-)</td>
</tr>
</tbody>
</table>

Comparison between the attempt frequencies (obtained using DFT) shows that the attempt frequency for Cu adatom diffusion on Cu(111) is 0.3 THz higher than that of Cu on Ag(111). The analysis of the individual frequencies shows that the vibrational frequencies in the surface plane are close to each other. The vibrational frequency along the direction perpendicular to the surface is 0.8 THz higher when the Cu adatom is adsorbed on Cu(111) than on Ag(111). One factor is that, for Cu on Cu(111), the adsorbate couples more strongly with the surface atoms in the perpendicular direction ($z$) than that for Cu on Ag(111). Moreover, Cu has smaller lattice constant and higher cohesive energy than does Ag so that the former is stiffer around the equilibrium [47]. For Cu adatom on Cu(111), we find that with the addition of the extra degrees of freedom from the neighbors ($3N=57$) the attempt frequency changes to 1.538 THz (Table 4.11), which is only about a factor of two lower than in the case for which only the single atom vibrations are considered. Even by adding the vibrational contributions of all the atoms of the first layer ($3N=111$) the attempt frequency becomes only 1.221 THz. Hence, we can conclude from our calculations that for the calculation of the prefactors and diffusion...
coefficients considering *only* the vibrations of the adatom is sufficient (to within a factor of two). The results for the Cu$_7$ cluster on Cu(111) also showed that inclusion of more degrees of freedom (3N=129) does not change the attempt frequency more than a factor of two. The same trend is observed as for the single atom case -- inclusion of more degrees of freedom slightly changes the attempt frequencies. Thus it is reasonable to proceed in the calculation of the prefactors using *only* the adsorbate vibrational frequencies.

Table 4.12 Prefactors ($D_0(T)$ ($10^{-4}$ cm$^2$/s)) and diffusion coefficients ($D(T)$ ($10^{-4}$ cm$^2$/s)) for single atom diffusion from an fcc to an hcp site using DFT considering only adatom degrees of freedom

<table>
<thead>
<tr>
<th>Systems</th>
<th>$D_0$(T) (300 K)</th>
<th>$D_0$(T) (550 K)</th>
<th>$D_0$(T) (700 K)</th>
<th>$D$(T) (300 K)</th>
<th>$D$(T) (550 K)</th>
<th>$D$(T) (700 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu on Ag(111)</td>
<td>12.08</td>
<td>11.99</td>
<td>11.98</td>
<td>0.645</td>
<td>2.435</td>
<td>3.399</td>
</tr>
</tbody>
</table>

In Table 4.12, we summarize the DFT results for the prefactors and diffusion coefficients obtained using equations 4.19-4.23 for a Cu adatom diffusion on Cu(111) and on Ag(111) using *only* the vibrational frequencies of the adatom. The results show that the prefactor for Cu on Ag(111) is a factor of 1.3 *higher* than that for Cu on Cu(111). The difference in the prefactors is clearly negligible given the fact that the degree of freedom allowed in the calculations is sufficient (Table 4.11). At relatively low temperature (300 K), we find that the diffusion coefficient for Cu on Cu(111) is about a factor of two *higher* than that for Cu on Ag(111). This slight difference emerges from the fact that the latter has a large diffusion barrier that compensates for the difference in the
prefactor (see equation 4.23). The prefactors can also be calculated from the obtained attempt frequencies using equation 4.25. Our calculations show that at high temperature the prefactors obtained from equation 4.25 are the same as those obtained from equation 4.22. In an earlier publication [90] we have shown for Cu adatom diffusion on Cu(100) and on Cu(110) that the prefactors determined using equation 4.25 converge (at high temperature) with those obtained using equation 4.22.

In Table 4.13, we present the results for the prefactors and the diffusion coefficients obtained using EAM for the diffusion of Cu adatom on Cu(111) and on Ag(111) first using only the vibrational frequencies of the adatom on a rigid substrate, then using only the adatom vibrations on non-rigid substrate and finally including the vibrational contributions from the rest of the system using the VDOS determined from the RSGF (see equations 4.17 to 4.23). In agreement with the DFT results (Table 4.12), we find the prefactors obtained using only the adatom vibrational frequencies (on a rigid substrate) to be higher by factor of 1.7 for Cu on Ag(111) than that for Cu on Cu(111). We find that the diffusion coefficients follow the same trend as in the DFT results: slightly lower for Cu on Ag(111) than that of Cu on Cu(111). Notice from the Table 4.13 that the prefactors obtained allowing only the adatom vibrations (on a non-rigid substrate) and those obtained by taking into account the contributions of all the atoms in the system differ by a factor of less than two. This result confirms that the vibrational contributions from the substrate atoms are negligible and that the presence of an adatom affects only locally the vibrational properties of the system. Note that in an earlier publication we have reached the same conclusion about the effect of substrate vibrations on the prefactors for the diffusion (single atom) of Cu on Cu(100) and Ag on Ag(100) [227].
Table 4.13 Prefactors \( (D_0(T) \ (10^{-4}\ \text{cm}^2/\text{s})) \) and diffusion coefficients \( (D(T) \ (10^{-4}\ \text{cm}^2/\text{s})) \) for single atom diffusion from an fcc to an hcp site using EAM considering only adatom frequencies on a rigid substrate (in parenthesis), on a non-rigid substrate [in square brackets], and including the vibrational contribution of all atoms using RSGF.

\[
D_0(T) \ (300 \text{ K}) \quad D_0(T) \ (550 \text{ K}) \quad D_0(T) \ (700 \text{ K}) \quad D(T) \ (300 \text{ K}) \quad D(T) \ (550 \text{ K}) \quad D(T) \ (700 \text{ K})
\]

<table>
<thead>
<tr>
<th>Systems</th>
<th>Cu on Cu(111)</th>
<th>Cu on Ag(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(4.545)</td>
<td>(7.719)</td>
</tr>
<tr>
<td></td>
<td>(2.259)</td>
<td>(1.752)</td>
</tr>
<tr>
<td></td>
<td>1.729</td>
<td>2.239</td>
</tr>
<tr>
<td>(300 \text{ K}))</td>
<td>(4.534)</td>
<td>(7.640)</td>
</tr>
<tr>
<td></td>
<td>(2.244)</td>
<td>(1.751)</td>
</tr>
<tr>
<td>(550 \text{ K}))</td>
<td>(4.533)</td>
<td>(7.628)</td>
</tr>
<tr>
<td></td>
<td>(2.241)</td>
<td>(1.751)</td>
</tr>
<tr>
<td>(700 \text{ K}))</td>
<td>(1.429)</td>
<td>(0.544)</td>
</tr>
<tr>
<td></td>
<td>(0.711)</td>
<td>(0.561)</td>
</tr>
<tr>
<td>(300 \text{ K}))</td>
<td>(2.416)</td>
<td>(1.834)</td>
</tr>
<tr>
<td></td>
<td>(1.195)</td>
<td>(0.925)</td>
</tr>
<tr>
<td>(550 \text{ K}))</td>
<td>(1.363)</td>
<td>(1.057)</td>
</tr>
<tr>
<td>(700 \text{ K}))</td>
<td>(2.757)</td>
<td>(2.471)</td>
</tr>
<tr>
<td></td>
<td>(1.729)</td>
<td>(2.238)</td>
</tr>
<tr>
<td>(300 \text{ K}))</td>
<td>(1.729)</td>
<td>(2.238)</td>
</tr>
<tr>
<td></td>
<td>(0.544)</td>
<td>(1.738)</td>
</tr>
<tr>
<td>(550 \text{ K}))</td>
<td>(0.711)</td>
<td>(0.544)</td>
</tr>
<tr>
<td>(700 \text{ K}))</td>
<td>(1.057)</td>
<td>(0.925)</td>
</tr>
<tr>
<td></td>
<td>(0.572)</td>
<td>(0.544)</td>
</tr>
<tr>
<td>(300 \text{ K}))</td>
<td>(0.727)</td>
<td>(0.572)</td>
</tr>
<tr>
<td></td>
<td>(0.772)</td>
<td>(0.772)</td>
</tr>
<tr>
<td>(550 \text{ K}))</td>
<td>(0.567)</td>
<td>(0.567)</td>
</tr>
<tr>
<td>(700 \text{ K}))</td>
<td>(0.772)</td>
<td>(0.772)</td>
</tr>
</tbody>
</table>

In order to understand why the contributions of substrate vibrations are negligible in the calculation of prefactors, we re-write equation 4.22 in terms of vibrational free energy differences (calculated at the fcc site and the transition state configurations) and find:

\[
D_0(T) = \frac{k_B T}{h} \frac{m d^2}{2\alpha} \exp \left( -\frac{\Delta F_{\text{vib}}}{k_B T} \right)
\]  

(4.26)

where \(\Delta F_{\text{vib}}\) is the vibrational free energy difference between two configurations of the system when the adsorbate sits at an fcc site and when it is in the transition state. As the equation makes it clear even slight change in the \(\Delta F_{\text{vib}}\) significantly affects prefactors. Hence, we will analyze the change in the free energy of each individual atom in the system when the adatom is adsorbed at an fcc site (on top of the atom labeled 32 in Figure 4.25.a) and when it sits in the transition state (in between the atoms labeled 32 and 22 in Figure 4.25.a).
In Table 4.14, we summarize the vibrational free energies of the adatom, of the neighbors in the first layer (atoms 1-15 in Figure 4.25.a), of the neighbors in the second layer (atoms 16-27 in Figure 4.25.a) and of those in the third layer (atoms 28-39 in Figure 4.25.a) for both the fcc site and the transition states for temperatures 300 K and 700 K. The table shows that the highest vibrational free energy contribution comes from the adatom itself. For Cu on Cu(111), the vibrational free energy contributions are +39 meV (at 300 K) and +143 meV (at 700 K). For Cu on Ag(111), the vibrational free energy contributions are +34 meV (at 300 K) and +131 meV (at 700 K). Analysis of the vibrational free energy contributions from the rest of the atoms of the system shows that the significant contributions come only from the closest neighbors (atoms labeled 2,3,7,8,12 in Figure 4.25.a), which are in the first layer, while the contributions from the atoms far from the adatom cancel each other at the fcc site and the transition state, so that they make no contribution to the prefactor.

![Figure 4.25 Adatom neighbors contributing to the vibrational free energies for a) a single atom and b) 7-atom cluster](image)

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Table 4.14 Vibrational free energies per Cu atom at the two configurations of the system when the adatom is adsorbed on Ag(111) and on (Cu(111))

<table>
<thead>
<tr>
<th>Atoms</th>
<th>$F_{\text{vib}}$ (meV) fcc site 300 K</th>
<th>$F_{\text{vib}}$ (meV) saddle point 300 K</th>
<th>$F_{\text{vib}}$ (meV) fcc site 700 K</th>
<th>$F_{\text{vib}}$ (meV) saddle point 700 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adatom</td>
<td>-101 (-58)</td>
<td>-67 (-19)</td>
<td>-389 (-291)</td>
<td>-258 (-148)</td>
</tr>
<tr>
<td>2</td>
<td>- (-35)</td>
<td>- (-22)</td>
<td>- (-237)</td>
<td>- (-209)</td>
</tr>
<tr>
<td>3</td>
<td>-85 (-25)</td>
<td>-98 (-37)</td>
<td>-351 (-216)</td>
<td>-380 (-241)</td>
</tr>
<tr>
<td>7</td>
<td>-85 (-26)</td>
<td>-81 (-22)</td>
<td>-351 (-216)</td>
<td>-344 (-208)</td>
</tr>
<tr>
<td>8</td>
<td>-85 (-26)</td>
<td>-81 (-34)</td>
<td>-351 (-216)</td>
<td>-344 (-234)</td>
</tr>
<tr>
<td>12</td>
<td>-94 (-35)</td>
<td>-97 (-33)</td>
<td>-373 (-237)</td>
<td>-379 (-233)</td>
</tr>
<tr>
<td>1-2, 4-6, 9-15</td>
<td>-93 (-33)</td>
<td>-93 (-33)</td>
<td>-369 (-233)</td>
<td>-369 (-233)</td>
</tr>
<tr>
<td>16-39</td>
<td>-80 (-20)</td>
<td>-80 (-20)</td>
<td>-341 (-206)</td>
<td>-341 (-206)</td>
</tr>
</tbody>
</table>

Let us now turn the attention to the diffusion dynamics of a 7-atom cluster via concerted motion. In Table 4.15, we summarize the DFT results for the prefactors and diffusion coefficients obtained using only the vibrational frequencies of the cluster atoms, $3N=21$ at an fcc site and $3N=20$ at the transition state. For Cu$_7$ on Cu(111), the results show that the prefactor is higher by a factor of 1.5 than that for the single atom diffusion (Table 4.12). But for the hetero system the ratio of the prefactor for a 7-atom cluster and that for a single atom is 0.42 -- a difference we shall see shortly undertake to explain. The change in the prefactor for 7-atom cluster as compared to the single atom (for the homo system) is in the same direction as that reported in the earlier MS studies for other metal surfaces [229]. To the best of our knowledge there are no MS studies examining the differences in the diffusion dynamics between the homo and hetero systems.
Table 4.15 Prefactors ($D_0(T)$ ($10^{-3}$ cm$^2$/s)) and diffusion coefficients $D(T)$ for 7-atom cluster concerted motion diffusion from an fcc to an hcp site using DFT considering only cluster atoms degrees of freedom

<table>
<thead>
<tr>
<th>System</th>
<th>$D_0(T)$ (300 K)</th>
<th>$D_0(T)$ (550 K)</th>
<th>$D_0(T)$ (700 K)</th>
<th>$D(T)$ (300 K)</th>
<th>$D(T)$ (550 K)</th>
<th>$D(T)$ (700 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_7$ on Cu(111)</td>
<td>1.480</td>
<td>1.466</td>
<td>1.464</td>
<td>3.999x10^{-11}</td>
<td>1.114x10^{-7}</td>
<td>8.149x10^{-7}</td>
</tr>
<tr>
<td>Cu$_7$ on Ag(111)</td>
<td>0.511</td>
<td>0.527</td>
<td>0.529</td>
<td>2.796x10^{-10}</td>
<td>2.056x10^{-7}</td>
<td>1.074x10^{-6}</td>
</tr>
</tbody>
</table>

In Table 4.16, we present the results for the prefactors and diffusion coefficients for 7-atom cluster diffusion obtained using RSGF with the interactions derived from EAM. The results taking into account the contributions from all atoms in the system show that for Cu$_7$ on Cu(111), the prefactor is higher by a factor of 7.3 than that of the single atom, while for Cu$_7$ on Ag(111) it is higher by a factor of only 0.41. Note that the EAM results are in good agreement with those obtained from the DFT calculations.

Table 4.16 Prefactors ($D_0(T)(10^{-3}$ cm$^2$/s)) and diffusion coefficients $D(T)$ for 7-atom cluster concerted motion diffusion from an fcc to an hcp site using EAM for the cluster vibrations using the vibrational contribution of all atoms using RSGF and considering a non-rigid substrate [in brackets]

<table>
<thead>
<tr>
<th>System</th>
<th>$D_0(T)$ (300 K)</th>
<th>$D_0(T)$ (550 K)</th>
<th>$D_0(T)$ (700 K)</th>
<th>$D(T)$ (300 K)</th>
<th>$D(T)$ (550 K)</th>
<th>$D(T)$ (700 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_7$ on Cu(111)</td>
<td>1.260</td>
<td>1.261</td>
<td>1.260</td>
<td>4.922x10^{-9}</td>
<td>1.435x10^{-6}</td>
<td>5.958x10^{-6}</td>
</tr>
<tr>
<td>[0.858]</td>
<td>[0.846]</td>
<td>[0.844]</td>
<td>[3.353x10^{-9}]</td>
<td>[0.963x10^{-6}]</td>
<td>[3.988x10^{-6}]</td>
<td></td>
</tr>
<tr>
<td>Cu$_7$ on Ag(111)</td>
<td>0.092</td>
<td>0.093</td>
<td>0.094</td>
<td>6.544x10^{-12}</td>
<td>1.199x10^{-8}</td>
<td>0.788x10^{-7}</td>
</tr>
<tr>
<td>[0.103]</td>
<td>[0.104]</td>
<td>[0.104]</td>
<td>[7.292 x10^{-12}]</td>
<td>[1.335x10^{-8}]</td>
<td>[0.877x  x10^{-7}]</td>
<td></td>
</tr>
</tbody>
</table>
In order to reveal the origin of the different behavior for the prefactors between the homo and the hetero cases, we analyze the vibrational free energy contributions of the atoms in the systems when the cluster adsorbs at an fcc site and at the saddle point. In Figure 4.25.b, we present the atoms that contribute to the calculation of the prefactors in the first, the second and the third layers. We find the vibrational free energy difference ($\Delta F_{\text{vib}}$) for the Cu$_7$ cluster itself to be +4.4 meV at 300 K and +62 meV at 700 K when adsorbed on Cu(111), and +66 meV at 300 K and +204 meV at 700 K when adsorbed on Ag(111). Analysis of the vibrational free energy contributions from the rest of the atoms in the system (Figure 4.25.b) shows that, in accord with the single atom diffusion result, we find the total vibrational contribution to be negligible as compared to that of the cluster. For instance, for Cu$_7$ on Ag(111), the total vibrational free energy contribution (from the atoms labeled in Figure 4.25.b) is +69 meV at 300 K and +210 meV at 700 K. Note that the vibrational free energy contribution from the cluster itself is +66 meV at 300 K and +204 meV at 700 K. The contributions from the atoms that are far from the cluster cancel out each other.

Analysis of the vibrational free energies of Cu$_7$ cluster itself reveals significant difference when it is adsorbed on Cu(111) and Ag(111). As noted above, the vibrational free energy contribution at 300 K for Cu$_7$ on Ag(111) is 62 meV higher than that of Cu$_7$ on Cu(111). Equation 4.26 indicates that this large difference in $\Delta F_{\text{vib}}$ will play a major role in determining the prefactor value: since $-\Delta F_{\text{vib}}$ functions exponentially, the contribution comes from the exponent is significantly reduced for Cu$_7$ on Ag(111). What then in turn determines the magnitude of $\Delta F_{\text{vib}}$? Note that at relatively low temperature
the vibrational contribution to the free energy is controlled by the low-frequency end of the vibrational spectrum (see equation 4.19). The analysis of this low-frequency region may explain the observed large deviation in the vibrational free energy contributions between Cu$_7$ on Cu(111) and on Ag(111). We examine the VDOS at the low frequency end of the spectrum when the cluster is adsorbed at an fcc site. In Figure 4.26.a-b, the LVDOS of the cluster atoms for Cu$_7$ on Cu(111) and Cu$_7$ on Ag(111) are plotted, respectively. Notice from Figure 4.26.b that for the latter there is an enhancement at the low frequency end of the spectrum, indicating a softening of some of the force-constants.
To quantify the effect of the enhancement at the low frequency end of the spectrum on the vibrational free energy, we plot in Figure 4.27 the integrand in the equation 4.19 for the cluster at 300 K. Notice from the figure that the contribution at low temperature is much higher in the case for Cu$_7$ on Ag(111) than that of Cu$_7$ on Cu(111). This confirms the large vibrational free energy contribution in the former case. The origin of this
The difference is the presence of strong intra-cluster interaction that causes weak interaction with the substrate atoms. It induces softening of some of the modes, which then results in increase in population at the low frequency end of the spectrum.

Figure 4.27 Integrand (in equation 4.19) is plotted at 300K when the cluster is adsorbed at an fcc site.

### 4.5.7 Atomistic Processes and Diffusion Parameters From MD Simulations

MD simulations are performed for five temperatures (400 K-700K) for 200 ns in order to collect enough statistics to determine the diffusion energetics and dynamics for the diffusion of Cu\textsubscript{7} cluster on Cu(111) and on Ag(111). In Figures 4.28.a-b, we have plotted the center of mass motion (for the temperatures 400 K, 550 K and 700 K) for Cu\textsubscript{7} cluster diffusion on Ag(111) and on Cu(111), respectively. The figures show that the cluster motion is a random walk. For Cu\textsubscript{7} cluster diffusion on Ag(111), at relatively low temperature (400 K), the motion of the cluster involves stick-slip motion owing to the fact that the interaction among the cluster atoms is stronger than those with substrate
atoms -- substrate atoms are larger than those of the cluster. This feature is not observed for the Cu$_7$ cluster diffusion on Cu(111).

Figure 4.28 The center of mass trajectories for the Cu$_7$ cluster diffusion from the MD simulations for 200 ns a) on Ag(111) and b) on Cu(111)
In order to reveal possible shape change of the cluster during diffusion, one has to extract in detail the atomistic processes. To do that, one has to decrease the write out time of the positions from the simulations. To determine whether the 7-atom cluster encounters shape change during its diffusion, we have performed MD simulations for 500 ps and extracted the positions at every 0.5 ps. We have then calculated the maximum average bond lengths between the cluster atoms with the aim in revealing any large deviation in the average bond lengths from those of the compact shaped case. Note that if the cluster goes under any shape transition, the bond lengths between the atoms will be different than those for the compact shaped cluster. In Figures 4.29.a-b, we have plotted the average bond lengths between the cluster atoms during 500 ps simulation time for 400K and 550K when the cluster is adsorbed on Cu(111) and on Ag(111), respectively. Notice from the figures that the average bond length changes between 4.9 Å to 5.8 Å for Cu cluster on Cu(111) at 400K and 550K, while the average bond length varies between 4.9 Å to 7.8 Å for Cu cluster on Ag(111) at 550K. The largest bond length among the cluster atoms (when it is in compact shape) is equal to the two nearest-neighbor distance (5.12 Å). Note from the figures that, although large fluctuations are seen in the average bond length, it is also clear that the average bond length becomes shorter than that of the compact shaped. This indicates that during the simulations the cluster atoms get closer to each other and preserve its compact shape. Cluster’s motion consists of vibrations of atoms at fixed point and breathing mode for Cu cluster on Cu(111). At these temperatures, for 500ps duration of simulation time, there is no shape change observed. For Cu cluster on Ag(111), at 550K, we see that the average bond length can reach up to 7.8 Å. In Figure 4.30.a-c, we plot the cluster’s shape corresponding to the largest change.
observed in the bond length indicating that the cluster encounters shape change, however, it is short-lived. Note from Figure 4.30.a-c that cluster goes from a compact shape to a distorted shape. This yields an increase in the maximum bond lengths among the cluster atoms.

Figure 4.29 Change in the average bond lengths among the cluster atoms for a) Cu₇ cluster on Cu(111) and b) Cu₇ cluster on Ag(111)
Figure 4.30 Change in cluster shape at particular simulation times for Cu$_7$ cluster on Ag(111) at 550K: (a) from 92ps to 93.5ps, (b) from 397ps to 398ps, and (c) from 405ps to 407ps.
Figure 4.31 Change in the average bond lengths among the cluster atoms at 700K. 

a) Cu$_7$ cluster on Ag(111) 

b) Cu$_7$ cluster on Cu(111)
In Figures 4.31.a-b, we plot the average bond length as a function of time of the simulation at 700K for Cu$_7$ cluster on Ag(111) and Cu$_7$ cluster on Cu(111), respectively. Analyses of the average bond lengths between the cluster atoms show that for both cases, the cluster encounters shape -- becomes distorted. Notice from the figures that although the cluster becomes distorted; time to time it goes back to its compact shape. The analyses show that at this temperature, cluster atoms do not like to be close to each other. It is clear from the figures that for both cases, at these temperatures, these distorted states compete with the compact shape states.

In Figures 4.32.a-f, we have plotted transitions from a distorted to compact shapes or vice versa for particular times -- corresponding to short/large bond lengths between the cluster atoms -- during the simulations for Cu$_7$ cluster diffusion on Cu(111) and on Ag(111). Notice from the figures that the (large) average bond length between the clusters atoms are observed for the distorted cluster shape, while the short bond lengths are for the compact shape. It is clear that the temperature has direct effect on the shape of the cluster during its diffusion. It is worth noticing that for Cu$_7$ cluster diffusion on Ag(111), the number of distorted states are less as compared to that for Cu$_7$ cluster diffusion on Cu(111). This can be attributed to the fact that owing to the misfit between the cluster atoms and the substrate atoms -- strong intra-cluster interaction -- forces the cluster atoms to get closer to each other for the former.

Note that this short simulation time gives great detail for the atomistic process responsible for the diffusion of this compact cluster.
Figure 4.32 Change in cluster shape at particular simulation times for Cu\textsubscript{7} cluster on Cu(111) [on the right] and on Ag(111) [on the left] at 700 K at a) 85.5 ps to 90.5 ps b) 166 ps to 168.5 ps c) 380 ps to 388 ps d) 173.5 ps to 182 ps e) 262.5 ps to 285.5 ps and f) 486 ps to 494 ps
Analyses of the movie generated from the result of the 500 ps MD simulation at 400 K for Cu$_7$ cluster diffusion on Cu(111) revealed that the cluster does not encounter shape change during its diffusion. It diffuses slightly by concerted motion -- for most of the simulation time its motion consists of vibrations of atoms around a fixed position. Its motion also includes a breathing mode [230]. Analyses of the movie generated for 550 K for 500 ps showed that the cluster diffuses via concerted motion. As expected, cluster is more diffusive as compared to the case of 400 K. During its diffusion, the motion of the cluster consists of rotation and breathing. There are also several attempts observed for detachment of a periphery atom from the cluster, however, the cluster gets back to its compact shape in sudden. Note that at 400 K, this feature is not observed.

The analyses of the movie generated from the MD simulation at 700 K for 500 ps revealed that during most of the simulation time, cluster undergoes shape change. It becomes distorted by detachment of a periphery atom. The movie also shows that cluster diffuses as distorted for some time, and then later it goes back to its compact shape. This is repeated very many times during the simulation. Since for both 400 K and 550 K, the simulations did not show any shape change, and limited number of known atomistic processes, the snapshots are not of much interest. We will only present the snapshots from the movie generated for 700 K.
Figure 4.33 Atomistic process observed for the diffusion of Cu$_7$ cluster on Cu(111) at 700K, for 500 ps with 0.5 ps write out time.

In Figure 4.33, we present several snapshots are extracted from the simulations (for 500 ps with 0.5 ps write out) for the diffusion of Cu$_7$ cluster on Cu(111). The figure makes it clear that the cluster’s shape change involves variety of such diffusion processes as the rotation, dimer shear, and edge diffusion. The analysis of all the snapshots shows
that from the beginning of the simulation, the cluster undergoes a shape change and becomes distorted around 15 ps. It goes from a compact to an elongated shape by detachment (15 ps) of a single atom at the periphery (an energetically costly process). The cluster stays distorted for about 70 ps, during which one can see such diffusion processes as dimer shear (33 ps – 33.5 ps), rotation (33.5ps - 36 ps) and edge diffusion. Cluster stays compact for a very short time (5ps) then becomes distorted again by detachment of an atom and stays distorted for about 100 ps. During this time, the above mentioned diffusion processes and more can be seen. Once again, cluster goes back to its compact shape and maintains its shape for about 80ps. After that it gets distorted and goes back to the compact shape and again distorted. For this relatively short simulation time, one notices that the cluster’s shape changes continuously, and that there is a competition between the compact and distorted shapes. In the light of these observations, at high temperature, it is clear that the cluster will not diffuse only via concerted motion but also as a distorted cluster.

Analyses of the movies generated for the diffusion of Cu7 cluster on Ag(111) at 400K showed that the cluster does not encounter shape change during its diffusion. Its motion involves vibration of the atoms and breathing. The movie generated at 550K showed that for most of time cluster diffuses as concerted motion, while for very short time it is distorted. Note that these distorted states are very short-lived. In Figure 4.34, we present several snapshots of the movie extracted from the simulations (for 500 ps with 0.5 ps write out) for the diffusion of Cu7 cluster on Ag(111) at 700K. The snapshots reveal that at this temperature for this cluster too, there is a shape change. The motion of cluster involves such atomistic processes as tendency to form of 3D cluster, rotation,
dimer shear, rotation plus shear, and edge diffusion. The cluster becomes distorted by detachment of a periphery atom as shown in the snapshot taken at 7ps. Then the cluster goes back to its compact shape (16ps). Right after coming to a compact shape, the cluster becomes elongated yielding the middle cluster atom to be popped up (16.5ps). At this stage one sees that the cluster tends to form itself as 3D. Similar feature is also obtained later during the simulation (see the snapshots taken at 30.5ps, 36.5ps, 113ps, 188ps, and 264 ps). From the elongated shape, cluster goes back to its compact shape by individual atoms rotation and shear mechanism (see the snapshots taken at 17ps to 25 ps). The rotation mechanism is also observed at later times during the simulation (see 32ps to 35ps). The dimer shear mechanism is one of the most frequently observed mechanisms. In our KMC simulations [230] concerning the diffusion of 2D Cu clusters (4 to 30 atoms) on Ag(111) substrate, we showed that the shear is a common mechanism for large cluster diffusion. The snapshots taken at the simulation times at 69-70.5ps, 93-94.5ps, 184ps, 208.5ps and 209ps show the dimer shear mechanism. From the snapshots taken at 136.5ps and 137.5ps, one sees the edge diffusion mechanism. Combination of rotation and shear mechanisms is clearly seen in the snapshots taken at 365.5ps and 362.5ps. The other times during the simulation, for instance, 111ps to 152ps and 297ps to 387ps, the cluster preserves its compact shape. Note that these short time MD simulations with small steps for write out is important to reveal the details of atomistic processes responsible for the diffusion of multi-atoms clusters. For the calculation of accurate thermodynamical properties, much longer simulation times are needed as discussed above. In the present study, we use these short time simulations to obtain details of the processes, and the simulation times reaching to 200 ns are used to calculate the diffusion parameters.
Figure 4.34 Atomistic process observed for the diffusion of Cu$_7$ cluster on Ag(111) at 700K for 500 ps with 0.5 ps write out time.
Figure 4.35 Arrhenius plots for Cu adatom diffusion (obtained from 1ns MD simulations) a) on Cu(111) and b) on Ag(111)
In order to calculate the diffusion barriers and prefactors, we have performed long time MD simulations for both single atom and cluster diffusion. In Figure 4.35.a-b, we present the Arrhenius plot for the diffusion of single Cu atom on Cu(111) and on Ag(111) generated from the results of several MD simulations of 1ns for temperatures ranging from 400K to 700K. Note that for each temperature, for better collection of statistics, we have performed the calculation for different initial configurations (about 10 configurations for each temperature). The resulting diffusion activation barriers are obtained from the slope of the Arrhenius plot, while the prefactors are obtained from the intercept. The similar analyses are also repeated for the diffusion of Cu$_7$ cluster on Cu(111) and on Ag(111) substrates. The resulting activation barriers and the prefactors for both single atoms and the cluster diffusion are summarized in Table 4.17.

Table 4.17 Effective diffusion barriers from MD simulation for single-atom and 7-atom cluster

<table>
<thead>
<tr>
<th>System</th>
<th>$E^{\text{eff}}_{\text{diff}}$ (meV)</th>
<th>$E^{\text{eff}}_{\text{diff}}$ (meV)</th>
<th>$\text{Prefactor}$ (cm$^2$/s)</th>
<th>Prefactor (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu on Cu(111)</td>
<td>41</td>
<td>615</td>
<td>1.11x10$^{-4}$</td>
<td>57.0x10$^{-3}$</td>
</tr>
<tr>
<td>Cu on Ag(111)</td>
<td>85</td>
<td>279</td>
<td>5.26x10$^{-4}$</td>
<td>0.18x10$^{-3}$</td>
</tr>
</tbody>
</table>

The effective diffusion barriers for the diffusion of single atoms are found to be about 10-15 meV higher than those obtained from static calculations. Note that the barriers obtained from MD simulations are in good agreement with the earlier reports [231]. The activation barrier for the Cu$_7$ cluster diffusion on Cu(111) is found to be about 300 meV higher than that for the static barrier value (for concerted motion process). Note
that during its diffusion, the cluster encounters shape change several times. These shape changes are initiated by detachment of a periphery atom. This diffusion process and those others (rotation, shear, etc.) observed for the diffusion of Cu$_7$ cluster on Cu(111) are energetically more costly than that for the concerted motion (compact shaped). Note also that for relatively low temperatures (400K and 550K), the results showed that the cluster simply vibrates at a fixed position and it is not diffusive. Hence it is understandable that the effective diffusion activation barrier -- corresponds to all the process observed in given simulation time -- obtained from MD simulation is much higher than that for the concerted motion process (as compact shaped). It is interesting and puzzling to note that the activation barrier for the Cu$_7$ cluster diffusion on Ag(111) obtained from MD simulation is found to be less than that for the concerted motion process (as compact shaped). Although for this case too, the simulations have revealed several dominant diffusion mechanisms that are energetically costly (frequent single atom processes), the resulting activation barrier is less than that of the concerted motion process. One reason could be the fact that there are processes for which the diffusion barriers are much less than that calculated for the concerted motion. For a conclusive argument of the underlying reason(s) behind this peculiar case, large number of energetic calculations is needed. It is reasonable to start with careful analysis of the observed diffusion mechanisms from MD simulation. For each mechanism one performs the static calculations to determine the corresponding activation energy barrier and compares with the effective diffusion barrier. This part of the study will be undertaken in the future. Note that there are no data available in the literature for comparison.
The prefactors obtained from MD simulations for the single atom diffusion are in excellent agreement with the available data [231]. The ratio between the prefactors for Cu₇ cluster diffusion on Cu(111) and that for the single atom is 514 indicating that the prefactor for the cluster diffusion is three orders of magnitude larger than that for the single atom. A similar result was reported in an earlier study [224, 226]. Note that the ratio obtained for the hetero case is only 0.34. Note that the static calculations considering only the concerted motion showed that ratios are 7.3 and 0.41 for homo and hetero cases, respectively. This indicates that the concerted motion (as compact shape) is not the governing diffusion mechanism for this particular cluster.

4.5.8 Conclusions

Atomic relaxations are found to be more pronounced when using DFT as compared to EAM. We find that the intra-cluster interaction is more enhanced for the hetero system as compared to that for the homo as a result of the large misfit presence. Electronic DOS present narrowing of the bands for under coordinated atoms and stronger hybridization for the hetero system. The narrowing of the band is more enhanced for the periphery atoms than for the middle atom reflecting the coordination effect. The electronic DOS of the middle cluster atom for the Cu₇ on Ag(111) presents discrete states originating from the strong interaction among the cluster atoms as compared to between cluster and substrate. The calculated diffusion barriers for the 7-atom diffusion via concerted motion revealed that the barrier to diffuse from an fcc to an hcp site is higher for both cases. Analyses of the binding energies also revealed the same trend. For Cu₇ cluster on Cu(111), the binding energy per cluster atom is higher
than that for the single atom. This can be understood on the basis of the differences in their coordination. However, for Cu₇ cluster on Ag(111), the binding energy per cluster atom is lower than that for the single atom indicating that coordination argument does not apply for this system. This feature originates from the fact that for this case, the intra-cluster interaction reduces the binding energy relative to the substrate.

We find using static simulations that the prefactors for the diffusion of single atom and 7-atom cluster (via concerted motion) -- with or without inclusion of partial substrate dynamics -- are found to be around the usual value (10⁻³ cm²/s) indicating that substrate contributions to the prefactors are negligible within a factor of 2. The results obtained using dynamic simulations provides different prefactors for homo systems. The prefactor for the diffusion of Cu₇ cluster on Ag(111) is smaller than that for the diffusion of Cu₇ cluster on Cu(111). The analysis of the vibrational free energy contribution showed that it is higher for the hetero case than the homo. This originates from the fact that strong intra-cluster interaction for the hetero case increases the population at the low frequency end of the spectrum that governs the vibrational free energy. This then leads to smaller prefactor. From the static simulations, we find that comparison of the prefactor for the single atom diffusion, the prefactor for the 7-atom cluster (for concerted motion only) shows small deviation -- a factor of less than 10 is observed for the homo, while much smaller value (0.4) is found for the hetero case.

Short time MD simulations revealed that the cluster diffuses via concerted motion for 400K and 550K. The cluster’s motion mostly involves vibrations around a fixed point and breathing mode. For higher temperature (700K) we find that the cluster encounters shape change frequently during its diffusion. It diffuses as distorted via such
diffusion mechanism as rotation, dimer shear, and edge diffusion. For the hetero case, we find that cluster tends to become 3D. Note that the cluster always goes back to its compact shape during its diffusion hence indicating the competition between the compact and distorted shapes. Effective diffusion parameters obtained from long time MD simulations revealed that for high temperature (700K) the diffusion of the cluster governed by the motion of single atoms and dimers. For the homo case, we find the prefactor for the cluster diffusion to be much larger than that for the single atom, while diffusion prefactor obtained for the hetero case does not show the same trend. Our calculations shows that the static simulations used to calculate the prefactors that involves only certain number of degrees of freedom not the whole substrate dynamics do not provide the same conclusions as the dynamic simulations. This reveals that for the diffusion of multi-atoms, incorporating the whole substrate dynamics is important revealing the limitations of the static calculations.
We report results of a systematic study of structural, vibrational and thermodynamical properties of 34-atom bi-metallic nanoparticles from the $\text{Ag}_n\text{Cu}_{34-n}$ family using model interaction potentials as derived from the embedded atom method and invoking the harmonic approximation of lattice dynamics. Systematic trends in the bond length and dynamical properties can be explained largely from arguments based on local coordination and elemental environment. Thus an increase in the number of silver atoms in a given neighborhood introduces a monotonic increase in bond length, while an increase of the copper content does the reverse. Moreover, for the bond lengths of the lowest-coordinated (six and eight) copper atoms with their nearest neighbors (Cu atoms), we find that the nanoparticles divide into two groups with the average bond length either close to ($\sim 2.58 \text{ Å}$) or smaller than ($\sim 2.48 \text{ Å}$) that in bulk copper, accompanied by characteristic features in their vibrational density of states. For the entire set of nanoparticles, we find vibrational modes above the bulk bands of copper/silver. We trace a blue shift in the high-frequency end of the spectrum that occurs as the number of copper atoms increases in the nanoparticles, leading to shrinkage of the bond lengths from those
in the bulk. The vibrational densities of states at the low-frequency end of the spectrum scale linearly with frequency as for single-element nanoparticles, with a more pronounced effect for these nanoalloys. The Debye temperature is found to be about one-third of that of the bulk for pure copper and silver nanoparticles, with a non-linear increase as copper atoms increase in the nanoalloy.

5.1 Introduction

It has been widely accepted that a solid’s surface representing the interface with the surrounding environment introduces differences in properties from those of the bulk form. These differences have opened new avenues through which one can fine-tune the physical and chemical properties and so approach the goal of designing materials with tailored characteristics. Because of their large surface-to-volume ratio, NPs are good candidates for materials with novel and controllable properties. Efforts have thus been made to understand the size-dependent evolution of the physical, chemical, and electronic properties of these NPs [232]. These studies also point to the possibility of using NPs as building blocks for cluster-assembled materials [5] with tailored properties and possible applications [233] in the biomedical, catalytic, optical, and electronic industries. Since alloying offers a natural avenue for further controlling and modifying properties of NPs, attention has been directed to synthesis, characterization, and observation of novel properties of bimetallic NPs [234]. The latter have also found themselves to be the arena for testing theoretical developments in techniques that aim at sketching multidimensional potential energy surfaces to search for the equilibrium structures of atoms and molecules in complex environments. Competing roles of elemental specificity, relative strengths of
bonds and cohesive energy, local coordination, and electronic and geometric structure interplay in providing materials whose stability are not always transparent or easily controllable. Hence, developing an understanding of the microscopic factors that relate structure to functionality is at the basis of the increasingly important field of computational material design. Nanoalloys provide a bottom-up approach to tailoring the properties of materials through a systematic understanding of the relative importance of the diverse factors that constitute a local environment. The issues at the theoretical level extend from the description of the geometric structure of the nanoalloy, to establishment of stability criteria, to extraction of the relative effects of structural, electronic, and vibrational contributions in controlling alloy novel properties. In the case of bimetallic NPs, symmetry and elemental size are also expected to play a role in influencing the geometric structure.

Recently, Rossi et al [235] have applied global optimization techniques to several bimetallic clusters of transition metal elements consisting of 30–40 atoms, using semi-empirical inter-atomic potentials [236]. They found very stable ‘magic’ NPs, characterized as core–shell polyicosahedra with high (calculated) melting points. Earlier MD simulations [167, 168, 237] concerning the growth of core–shell structures of larger clusters (a few hundred atoms) showed that Ni and Cu impurity atoms prefer subsurface locations inside Ag clusters and induce higher stability and high melting temperatures. For six binary systems (Ag–Ni, Ag–Cu, Au–Cu, Ag–Pd, Ag–Au, and Pd–Pt), Rapallo et al [13] also examined the effects of size mismatch, alloying tendency (as compared to that in the bulk phase of Ag–Ni and Ag–Cu), and the tendency for surface segregation. Among these binary systems, Ag–Cu has the largest size mismatch. These pioneering
studies have been very helpful in developing the framework for a systematic methodology for determining the geometric structure and stability criteria for nanoalloys [238]. The stage is now set for complementary studies; in particular, the effect of alloying on the vibrational characteristics of the NPs remains to be explored. Such an examination is needed because of its relevance in determining relative structural stability in bulk [239] and surface alloys [240].

In this work we have thus undertaken a systematic examination of the effect of changing elemental composition on the local structure (bond lengths), vibrational dynamics, and thermodynamics for the case of 34-atom Ag–Cu NPs (namely AgₙCu₃₄₋ₙ family). As a starting point we take the geometric structure of each NP to be that obtained by Rossi et al [235], while recognizing that a priori inclusion of vibrational entropy in initial searches for equilibrium configurations could have produced a different outcome. For the rest of the chapter, we proceed as follows. In section 5.2 we discuss the theoretical details, while in section 5.3 we summarize the results in four sub-sections:

1. Section 5.3.1 describes the results of the analysis on the coordination and the bond lengths;
2. Sections 5.3.2-5.3.4 present the alloying effect on the VDOS of the sample NPs and LVDOS of some particular atoms, respectively;
3. Section 5.3.5 summarizes the results of the analysis of the vibrational free energies, and discusses the progressive alloying effect;
4. Section 5.3.6 discusses the mean-square vibrational amplitudes of the particular atoms, and the Debye temperatures of each NP and the average Debye
temperature of Cu and Ag atoms in the NPs; finally, in section 5.4, we will present the comprehensive conclusions.

5.2 Theoretical Details

The starting configurations (optimized global-minimum energy structures) of the 35 NPs form the family of Ag$_n$Cu$_{34-n}$ were established by Rapallo et al [13], who used a genetic algorithm scheme to find the global minimum energy configurations using an empirical potential [236]. They showed that this family consists of “magic” NPs, most of which are characterized by the common property of a perfect core–shell structure with Ag atoms on the shell and Cu atoms in the core.

In Figures 5.1.a–j, we present the geometric structures of 10 representative (from the structure point of view) NPs revealing the differences in the stoichiometry. As one can note from the Figures 5.1.f-h that, as the Cu-atom content increases in the NP, more Cu atoms becomes exposed to the shell. The figure makes it clear that there are NPs in this family with both complete and incomplete close shells. For those NPs with incomplete close shells, there is a partial symmetry. Among the NPs, Ag$_{17}$Cu$_{17}$ and Ag$_{27}$Cu$_{7}$ has perfect mirror symmetry. As we proceed through the thesis, one sees that these NPs show distinct electronic properties (Chapter 6). In our calculations, the starting configuration of each NP has been subjected to a further relaxation using the CG method [91] with interaction potentials derived from the EAM [50]. For Cu and Ag and their alloys, these potentials have proven to provide accurate structural as well as vibrational properties for bulk and surface systems [51].
Figure 5.1 Structure of sample NPs for a) Ag$_{34}$ b) Ag$_{31}$Cu$_3$ c) Ag$_{27}$Cu$_7$ d) Ag$_{24}$Cu$_{10}$ e) Ag$_{17}$Cu$_{17}$ f) Ag$_{14}$Cu$_{20}$ g) Ag$_{10}$Cu$_{24}$ h) Ag$_7$Cu$_{27}$ i) Ag$_3$Cu$_{31}$ and j) Cu$_{34}$

For the calculation of vibrational dynamics and thermodynamics the force-constant matrix has to be constructed. As the first step, we calculate the force-constant matrix of each NP (in their equilibrium configuration) from the partial second derivatives of the interaction potential. The VDOS of each NP is determined from the force constant matrix ($D$) by means of constructing the corresponding Green’s function. From the trace of the Green’s function matrix, the normalized VDOS (\(g(w)\)) is obtained:

\[
G(w^2 + i\varepsilon) = (I(w^2 + i\varepsilon) - D)^{-1}
\]

\[
g(w^2) = \lim_{\varepsilon \to 0} \frac{1}{\pi} \text{Im} \text{Tr}[G(w^2 + i\varepsilon)]
\]

\[
g(w) = 2w\rho(w^2)
\]

The LVDOS (\(g_i(w)\)) of each atom in the NP is such that \(\sum_{i=1}^{N} g_i(w) = g(w)\), where \(n\) is the number of atoms in the NPs, and can be determined from the diagonal elements of the imaginary part of the Green’s function matrix. Once the VDOS are calculated, the
thermodynamical functions can be determined in the harmonic approximation of lattice dynamics. The local vibrational free energies of each atom $i$, their vibrational mean-square amplitudes, and Debye temperatures are thus calculated using the equations below:

$$F_i^{\text{vib}} = k_B T \int_{0}^{\infty} \rho_i(w) \ln(2 \sinh(\frac{\hbar w}{2k_B T})) dw$$

(5.4)

$$\langle u_i^2 \rangle = \frac{\hbar}{2M} \int_{0}^{\infty} \frac{1}{w} \coth(2\hbar w k_B T) \rho_i(w) dw$$

(5.5)

$$\theta_i^2 = \frac{3\hbar^2 T}{Mk_B \langle u_i^2 \rangle}$$

(5.6)

In consideration of vibrational contributions to the relative stability of the system, the quantity of interest is the excess vibrational free energy, which is defined as the excess over the values associated with the bulk system. Thus the local contribution to the vibrational excess free energy is given by:

$$\Delta F_i^{\text{vib}} = F_i^{\text{vib}} - F_{\text{bulk}}^{\text{vib}}$$

(5.7)

where $F_{\text{bulk}}^{\text{vib}}$ is the bulk value (per atom) for the species (Cu or Ag), and is obtained from earlier calculations [131]. The total excess free energy (over the bulk), of course, contains a major contribution from the structural or potential energy and from configurational entropy. The excess potential energy portion is introduced by Ferrando et al [236] through the term $\Delta_{\text{pot}}$ as expressed below in equations 5.8. We have introduced a similar term, which corresponds to the vibrational component of the excess energy ($\Delta_{\text{vib}}$).
\[
\Delta_{pot} = \frac{E_{tot}^{N,N_1} - N_1 \varepsilon_1^{coh} - N_2 \varepsilon_2^{coh}}{N^{2/3}}
\]

\[
\Delta_{vib} = \frac{F_{tot}^{vib} - N_1 F_{bulk,Ag}^{vib} - N_2 F_{bulk,Cu}^{vib}}{N^{2/3}}
\]  

(5.8)

where \(E_{tot}^{N,N_1}\) is the minimum energy for a given composition of the NPs, \(\varepsilon_1^{coh}\) and \(\varepsilon_2^{coh}\) are the cohesive energies of the species (Ag and Cu), \(N_1\) and \(N_2\) are the numbers of Ag and Cu atoms, and \(N (N=N_1+N_2)\) is the total number of atoms in the NP. Dividing by \(N^{2/3}\) (approximately the number of surface atoms) yields the excess energy per surface atom.

Here \(F_{tot}^{vib}\) is the total vibrational free energy of the NP and expressed as:

\[
F_{tot}^{vib} = \sum_{i=1}^{N_1} F_{i,Ag}^{vib} - \sum_{i=1}^{N_2} F_{i,Cu}^{vib}
\]  

(5.9)

\(F_{bulk,Ag}^{vib}\) and \(F_{bulk,Cu}^{vib}\) are the vibrational free energies of bulk Ag and Cu atoms, respectively. The total excess energy is thus expressed as:

\[
\Delta_{tot} = \Delta_{pot} + \Delta_{vib}
\]  

(5.10)

In the above, we have not included explicitly the contributions from configurational entropy, which come into play when deciding the relative stability of isomers corresponding to specific nanoalloy compositions. Such contributions were included by Rapallo et al [13] in their energetic considerations. Our interest here is a specific isomer.

5.3 Results and Discussions

With the aim of investigating the effect of alloying and the local elemental environment and coordination in determining the structural, vibrational and
thermodynamical properties of this particular set of NP family, we first employ a global analysis of the bond lengths between the atoms and their neighbors in these 35 NPs. We then calculate the total VDOS of each bi-metallic NPs, and compare with that of the two single-element NPs in the family. Selecting particular atoms whose coordination and elemental environments are distinct, we also calculate their VDOS to gain insights into the local contributions. Finally, we analyze such global (averages) and local thermodynamical quantities as free energy, mean-square vibrational amplitudes and Debye temperatures.

5.3.1 Coordination and Bond-length Distribution

Since it is neither feasible nor desirable to present results of the bond lengths for all atoms with their neighbors in each of the 35 NPs that form the AgₙCu₃₄₋ₙ family, we choose to present those with the most dominant coordination. In contrast to the extended systems, the bond-length distribution is very broad in these NPs; hence a criterion for counting neighbors is necessary. We have set the cut-off in the nearest-neighbor bond-length count as 2.7 Å and 3.1 Å, for Cu and Ag atoms, respectively. With these cut offs in mind, we first tabulate the coordination of all atoms in each NP. The total number of Ag and Cu atoms in the set of 35 NPs with particular coordination is counted and divided by the total number of Ag and Cu atoms in the set (34×35) to obtain the number density. In Figures 5.2.a-b, we have plotted the number density as a function of coordination. Notice from the figures that Cu atoms with coordination 6, 8, 9 and 12 (with corresponding number densities of 0.2, 0.15, 0.27 and 0.29) and Ag atoms with coordination 6, 8 and 9 (with number densities of 0.51, 0.23 and 0.12) are the dominant
ones. The number densities reveal that most of these nanoalloys are core -- shell type in which Cu atoms populate the core and Ag atoms favor the shell. Moreover, one notes that in these small NPs only 3% of the Cu atoms and 7% of the Ag atoms form steps (with coordination 7). Corner/kink atoms with coordination 6 have a large density and even dominate (51%) in the case of Ag atoms. As for facets, in the case of Cu atoms it is the dense (111) geometry that is favored with 27% of the atoms (coordination 9), versus only 15% for the (100) geometry (atoms with coordination 8). The reverse is true for Ag atoms -- preference for more open structures with 23% of the atoms on a (100) facet, while only 12% are on the (111).
Figure 5.2 Number density as a function of coordination for a) Cu atoms and b) Ag atoms

Since there is a large deviation in coordination and bond lengths for each atom in the NPs, one expects that there is a range of values for the average nearest-neighbor bond length for the Cu (Ag) atoms with the coordination of 6, 8 and 9 (12, 9, 8 and 6). These variations in the average bond lengths for each coordination (changing the number of atoms of either species in the bonding) are shown in Figures 5.3.a-b for Cu and Ag,
respectively. Notice from Figure 5.3.a that especially for coordination 12, there is a monotonic increase in the bond length as the number of Ag atoms increases in the neighborhood. We also find the similar behavior for the Cu atoms with coordination 9 and 8, while for coordination 6 the statistics are too sparse to draw any specific conclusion.

![Figure 5.3](image1.png)

**Figure 5.3** Change in average nearest-neighbor bond length with coordination and elemental environment for **a)** Cu atoms and **b)** Ag atoms
For Cu atoms with coordination 12 with zero Ag atom neighbors, we find the average nearest-neighbor bond length to lie between 2.43 Å and 2.47 Å, with the exception of the Cu_{34} NP for which the average bond length is 2.50 Å. Increase in Ag atom neighbors yields the average nearest-neighbor distance to increase monotonically from 2.43 Å (0 Ag neighbors) to 2.70 Å (12 Ag neighbors), an increase of about 0.02 Å per Ag atom. This trend is obviously related to the fact that the bulk lattice constant of Ag is larger than that of Cu. As we proceed throughout the chapter, one sees that the effect of the change in the bond length is reflected in the local thermodynamical properties. Note that the spread in the average bond length for any particular environment (for Cu atoms with fixed number of Ag neighbors from any NP) is found to be small (of the order of 0.01–0.05 Å. For Cu atoms with coordination 9, the average bond length also increases with the number of Ag atoms in the neighboring sites from 2.54 Å (no Ag neighbors) to 2.71 Å to (six Ag neighbors) with variations in the average bond length between 0.02 Å and 0.07 Å. Similarly, for Cu atoms with coordination 8 the total increase in the average bond length is 0.14 Å as the number of neighboring Ag atoms changes from 0 (2.53 Å) to 4 (2.67 Å) with a small variation within any given neighborhood (0.03–0.06 Å). Finally, for coordination 6 the same trend is found as for the case of other coordination -- an increase in the bond length with increasing the number of Ag atoms.

On the other hand, for Ag atoms since the neighborhood shows a limited range of variation of the number of Ag atoms, the increase in the average bond length is not substantial. For Cu atoms with coordination 8 and 6, an interesting trend in bond lengths is observed, particularly for those with no Ag atoms neighbors, the bond lengths divide into two groups. For atoms with coordination 8, the first group of NPs has the average
bond length between 2.52 Å and 2.54 Å (smaller than bulk Cu), whereas for the second group the bond length varies from 2.56 Å to 2.59 Å (larger than bulk Cu). For atoms with coordination 6, in the first group of NPs the bond length lies between 2.48 Å and 2.51 Å. As the number of Ag atoms in the NPs increases from 9 to 18, the average bond length varies from 2.52 Å to 2.58 Å with a sudden shift for Ag₉Cu₂₅ (perhaps structure related). This is also confirmed by our *ab-initio* electronic structure calculations based on the DFT -- the results of which are summarized in Table 5.1 in parenthesis. Note that such behavior in the average bond lengths is not found for Ag atoms. A detailed analysis of the DFT results will be presented in Chapter 6, and a recent DFT study of particular nanoalloy (Ag₂₇Cu₇) is reported in [241].

Table 5.1 Average bond lengths for Cu atoms (coordination 6) in each NP along with their elemental environments. DFT results are in parenthesis.

<table>
<thead>
<tr>
<th>Cu coordination 6</th>
<th>Number of Ag atoms and Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0Ag</td>
</tr>
<tr>
<td>Ag₁₈Cu₁₆</td>
<td>2.57(2.55)</td>
</tr>
<tr>
<td>Ag₁₆Cu₁₈</td>
<td>2.58(2.56)</td>
</tr>
<tr>
<td>Ag₁₅Cu₁₉</td>
<td>2.54(2.55)</td>
</tr>
<tr>
<td>Ag₁₄Cu₂₀</td>
<td>2.55(2.56)</td>
</tr>
<tr>
<td>Ag₁₃Cu₂₁</td>
<td>2.58(2.58)</td>
</tr>
<tr>
<td>Ag₁₂Cu₂₂</td>
<td>2.57(2.57)</td>
</tr>
<tr>
<td>Ag₁₁Cu₂₃</td>
<td>2.55(2.57)</td>
</tr>
<tr>
<td>Ag₁₀Cu₂₄</td>
<td>2.52(2.51)</td>
</tr>
<tr>
<td>Ag₈Cu₂₅</td>
<td>2.57(2.58)</td>
</tr>
<tr>
<td>Ag₇Cu₂₆</td>
<td>2.51(2.51)</td>
</tr>
<tr>
<td>Ag₆Cu₂₇</td>
<td>2.51(2.51)</td>
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<tr>
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<tr>
<td>Ag₃Cu₃₁</td>
<td>2.49(2.48)</td>
</tr>
<tr>
<td>Ag₂Cu₃₂</td>
<td>2.49(2.49)</td>
</tr>
<tr>
<td>Ag₁Cu₃₃</td>
<td>2.48(2.49)</td>
</tr>
<tr>
<td>Cu₃₄</td>
<td>2.49(2.49)</td>
</tr>
</tbody>
</table>
As plotted in Figure 5.3.b, the average bond length of Ag atoms (with change in the number of Cu atom neighbors) shows that the effect of altering the elemental environment is in general much less pronounced than that for Cu atoms. There is almost a linear decrease in the bond length with the addition of Cu atoms to the bonding. For Ag atoms with coordination 9 (seven Cu neighbors) appears to violate the above trend (Figure 5.3.b). However, for this coordination, the small number of such atoms in the family of NPs does not produce sufficient statistics for drawing a definite conclusion. Note also that there is little variation in the bond length for Ag atoms with zero Cu atoms in the neighborhood. For the Ag atoms, the average bond length decreases with more Cu atoms in the elemental environment from 2.84 Å (0 Cu) to 2.78 Å (0 Cu) to 2.77 Å (5 Cu) for coordination 9, 2.84 Å (6 Cu) for coordination 8, and finally 2.83 Å (0 Cu) to 2.65 Å (6 Cu) for coordination 6.

In summary, for the sets of Cu (Ag) atoms with coordination 12, 9, 8 and 6 (9, 8 and 6), the variation in the bond length is 0.27, 0.17, 0.14 and 0.1 Å (0.07, 0.09 and 0.2 Å), respectively. We find characteristic trends in bond-length variations induced by alloying, thereby providing the effect of coordination and local elemental environment as its (bond-length) measure. The average bond length distribution for Cu and Ag atoms is summarized in Tables C1 to C7 in Appendix C: Chapter 5. We will now proceed to examine whether the local coordination and the elemental environment is an effective measure for determining other characteristics of the nanoalloys.
5.3.2 Vibrational Densities of States (VDOS) of Sample NPs

When surface-to-volume ratio of a solid system becomes high as is the case with matter at the nanoscale, it is to be expected that a substantial contribution to the properties comes from the surface atoms. Earlier studies on nanoalloys by Ferrando and co-workers [16] showed that the melting temperature of these NPs is relatively high with respect to that of single-element NPs of the same size. This may be a signature of stiffening of some of the bonds between atoms, which will have consequences for the VDOSs; hence for their thermodynamical properties. This fact hence justifies the need to study the vibrational dynamics and thermodynamics of these finite-sized systems in order to build understanding how composition effect correlates to the characteristics in the VDOS. It will also be of interest to compare our findings with those already known for Ag and Cu surfaces, NPs and their bulk forms [8, 131, 132]. In an earlier study of single-element metal (Ag) NP of varying size (2–3.5 nm) [8], two features of the VDOS were reported to be different from those of the bulk. One concerns the high-frequency end of the spectrum and the other the low-frequency portion. Similar findings have also been reported in several experiments for metal and magnetic NPs [9]. For the Ag NP, it was shown that the high-frequency end of the VDOS is shifted above that of the top of the bulk band and it is attributed to the shrinking of the nearest-neighbor distance of the some particular atoms in the NP [8]. The shift in the high-frequency end was shown to be localized and to drop sharply with increasing size of the NP. At the low-frequency end, these NPs exhibited substantial enhancement in the VDOS relative to that of the bulk spectrum. This enhancement was reported to originate from the contribution of the outer
atoms (surface atoms). For the bi-metallic nanoalloys, since the properties are governed by the interplay between the local coordination and elemental environment, the role of elemental environment on the characteristic of the VDOSs can be tested by means of studying a fixed size NP with different composition as we proceed in this study.

To illustrate the effect of progressive alloying, we present in Figures 5.4.a-f the VDOS of six sample NPs namely Ag₃₁Cu₃, Ag₂₇Cu₇, Ag₁₇Cu₁₇, Ag₁₀Cu₂₄, Ag₇Cu₂₇ and Ag₃Cu₃₁ and compare the results to those of the two single-element NPs in the family, Cu₃₄ and Ag₃₄. Notice from the figures that there is a correlation between the increase in population at high-frequency end of the spectrum and the increase in the Cu-atom content in the NPs. From Figure 5.4.a, for the NP (Ag₃₁Cu₃) with only three Cu atoms, one can note a slight shift towards the high-frequency end of the spectrum as compared to the case of the single-element Ag NP (Ag₃₄). This alloying effect becomes stronger for the other cases at which the ratio of Cu to Ag atoms in the NPs increases. One should also note that the shift towards the high-frequency end of the spectrum is found to extend over few Terahertz (over the top of the bulk band) confirming the earlier theoretical and experimental observations [8, 18]. As one can note from Figures 5.4.a-f, increase in the number of Cu atoms leads the spectrum to become close to that of the single-element Cu NP (Cu₃₄). In order to quantify the effect of alloying in these NPs, we have calculated the percentage change (relative partial integral) in the VDOS in the high-frequency region above 5.1 THz (the frequency at which the VDOS of Ag₃₄ is almost zero). In Figure 5.5, we plot percentage change as a function of the number of Cu atoms in the system and find the dependence to be nearly linear. A small deviation from linear behavior (shown in Figure 5.5) is understandable given the simplicity with which the information has been
extracted. The behavior at the low-frequency end of the spectrum for the chosen nanoalloys is found to be similar to that for single-element NPs for which the VDOS scales linearly with the frequency [8]. Below, we examine more closely the effect of elemental environment on the dynamical properties of these nanoalloys by means of calculating the LVDOSs for chosen Cu (Ag) atoms with coordination 12, 9, 8 and 6 (9, 8 and 6) with large diversity in their neighborhood, respectively.
Figure 5.4 VDOS of the sample NPs for (a) Ag$_{31}$Cu$_3$, (b) Ag$_{27}$Cu$_7$, (c) Ag$_{17}$Cu$_{17}$, (d) Ag$_{10}$Cu$_{24}$, (e) Ag$_7$Cu$_{27}$ and (f) Ag$_3$Cu$_{31}$. 
5.3.3 Local Vibrational Density of States (LVDOS) of Cu Atoms in Sample NPs

Analysis performed here for the local vibrational dynamics is based on the bond length analysis that is just presented above. The vibrational dynamics of the Cu atoms (with coordination 12, 9, 8 and 6 with varying elemental environment) from the NPs of selected compositions is plotted in Figures 5.6.a–e with the VDOS of the bulk Cu atom. For the atoms with coordination other than 6, we have chosen arbitrarily one such atom from the family of the NPs, since we find that there is a slight spread in the bond lengths. However, for atoms with coordination 6, the choice has to be done more carefully since the bond lengths (Table 5.1) fall into two categories; those larger and smaller than the bulk value. We analyze the vibrational dynamics of these representative atoms from each of the two categories to ascertain any differences in the spectra.
From the LVDOS of Cu atoms with coordination 12 (Figure 5.6.a), the first observation is the appearance of new peaks at 8.5 THz and 9.1 THz for environments containing zero and 6 Ag neighbors (no peaks appear in these high-frequency range when there are 12 Ag neighbors). The latter reflects softening in the Cu–Ag coupling introduced by the larger number of Ag atoms. At the low-frequency end, note an enhancement of the VDOS revealing the induced softening of the bonds by the presence of Ag atoms. These features can be rationalized using the bond-length arguments. Note that the bond length for Cu atoms in these three environments is in the range of (2.41 Å – 2.53 Å) for zero, (2.50 Å –2.74 Å) for 6 and finally (2.64 Å –2.74 Å) 12 Ag neighbors. The shorter bond lengths are responsible for the high-frequency peaks at 8.5 and 9.1 THz (zero and 6 Ag neighbors). For 12 Ag neighbors, the shortest bond length (2.64 Å) is higher than the bond length in bulk Cu (2.56 Å) thus explaining the absence of modes with frequencies above the Cu bulk band (Figure 5.6.a). Larger bond lengths tend to indicate a softer bonding that enhances the low-frequency end of the density of states. For example, for those Cu atoms with 6 and 12 Ag neighbors with large bond length (2.74 Å), there is an enhancement around 3 THz, which is absent for zero Ag neighbors, whose maximum bond length is 2.53 Å. Similar arguments explain the features in the LVDOS of Cu atoms with coordination 9 with zero, three and six Ag neighbors (Figure 5.6.b).

Let us now turn to the case of Cu atoms with coordination 8 (with zero, two and four Ag neighbors) for which the LVDOS is shown in Figure 5.6.c. At the high-frequency end, the largest shift is found for the case of Cu atoms with two Ag neighbors that is followed by those with four Ag neighbors. The smallest shift in the high-frequency region is found for the Cu atom with zero Ag neighbors the bond lengths ranging from
2.40 Å to 2.80 Å, for two Ag neighbors 2.41 Å to 2.78 Å and for four Ag neighbors 2.43 Å to 2.82 Å. These results diverge from the trend seen above. The effect of local environment on the features obtained at the high-frequency end of the LVDOS thus points to the need for more accurate analysis based on electronic structure calculations. At the low-frequency end, there is more pronounced deviation of the VDOS from the bulk with the loss of coordination -- the increase of Ag atoms enhances the shift towards low frequency.

Finally, we discuss the vibrational dynamics of Cu atoms with coordination 6. In Figure 5.6.d, the LVDOS is shown (for the first category of large bond length) with zero, one and two Ag neighbors. At the high-frequency end, the largest shift is found for atoms with zero and one Ag neighbor, with the shortest bond lengths being 2.29 Å and 2.31 Å respectively. For Cu atoms with two Ag neighbors, the shortest bond length is 2.41 Å, which shows the smallest shift at the high-frequency end. For the low-frequency end, one notices the complexity of the spectra. However, one can still extract a few trends: the order of enhancement is for Cu atoms with zero, one and two Ag neighbors with the largest bond length being 2.65 Å, 2.73 Å, and 2.75 Å, respectively. One would intuitively expect that the larger the bond, the larger would be the frequency softening.
Figure 5.6 LVDOS of selected Cu atoms with coordination (a) 12 (b) 9 (c) 8 (d) 6 (large bond length), and (e) 6 (short bond length) with varying elemental environment.
This is not however the case here. In Figure 5.6.e, we report the LVDOS of atoms with coordination six (from the category of short bond lengths) containing zero, one and two Ag neighbors. Note that a shift in high frequencies is found only for Cu atoms with two Ag neighbors (Table 5.1). It is interesting to note that even for the atoms with zero and one Ag neighbors with relatively short bond lengths (2.44 Å and 2.39 Å, respectively) the corresponding LVDOS does not show any new features at high frequencies. At the low-frequency end, we note the same trend as shown in Figure 5.6.d for which the increasing number of Ag neighbors combined with the large bond length, for example, for two Ag (2.73 Å), one Ag (2.64 Å) and zero Ag neighbors (2.52 Å) does not enhance the low-frequency modes. In summary, in addition to the obtained useful trends, the above analysis also points to the fact that complex correlations between coordination and environment introduce some features in the LVDOS that cannot be adequately accounted for solely on the basis of local environment and bond-length arguments. Further work is needed to address these issues.

### 5.3.4 Local Vibrational Density of States (LVDOS) of Ag Atoms in Sample NPs

In Figures 5.7.a–c, the LVDOS of Ag atoms with coordination 9, 8 and 6 is presented following the same procedure used for Cu atoms discussed above. Here again the choice of the NPs -- from which the atoms in question are extracted -- is reported in the figures. For example, for coordination 9, the Ag atom with zero Cu neighbors is chosen from Ag34, while those with three and five Cu neighbors are from Ag23Cu11. From Figure 5.7.a, a shift in the VDOS towards high frequencies above the bulk Cu band is found for the Ag atoms with three and five Cu neighbors. Higher shift is found for the
latter that can be explained by the bond-length analysis given above. The enhancement at the low-frequency end simply reflects the reduction in the coordination. From Figure 5.7.b, we conclude that the features at the high and the low frequency ends for the atoms with coordination 8 are quite similar to those with coordination 9. The most striking features at both high-and low-frequency ends of the spectrum are associated with Ag atoms with coordination 6. As for coordination 9 and 8, the high-frequency end contains new modes that are well resolved and arise from environments in which Cu atoms are present (Figure 5.7.c). The lowest bond lengths are 2.47 Å and 2.5 Å and 2.77 Å, for six, three and zero Cu neighbors, respectively.

Note the fact that the bond length associated with zero Cu neighbors is distinct and larger than that associated with three and six Cu neighbors explains the presence of high-frequency modes for the last two cases. It is at the low-frequency end at which there is a large enhancement for all three cases. This feature is much more pronounced than that for the atoms with coordination 9 and 8. From the same arguments used for coordination 9 and 8, however, one would expect to find enhancement for the atoms with the highest number of Ag neighbors. Note that this is not the case here: instead, the highest enhancement of the density of states at the low-frequency end of the spectrum is associated with a Ag atom with six Cu neighbors.
5.3.5 Vibrational Contributions to the Excess Free Energy

The stability of a system and its phase transitions can be explored by studying its thermodynamical properties, for which the vibrational dynamics of a system may play a substantial role. For instance, the role of vibrational free energy in determining the equilibrium structures of bulk-alloy systems has been explored and reported to be important [242]. A recent study for the stepped metal surfaces of Cu and Ag showed the vibrational contributions to be a substantial fraction of the step free energy [131].
equally important and sometimes dominant contribution may arise from configurational entropy. If we were to be comparing the relative stability of a set of isomers for each NP of a given composition, then a discussion devoted on the role of configurational entropy would be appropriate. However, in this study, we narrow the analysis to the specific NPs whose configurations have already been established by Rapallo et al [13], as the candidates with the lowest energy for a given set of isomers. Hence, we focus only on the assessment of vibrational entropy of a NP of a fixed configuration. The task here is to determine whether the above trends in the contribution of the local vibrational properties to the excess free energy also applies to NPs with only 34 atoms, and whether alloying brings some additional characteristics. For this purpose, the average free energy contribution distribution as a function of elemental environment for Cu and Ag atoms is summarized in the Tables C8 to C14 in Appendix C: Chapter 5. We have also calculated the contribution to the total vibrational free energy from each NP and tabulated in Table C15 in Appendix C: Chapter 5. The change in the vibrational free energy as a function of the number of Cu atoms in the NPs is plotted in Figure 5.8. The figure shows that the contribution increases monotonically with the number of Cu atoms. The contributions to the low-frequency end of the spectrum of VDOS determine vibrational free energy at (relatively) low temperatures. In order to reveal that feature, we have also calculated the percentage contribution of the low-frequency ends to the whole spectrum. To do that, the Debye frequencies of bulk Cu and Ag (6.56 THz and 4.48 THz, respectively) are used as the cut-off for the low-frequency “part” of the LVDOS. We have summarized the percentage contributions for some NPs Table C15 in Appendix C: Chapter 5. Increasing the number of Cu atoms (alloying) depletes the low-frequency end of the spectrum,
enhancing the contribution of the vibrational dynamics to the free energy. Note that using
the Debye frequency of bulk Cu instead of Ag gives the same trend with higher
contributions. In an earlier study [131], it was shown that the low-coordinated atoms (on
stepped Cu and Ag surfaces) have higher contributions to the excess free energy. It was
also reported that the atom below the step -- named as bulk nearest neighbor (BNN) --
has lower contribution than that of the atoms in the bulk (one would expect bulk atoms to
have the lowest contribution). This is attributed to over-coordination of atoms induced by
strong structural relaxations. In order to determine how coordination affects the excess
free energy, we examine the Cu atoms (no Ag neighbors) in Cu_{34} NP. For the
coordination (12, 9, 8 and 6), we find the corresponding local excess vibrational free
energy to be +12 meV/atom, -6 meV/atom, -6 meV/atom and -15 meV/atom,
respectively. The trend in the contribution of the under-coordinated atoms is thus in
accord with what was reported earlier [131]. The most interesting contribution comes
from the atoms with coordination 12, whose opposite sign reflects the effect of over-
coordination in agreement (except that here the contribution is much larger) with the
earlier study on extended systems. For NPs, the over-coordination of the core atoms
results from the local shrinking that the finite-sized systems experience [8]. For the case
of Ag atoms with coordination 9, 8 and 6, we turn to the contributions of the atoms in the
Ag_{34} NP (no Cu neighbors). We find the contributions to be 0 meV/atom, -4 meV/atom
and -7 meV/atom for coordination 9, 8 and 6, respectively. The observed trend here is
qualitatively similar to that found for the metal surfaces [132].
We present the results for the vibrational entropic contribution for the full set of 35 NPs in Figure 5.9, which shows that the inclusion of the vibrational contribution to the free energy does not introduce noticeable changes in the relative quantities for these NPs. Clearly, the complexity in the local environments leads to both positive and negative contributions to vibrational entropy, making the total contribution to be small relative to that of the structural energy of the NP.
5.3.6 Mean-Square Vibrational Amplitudes and Debye Temperatures

In an earlier study on vicinal metal surfaces [132], it was found that the mean square vibrational amplitude is enhanced for low-coordinated atoms, and the Debye temperature is reduced to about two-thirds of the bulk value. In this section we examine the mean-square vibrational amplitudes and the Debye temperatures of selected atoms in these nanoalloys in order to reveal the effect of coordination on these quantities, and compare with that was reported for those atoms of vicinal surfaces. The local mean-square vibrational amplitudes calculated within the harmonic approximation for Cu (Ag) atoms with coordination 12, 9, 8 and 6 (9, 8 and 6) are presented in Figure 5.10 (5.11). We will discuss the deviations from the bulk value at 300 K. Let us start with Cu atoms with coordination 12 (Figure 5.10.a). The largest deviation (0.005 Å²) from the bulk
value (0.0325 Å²) is found for the case which has the highest number of Ag neighbors. For atoms with coordination 9 and 8, we find that the higher the number of Ag neighbors yields larger mean-square vibrational amplitudes, which deviate from the bulk about 0.022 Å² and 0.04 Å², respectively. However, for Cu atoms with coordination 6 (in the large-bond-length regime) the trend is the opposite: an increase in the number of Ag neighbors results in a decrease in the mean-square vibrational amplitudes. This latter trend can be traced back to the low-frequency part of the VDOS for such atoms (Figure 6.d), which resembles the bulk atom VDOS. The largest deviation is found to be 0.15 Å² (30 times larger than that of the atom with coordination 12). For the short-bond-length case, the same trend is reported in Figure 5.10.e, with a deviation of 0.1 Å² (for zero Ag neighbors).
Figure 5.10 Mean square vibrational amplitudes of Cu atoms with coordination (a) 12 (b) 9 (c) 8 (d) 6 (large bond length) and (e) 6 (short bond length) and environment.
Turning to the case of Ag atoms with coordination 9, let us note from Figure 5.11.a that a decrease in the number of Cu neighbors brings an increase in the mean-square vibrational amplitude with a deviation from that of the bulk of about 0.04 Å². When the coordination is reduced to 8 (Figure 5.11.b), regardless of the number of Cu neighbors, the mean-square amplitudes become almost the same (~0.075 Å²), and the deviation is found to be the same as that for atoms with coordination 9 (0.04 Å²). Thus conclude that local coordination has less effect on the mean-square vibrational amplitude of Ag than it does on that of Cu atoms, as already reported [131]. For Ag atoms with coordination 6 (Figure 5.11.c), as in the case of Cu atoms for the same coordination, addition of more Cu atoms induces larger mean square vibrational amplitudes with a deviation of 0.1 Å² from the bulk value.
Figure 5.11 Mean square vibrational amplitudes of Ag atoms with coordination (a) 9 (b) 8 and (c) 6 and elemental environment

Note that mean-square vibrational amplitude being a local quantity, changes dramatically from one atom to another in NP. Experiments, on the other hand, would be more amenable to the measurements of a global quantity that reflects an averaged value such as the Debye temperature. It is related to the mean-square vibrational amplitude as expressed in equation 5.6. We have calculated the Debye temperature of each NP using the calculated mean-square vibrational amplitudes of all the atoms in each NP.
Figure 5.12 Average Debye temperatures of the NPs as a function of Cu-atom content

The calculated average Debye temperatures of each NP are summarized in Table C16 in Appendix C: Chapter 5, along with a breakdown into contributions from Cu and Ag atoms. In Figure 5.12, we have also plotted these average Debye temperatures for each NP as a function of Cu-atom content in the NPs. The upper and lower limits of the average Debye temperature are found to be 69 K and 88 K, respectively. For Cu (Ag) atoms, the average Debye temperatures are found to be in the range of 86 K–111 K (60 K–71 K), which is about one-third of the Debye temperature of the corresponding bulk atom. From the figure, it is clear that the average Debye temperature of the NPs does increase with the increase of Cu atoms. The increase is, however, not linear. In order to examine the critical role of the atomic coordination in controlling local dynamics, we have also calculated the Debye temperatures for Cu and Ag atoms with coordination ranging from 6 to 12.
We will present the Debye temperatures only for the atoms in Cu$_{34}$ and Ag$_{34}$ NPs. The Cu atoms with coordination 12, 9, 8 and 6 have Debye temperatures of 103 K, 83 K, 81 K–96 K, 73 K–87 K, respectively. The Debye temperatures for the atoms with coordination 8 and 6 have upper and lower limits reflecting the variations in bonding for these particular coordination. If we consider the lower limit in the temperature range, note that the same correlations are found as predicted for the vicinal surfaces [132]. For Ag atoms in the NP, the Debye temperatures are 87 K, 75 K, 72 K and 62 K for coordination 12, 9, 8 and 6, respectively. The correlation between the Debye temperature and coordination observed for Cu atoms is also present for Ag atoms.

From Table C16 in Appendix C: Chapter 5, it is worth noting that there is a sharp change in the average Debye temperatures for Ag$_{29}$Cu$_5$ and Ag$_{28}$Cu$_6$ NPs. Examining the individual contributions to the Debye temperature from the Cu and Ag atoms, we find that the contribution from the former ranges from 104.5 K to 110.4 K for Ag$_{28}$Cu$_6$, while it ranges from 84.5 K to 100.2 K for Ag$_{29}$Cu$_5$. The average contributions from the Cu atoms then become 107.9 K and 89.9 K for Ag$_{28}$Cu$_6$ and Ag$_{29}$Cu$_5$, respectively. The average Debye temperatures of the Ag atoms are found to be 71.0 K and 68.9 K, nearly the same as for Ag$_{28}$Cu$_6$ and Ag$_{29}$Cu$_5$, respectively. The calculated dip in the average Debye temperature thus arises mainly from the individual contributions of the Cu atoms in these NPs. The structural motifs of these two particles are different from each other, and neither is symmetric. Interestingly, the Cu atoms in the Ag$_{28}$Cu$_6$ have coordination 12, while those in Ag$_{29}$Cu$_5$ the coordination varies from 10 to 12.
5.4 Conclusions

A detailed study of the family of Ag<sub>n</sub>Cu<sub>34-n</sub> NPs reveals interesting trends “upon alloying” in bond-lengths, vibrational dynamics and thermodynamics. Through arguments based on local coordination and elemental environment, these characteristics can be systematically rationalized. In particular, the average bond length for Cu atoms is found to depend strongly on both coordination and elemental environment. It increases monotonically by 0.25 Å as the number of Ag neighbors varies from 0 to 12. However, these variations in the average bond length are less pronounced for Ag atoms. For the Cu atoms with low coordination (6 and 8), a global analysis of the bond length reveals two regions (with short and long average bond length). This bi-modal behavior, which goes beyond coordination and direct environment, is the subject of a second degree environmental analysis (second neighbors) and will be subject of future calculations.

We find that increasing the Cu atom ratio to Ag atoms (alloying) induces systematic stiffening in the force field that yields a shift towards high frequencies in the VDOS. On the other hand, the low-frequency end of the spectrum is found to be similar to that of single-element NPs, which shows a linear dependence on the frequency. The (total) vibrational free energy of the family of Ag<sub>n</sub>Cu<sub>34-n</sub> NPs increases monotonically as the number of Cu atoms in increases. The effect of coordination on the excess vibrational free energy shows qualitative similarities to the atoms on vicinal surfaces, and in single-element NPs, though substantial quantitative differences appear. The local vibrational mean-square amplitudes present strong correlations with coordination. We also find that the calculated average Debye temperatures of these NPs increase with the number of Cu
atoms, but this change is not linear. Also, the Debye temperature of Cu (Ag) atoms is found to be about one-third of the corresponding bulk atom as compared to a ratio of two-thirds of the bulk reported for the atoms on stepped surfaces of Ag and Cu.

The analyses of the vibrational and thermodynamical properties of these nanoalloys make it possible to reveal the effect of progressive alloying. Understanding these effects is important when one wants to use these alloys as building blocks of proposed functionalized materials with unique properties.
We report results of first principles calculations of the electronic structure of the AgₙCu₃₄₋ₙ bi-metallic nanoparticle family where n=0, 1, …, 34. We find that alloying of the pure Ag cluster with a few Cu atoms displays substantial changes in the electronic structure but the reverse is not the case when few Ag atoms are substituted in pure Cu clusters. We find that local environment control the length and the strength of the Cu-Ag bonds. The Cu atoms, which form the core display shortened bond length and present above 1 eV shift in their d-band center. The HOMO-LUMO gap for the set of nanoalloys falls in three regions: 0.19 eV to 0.31 eV, 0.40 eV to 0.57 eV, and 0.73 eV to 0.88 eV. For several nanoparticles slight change in composition may thus lead to a change of about 600 meV in the gap. The highest gap is found for the most symmetric nanoparticle Ag₁₇Cu₁₇. We present a systematic analysis of the changes in Cu-Ag, Ag-Ag and Cu-Cu bond lengths and hybridization with composition to understand their effect on the HOMO-LUMO gap and other characteristics of the nanoparticles. We find that the atoms with distinct coordination and bond length distribution mostly control the electronic structure of these nanoparticles.

6.1 Introduction

NPs -- aggregates of metal atoms of nano size -- have been the subject of intensive investigations both experimentally and theoretically from a variety of viewpoints [243].
For such finite-sized alloy structures, the physical and chemical properties have been shown to be size- and composition-dependent [244]. Owing to their size nanoclusters present peculiar thermal, optical, magnetic and electronic properties that are qualitatively different than those of their constituent parts -- whether atoms or molecules -- from those of macroscopic pieces of matter. Size dependence brings the possibility of controlling the nanocluster properties by modifying the formation processes in order to generate novel materials with properties controlled and adjusted in accordance with specific demands. For instance, it has been shown that the strong size dependence of the NPs induces peculiar behavior of metal to non-metal transition [245], magnetic to non-magnetic transitions, red or blue shift of optical gaps [3], and catalytic activity [4]. Some of these systems have been shown to have unusual stability from the energetic, electronic and thermodynamical points of view, indicating the possibility of using them as building blocks for cluster-assembled materials [5]. These features open up applications in such areas as catalysis, bio-medicine and electronic devices, to name a few [246].

The unusual properties of the mono-metallic systems originate from their finite size, the enhancement of surface-to-volume ratio, and quantum effects. For such nanoscale systems, understanding in detail the interplay between structure and chemical order is important for controlling and adjusting their properties. Achieving such understanding, however, requires atomically-resolved insights into their geometric structure, vibrations, thermodynamics and the electronic structures that are not trivial to obtain. Recent experimental and theoretical studies have provided contributions to the understanding of the role played by the size of these systems on the vibrational, thermodynamical and electronic structure properties [8, 18]. These studies have shown
that nanocrystals present two distinguished features in their VDOS: i) a higher population of the low frequency modes and ii) a high frequency tail extending beyond the bulk band. A theoretical study [8] has pinpointed the origin of these high frequency tails to be originating from the global shrinking, while the low frequency part of the spectrum is governed by surface atoms. A recent study has also showed that the thermodynamics of the mono-metallic NPs are different from those of single atoms or molecules [10].

When two or more elements of different radii are composed into a NP -- as in the case of nanoalloys -- that difference affects the way the atoms are arranged. The resulting picture is far more complicated than that for single-element NPs since many equilibrium structures are reported ranging from quasicrystals, amorphous crystals to well-ordered super lattices, onion-like multi-shell structures and core-shell arrangements [237, 247, 248]. Recent studies on bi-metallic NPs consisting of transition metals indicate that an icosahedral structure is preferred over all others [12, 25].

Recently, Rossi et al have used genetic optimization (GO) technique to study several bi-metallic clusters of transition metals in the size range of 30-40 atoms [13]. Their study revealed a family of the NPs whose most stable structures they characterized as core–shell polyicosahedra (pIh). In this structure, the element of smaller radius occupies the core, and the element with larger radius the shell of the NP. They [13] have studied six binary systems (Ag–Ni, Ag–Cu, Au–Cu, Ag–Pd, Ag–Au, and Pd–Pt) to reveal the effects of size mismatch, the tendency for alloying (as compared to the bulk phase), and the tendency for surface segregation. Among these systems, the most interesting is perhaps the Ag-Cu system, owing to the fact that these two elements have a wide miscibility gap [234] and have the largest misfit. Although Ag-Cu clusters have not been
extensively studied experimentally, there are indications that confirm the core-shell structure in which Cu atoms form the core surrounded by Ag atoms shell [249]. Their calculations using the 34-atom Ag$_n$Cu$_{34-n}$ NP family have revealed that this bi-metallic family of the NPs is energetically, thermodynamically (high melting points) and (some) electronically stable (large HOMO-LUMO gaps) [250]. This study is the first systematic study concerning the structure and the stability of the entire family of the bi-metallic nanoalloys.

It is not yet established how the interplay between the chemical order and size controls the properties of NPs. In the case of bi-metallic NPs, one faces an additional complexity that is brought into play by composition effects. The properties of the bi-metallic NPs are dictated by the size, ratio between the number of atoms of the species, and even the relative positions of the atoms within the whole. Thus their properties are expected to be quite different from those of their single-element counterparts. The core-shell NPs in particular have been under investigation since properties such as optical [251], catalytic [252], thermodynamical [88, 253, 254], magnetic [255] and electronic can be tuned by controlling the chemical composition of the core, the shell and the interface. These studies have shown that the catalytic activity of the bi-metallic NPs is enhanced as compared to that of the mono-metallic NPs. The core-shell structures are particularly economic owing to the fact that alloying with less expensive catalyst metal -- such as Pd and Pt alloyed with Co, Cu, and Ni (occupying the core) -- reduces the waste during reaction.

A recent DFT study concerning the electronic and magnetic properties of Ni$_{3n}$Al$_n$ NPs (with n=1,..8) reports that magnetic moment per atom in these clusters is
significantly enhanced with respect to the bulk [17]. It shows that the distribution of the magnetic charge is inhomogeneous, and depends on the number of Al and Ni neighbors. There is also charge transfer observed from Ni to Al. The authors find that the binding energy per atom increases (approaching the bulk cohesive energy) as n increases. Increase in the size of the clusters also affects the HOMO-LUMO gaps (large clusters have shown to have metallic character). Although this study has revealed the size effect on the properties, direct information regarding the composition effects is not transparent from their calculations. The same conclusions can be derived from the recent DFT study for (CoRh)ₙ NPs [18]. Another study for the electronic and magnetic properties of CoPd nanoclusters (of the sizes 7, 13, 19, 23, and 26 atoms and varying stoichiometry) has revealed that magnetic moment increases with Co concentration independently of cluster size [19]. It also shows that metallicity decreases almost monotonically as the Co concentration increases. For transition-metal NPs, a recent study has reported findings on the structural and chemical properties of Pt₁₂₋ₙCuₙ NPs (with n=0,1,…,12) [15]. It is found that the electronic and magnetic properties depend on the ratio of the Cu atoms (odd or even). The magnetic moment and the hardness of the NPs have an oscillatory dependence as a function of even or odd number of Cu atoms. Their analysis of the reactivity reveals that there is an important interplay between the structure and the reactivity. A recent DFT study [241] on the electronic properties of a particular NP from the 34-atom Ag-Cu NP family revealed the importance of understanding the bond strength hierarchy for the stability of this given composition. Although these studies provide key insights into the composition effects on the physical and chemical properties of the bi-metallic NPs, there is more to be explored.
In the present study, we have thus undertaken a systematic study of the electronic structure of fixed size (34-atom) \( \text{Ag}_n\text{Cu}_{34-n} \) NP family with the aim in revealing the effect of composition in controlling the electronic structure. The geometric structures are obtained from an earlier study at which GO optimization is performed to determine the global minimum energy structures of these alloys. The primary objective of our study here is to understand the influence of the relative concentration of Ag and Cu atoms on the geometric, electronic and chemical properties of the 34-atom Ag-Cu NPs family. The relative stability analysis is carried out by examining the excess energy and second difference in energy. The electronic structure properties are revealed by analyzing the electronic DOS (for tracing hybridized states), the position of the center of the d-states (for reactivity purposes), HOMO-LUMO gaps (for metal to non-metal transition) and charge density distributions.

The details of how the chapter is organized are given in the results and discussion session.

### 6.2 Details of Calculations

The electronic structure of bi-metallic \( \text{Ag}_n\text{Cu}_{34-n} \) NP family is obtained using DFT [48] implemented in the VASP code [171], which performs a self-consistent density functional calculation to solve the Kohn-Sham equations. For the exchange correlation functional, we have employed Perdew-Wang (PW) functional in GGA approximation [78]. The kinetic energy cut off is set to 273 eV, and for comparison purposes, we have also performed the calculations for some NPs using higher energy cut off (about 400 eV). We construct a cubic supercell with a side length of 21 Å. The NP is located inside this
cubic supercell. The size of the cubic cell makes us to ensure that as a result of periodic boundary conditions, atoms in the NP do not interact with their images; therefore the NP can be treated as isolated. The structural optimization is carried out using CG algorithm [91] that minimizes the total energy as a function of atomic positions. The atomic positions are all relaxed without any symmetry constraint until the forces on them are about 1x10^{-3} eV/Å. Integrations over BZ is obtained using one k-point.

6.3 Results and Discussion

The first section extracts the effect of alloying on the properties of the respective NPs. The method is “global”, in that the properties of each NP are systematically compared with those of all others in the series beginning with one single-element ending with the other NPs. The properties of focus on in Section 6.3.1 are geometric structure of the NPs, coordination distribution of the atoms, bond lengths between the atoms, and energetic stability of the NPs. As we shall see in the next subsection studying how the first three properties differ in each alloyed NP from the others in the series provides a basis for understanding the diversity in their electronic properties. To compare the effect of composition on energetic stability, we calculate and compare the binding energy per atom in each NP with a view towards seeing how addition of a foreign atom modifies the strength of bonding in these finite-sized systems. Extending an earlier analysis [235], we now calculate excess energy and second difference in energy to determine energetically the most stable NP (i.e that is at the minima of the excess energy and the maximum of the second difference in energy). In Sections 6.4-6.4.1, we address the effect of progressive alloying on the electronic densities of states (DOS), and examine how it relates to the
changes in elemental environment and the position of the center of the d-states for each individual atom. In Section 6.5, we turn to the effect of progressive alloying upon the relative reactivity of the NPs. We begin by comparing the \textit{averaged} center of the d-states for each element in each bimetallic NP with the center of the d-states for each of the two single-element NPs. Next in Section 6.6 we present the HOMO-LUMO gap for each NP and examine the effect various properties discussed so far in controlling these gaps. We will also show how, among the various properties discussed so far, it is the composition and the corresponding shape that control the diversity in these gaps. The global analysis of properties is helpful in determining the relative differences between the compositions. These analyses enable us to single out those NPs with properties of special interest. As we shall see later in Section 6.4, however, the differences observed in the electronic structure can be understood only if the properties of each atom are studied. Detailed analysis of the properties of these atoms helps us to extract common trends in each NP. But these extensive analyses produce a huge amount of data, it is not reasonable to discuss individually the properties of each atom in each NP. The analyses for sample NPs, the selection of which is described below, are presented in Section 6.3.1. The center of d-band, coordination distribution and the average bond lengths for each atom in each NP in the family are provided in Figures D.1 to D.35 in Appendix D: Chapter 6. In Section 6.7, we also present much deeper local analyses for the most symmetric NP, namely Ag$_{17}$Cu$_{17}$. 
6.3.1 Geometric Structure, Coordination Distribution, Bond Lengths, Formation Energies and Stability

There has been great interest in late transition metal alloys owing to their possible variety of applications ranging from catalysis to optics. Revealing the key parameters that control the properties of single-element NPs is somehow established as most of the studied cases for both magnetic and metal clusters have proven that the correlations among size of the particle, coordination of atoms and quantum effects are sufficient for understanding overall properties. For instance, coordination alone can be used to explain the differences in reactivity for atoms in environments, such as steps and kinks [256]. However, for bi-metallic alloys, this single parameter is far from being sufficient since the presence of a single foreign atom and even its location introduce a new dimension into the analysis, namely the elemental environment. Hence, the electronic structure of these alloys is controlled by the interplay between coordination and the elemental environment of the atoms in them.

As a start in the analysis, we first focus on examining the geometric structure of the NP family (Figure 6.1). From the whole family, we select to present the details of some of the NPs starting from the single-element Ag (Ag₃₄) NP to the single-element Cu (Cu₃₄) NP (Figure 6.2). The choice in presenting these specific NPs is not random but based on the results of the overall analysis. One of our criteria is based on the HOMO-LUMO gaps. As we will discuss later in Section 6.6, these gaps fall into three regions from which in Figure 6.2 we illustrate the NPs belonging to each group. A closer look into the structure of these alloys shows that single-element NPs (Figures 6.2.a and 6.2.l) do not have any particular symmetry. The addition of Cu atoms creates the core-shell
structure [167, 235, 237] in which the Cu atoms occupy the core while the Ag atoms form the shell. Among all NPs, only two, namely Ag$_{27}$Cu$_7$ (Figure 6.2.c) and Ag$_{17}$Cu$_{17}$ (Figure 6.2.f), have perfect mirror symmetry. The former is composed of five outer Ag rings (five atoms each), one inner Cu ring (consisting of five atoms) and a chain of two Ag terminal atoms and two core Cu atoms. The latter is made of three Cu rings (five atoms each), three Ag rings (five atoms each) and a chain of two Cu core atoms and two Ag terminal atoms. For Ag$_{27}$Cu$_7$, all the Cu atoms are inside the core, covered by the Ag shells, while for Ag$_{17}$Cu$_{17}$, some Cu atoms are beyond the core of the NP. It is worth noting that since both NPs have mirror symmetry, there are six non-equivalent atoms, the properties of the remaining atoms can be characterized by studying only these six. As we proceed in the analysis towards Cu-rich NPs in the family (Figure 6.2.g-l), one sees that core-shell structure is maintained for some NPs with completely closed shells, while for some others, the shell becomes incomplete (Figures 6.2.h, 6.2.j and 6.2.k). For these Cu-rich NPs, the shell becomes a mixture of Cu and Ag atoms. As we shall see in later sections that the geometric structure of these NPs and relative positions of its components are the key factors in shaping their electronic structure and chemical reactivity.
Figure 6.1 The structure of all the NPs in the $\text{Ag}_n\text{Cu}_{34-n}$ family
As noted above, changes introduced to NP’s electronic structure originate from the interplay between the coordination and elemental environment of the atoms in them. Before discussing the effect of elemental environment let us first examine the number density (a measure to reveal the dominant coordination) for Cu and Ag atom’s coordination in all NPs. In Figures 6.3.a and 6.3.b we plot the number density as a function of the coordination for Cu and Ag atoms, respectively. The figures reveal that for Cu atoms coordination 12 predominates, while for Ag atoms, coordination 6 is dominant. The number density reflects the core-shell structure of some of the NPs in which the small atom (Cu) occupies the core (where they are highly coordinated), while the large atom (Ag) form the shell (where fewer nearest-neighbors are available). That atoms with coordination 9, 8 and 6 are also present in the NPs points the presence of (111) and (100) facets and kinks. As we shall see later that highly coordinated core atoms...
show distinctive features in their electronic properties as compared to those for the bulk and low-coordinated atoms.

![Graph showing number density versus coordination number for Cu and Ag atoms.](image)

**Figure 6.3 Number density versus coordination number for a) Cu and b) Ag atoms**

The atoms in these NPs possess diverse coordination number and elemental environment; hence lead hierarchy in their bond lengths (Cu-Cu, Cu-Ag and Ag-Ag).
This hierarchy is expected to induce dissimilarities in the electronic structure owing to the fact that the degree of bond length contraction or expansion controls the degree of hybridization between the states of the two elements. We first analyze the effect of the Ag-atom concentration on the average bond lengths for each NP. For the single-element Cu NP (Cu\textsubscript{34}), the average bond length between the atoms is found to be 2.52 Å, while for Ag NP (Ag\textsubscript{34}), it is 2.82 Å. As expected, for the bi-metallic NPs the average bond lengths show a monotonic increase with the increase of Ag-atom concentration. We also examine the changes in the average Cu-Cu, Cu-Ag and Ag-Ag bond lengths in each NP.

In Figure 6.4.a we plot the change in each of these bond lengths with the increase in Ag-atom concentration. As seen from the figure, the average Cu-Cu bond length is almost the same, ranging from 2.53 Å to 2.55 Å with the exception of Ag\textsubscript{32}Cu\textsubscript{2} NP, for which the bond length is 2.69 Å. In this special case, both Cu atoms are highly coordinated (12) and have only one Cu atom to bond to. We also find the Cu-Ag bond length to be almost the same for each NP, ranging between 2.68 Å and 2.79 Å. The shortest average Ag-Ag bond length is 2.84 Å (for Ag\textsubscript{34} NP), while the largest bond length is 2.99 Å for the NPs, which consist of 11, 12, 13, 16 and 17 Ag atoms. In Figure 6.4.b, the average coordination of both Cu and Ag atoms is plotted as a function of Ag-atom concentration in the NPs. Notice from the figure that the increase in the number of Ag atom yields monotonic increase in the average coordination of Cu atoms up to Ag\textsubscript{27}Cu\textsubscript{7} NP. The increase in the average Cu atom coordination is understandable by the fact that when Ag to Cu ratio is high the Cu atoms are further embedded in the core that leads increase in their average coordination. Although the average coordination of the Ag atoms increases as the number
of Ag atoms increases in the NPs, especially for the Ag-rich NPs, nevertheless their average coordination does not vary as sharply as that of Cu atoms.

This global approach used here, however, gives a picture based only on the average coordination and bond lengths. Coordination and elemental environment of each atom in the NPs are diverse that should lead to strong deviation in their electronic structure. Hence, these key properties eventually need to be investigated for one atom at a time manner. We will show later in the text that some particular atoms (with distinctive coordination and bond lengths distribution) affect most the electronic structure of the NPs.
Figure 6.4  

a) Average Cu-Cu, Cu-Ag and Ag-Ag bond lengths versus Ag-atom concentration and  
b) Average coordination of the Cu and Ag atoms versus Ag-atom concentration  

An earlier study performed using model potentials [235] reported that for a family of NPs, the most stable structures are obtained at compositions corresponds to a perfect core-shell plh. In order to pinpoint those NPs with the most energetically stable
structures, it examined the relative stability of NPs of different sizes and compositions by monitoring the quantities $\Delta$ and $\Delta_2$ adapted to binary clusters. $\Delta$ is the excess energy with respect to $N$ bulk atoms divided by $N^{2/3}$ (the approximate number of atoms exposed at the surface of the alloys):

$$\Delta = \frac{E_{GM}^{N,N_1} - N_1^1 \varepsilon_{coh}^1 - N_2^2 \varepsilon_{coh}^2}{N^{2/3}}$$

(6.1)

where $N_1$ and $\varepsilon_{coh}^1$ are the number and the bulk cohesive energy of Ag atoms, $N_2 = N - N_1$ and $\varepsilon_{coh}^2$ are the same quantities for Cu, and $E_{GM}^{N,N_1}$ is the global-minimum energy at a given composition. One criterion used to highlight the most stable structures is that these structures have the lowest $\Delta$ values. A second criterion is that the most stable NPs are those that exhibit the maximum of the second difference in energy ($\Delta_2$) – global minimum energy with respect to that of the (two) NPs of the same family and immediately nearby compositions. $\Delta_2$ is expressed as:

$$\Delta_2 = E_{GM}^{N,N_1+1} + E_{GM}^{N,N_1-1} - 2E_{GM}^{N,N_1}$$

(6.2)

For this particular NP family ($\text{Ag}_n\text{Cu}_{34-n}$), they reported Ag$_{27}$Cu$_7$ to be the most energetically stable. This particle indicates a dip for the excess energy ($\Delta$) and a peak for the second difference in the energy ($\Delta_2$). They supplemented their model potential based simulations with DFT calculations for this particular NP and for a couple of NPs at some distance of either side of it ($\text{Ag}_{12}\text{Cu}_{22}$ and $\text{Ag}_{17}\text{Cu}_{17}$) [235].

In order to provide a more comprehensive basis for evaluating their results, we have carried out DFT calculations for $\Delta$ and $\Delta_2$. For the entire family of NPs, in Figure
6.5.a, we plot the difference between the excess energy ($\Delta$) and minimum excess energy ($\Delta_m$) as a function of Ag-atom content in the NPs. In accord with their results [235], our calculations also show that $\text{Ag}_{27}\text{Cu}_7$ shows a dip in the excess energy. The overall dependence of the excess energy on the number of Ag atoms is similar to their model potential results. In Figure 6.5.b, we plot the second difference in energy ($\Delta_2$) and find that $\text{Ag}_{27}\text{Cu}_7$ correspond to the maximum. Here, too, the systematic DFT calculations are in agreement with their model potential results. We encounter similar qualitative behavior with their results with some quantitative differences that might originate from the fact that the total energies obtained using DFT might be slightly different from those obtained using their model potentials.
Figure 6.5  

**a)** Excess ($\Delta$, in eV) and minimum excess energy ($\Delta_m$) difference versus Ag-content and **b)** Second difference in energy, $\Delta_2$ (in eV) versus Ag-atom content

In the context of energetic stability, in addition to the excess energy ($\Delta$), it is also important to examine the formation energy per atom, which is a measure for the cohesive energy of the NP. In order to determine the average strength of the bonds, we have calculated the formation energy per atom ($E_{\text{form}}$) in each NP which is expressed as:
where the first term in the right side of the equation is the total energy of the NP, \( N_1 \) and \( N_2 \) are the number of Ag and Cu atoms, and \( E(\text{Ag}_{\text{free}}) \) and \( E(\text{Cu}_{\text{free}}) \) are the energies of the isolated Ag and Cu atoms, respectively. In Figure 6.6, we plot the absolute value for the average formation energies per atom in each NP as a function of the number of Ag atoms in the NPs.

![Figure 6.6 Average formation energy (absolute value) versus Ag-atom content](image)

As shown in the figure, the formation energy per atom decreases monotonically from 2.88 eV (for Cu_{34} NP) to 2.09 eV (for Ag_{34} NP) with the increase in the number of Ag atoms from 0 to 34. This is in qualitative agreement with the results obtained using model potentials [235]. The increase in Ag to Cu ratio in the NPs weakens the average bond strength leading to a decrease in binding energy per atom. This originates from the fact
increase in the number of Ag atoms decreases the number of Cu-Cu bonds that is replaced by the formation of Cu-Ag and Ag-Ag bonds whose strength are relatively low. This is attributed to the fact that cohesive energy of Ag is much smaller than that of Cu. For Ag$_{27}$Cu$_{7}$, one of the two most symmetric NPs, we find the formation energy per atom to be 2.34 eV, which is similar to that reported by an earlier study [241]. The authors of this study also reported that the average formation energy of this NP is smaller than the bulk cohesive energies of Ag, Cu, and than those of Ag$_3$Cu and Cu$_3$Ag. At this point we turn to the formation energies of related systems for comparison. The calculated cohesive energies for bulk Ag and Cu atoms are 2.73 eV and 3.73 eV, respectively. The average formation energies per atom in Cu$_{34}$ and Ag$_{34}$ NPs are much lower than the cohesive energies of Cu and Ag bulk atoms, respectively.

6.4 Electronic Densities of States (EDOS)

The density of the electronic states can be used to reveal coordination of atoms, their bond lengths with neighbors, and elemental environment. It is well established that the change in coordination of atoms and bond lengths can be read out from their electronic DOS. For instance, for the transition metals with more than half-filled d-states, it is known that the atoms with lower coordination than that of their bulk counterparts present d-band narrowing along with an increase in intensity to maintain a fixed occupation number. For high-coordinated atoms, d-band becomes broader relative to that for low-coordinated atoms. Change in coordination re-arranges bond lengths between neighbors also reflected in the distribution of the DOS [241]. Moreover, the presence of different element species in the bonding introduces a new dimension to the analysis of
electronic DOS. In such cases, hybridization becomes an additional factor in broadening/narrowing of the bands. Indeed, the ratio between the two element species leads expansion and/or contraction of the various types of bond lengths, thus affecting the electronic DOS. The patterns in such change reveal the effect of progressive alloying.

### 6.4.1 Alloying Effect on the Electronic Densities of States (EDOS)

In this section we will present the results of the changes introduced to the electronic DOS of sample NPs by progressive alloying. We will do that through a comparison of the electronic DOS of the bi-metallic NPs with those of the single-element NPs. In order to trace the underlying reasons for the observed differences in their electronic DOS, we will also discuss the coordination distribution of the atoms, the average bond lengths of each type and the position of the center of the d-states, owing to the fact that the center of the d-states of the atoms can reflect the differences in their coordination, bond and binding strength of the atoms as well as the position of the HOMO level. The first step in the analysis must be to understand the non-alloyed NPs at the extreme ends of the family series. The aim is to develop an understanding of the effect of alloying on the electronic DOS to reveal the strength of hybridization between the states of Ag and Cu. In order to obtain the electronic DOS of these NPs from *ab-initio* electronic structure calculations, the states are broadened by using Gaussian functions of width 0.2 eV. In Figure 6.7.a-e, we plot the total electronic DOS of both single-element NPs, namely Cu$_{34}$ and Ag$_{34}$. In Figures 6.7.a-b, we compare the contributions from d and s-states to the total electronic DOS of Ag$_{34}$ and Cu$_{34}$ NPs, respectively. The figures make it clear that the total electronic DOS is mostly d-character and so that the contribution
from the s-states are negligible. Hence, further discussion and comparisons with the electronic DOS of bulk Cu and Ag atoms will be based on the d-states. In Figures 6.7.c-d, we compare the electronic DOS of the single-element Ag$_{34}$ and Cu$_{34}$ NPs with that of bulk Ag and Cu atoms, respectively. Notice from Figure 6.7.c that the distribution of the d-states for Ag$_{34}$ is strongly narrowed relative to that of Ag bulk and show increase in intensity to keep occupation number fixed. This originates from the fact that the average coordination of the atoms in Ag$_{34}$ NP is much less than that of bulk Ag atom. For Cu$_{34}$ (Figure 6.7.d), as with Ag$_{34}$, the distribution of d-states is narrowed with respect to that of Cu bulk atom, but in this case, narrowing is less enhanced. This is attributed to the fact that average coordination of the atoms in Cu$_{34}$ is larger than that of Ag$_{34}$. In Figure 6.7.e, we plot the total electronic DOS of Ag$_{34}$ and Cu$_{34}$ NPs along with their geometric structures.

For Cu$_{34}$ NP, the average coordination of the atoms is 8 (Figure 6.4.b) and the average position of the center of the d-states of the Cu atoms in the NP is at -2.31 eV. The position of the center of the d-states for these atoms is shifted (550 meV) towards lower binding energy relative to that (-2.86 eV) for the Cu bulk atom. The shift towards lower binding energy can be attributed to the fact that the majority of the Cu atoms in the NP are less than 12 coordinated, and that the average Cu atom coordination is 8. For the atoms with lower coordination than Cu bulk atom, we expect to observe band narrowing (Figure 6.7.d) that induces a shift towards lower binding energy. The average position of the center of the d-states of the Cu atoms in the NP is same as that of the Cu atoms of the (100) surface (8 coordinated). The average Cu-Cu bond length in this NP is 2.53 Å,
which is about 1.6% shorter than that of the bulk counterpart (2.57 Å) indicating stiffening of some of the bonds in the NP.

For Ag$_{34}$ NP, the average coordination of the atoms is 6 and the average position of the center of d-states is at -3.56 eV. In comparison with the position of the center of the d-states of Ag bulk atom (-4.41 eV), we find the NP’s average position of the center of the d-states is shifted towards lower binding energy (about 850 meV). Note that the shift towards lower binding energy in this case is more enhanced than that for Cu$_{34}$ NP. This can be explained by large deviation in the average coordination of Ag atoms in Ag$_{34}$ from Ag bulk atom coordination. For Cu$_{34}$, this deviation is much smaller. The coordination effect is further traceable when we compare the position of the center of the d-states of Ag atoms in this NP with that of the Ag atom of the (100) surface. We find that the center of the d-states of a (100) Ag surface atom (8 coordinated) is at -3.96 eV, which is 400 meV below (at a higher binding energy) than that for Ag atoms of the NP, indicating its larger coordination number. The average Ag-Ag bond length is 2.84 Å, which is 3.7% shorter than that of the bulk counterpart indicating even greater stiffening of some of the bonds in the NP.

In order to have a closer look into the details of the DOS, we analyze the properties of each atom in these mono-metallic NPs. For Ag$_{34}$, we plot in Figures 6.8.a-c the position of the center of the d-states, the coordination distribution and the average Ag-Ag bond lengths for each atom, respectively. Notice from Figure 6.8.a that for the majority of atoms the center of their d-states range from -3.4 eV to -3.7 eV, while for a small minority (only four) it sits at a slightly higher binding energy (-3.9 eV). A closer look into the coordination distribution shows that these four Ag atoms have the largest
coordination number (8 or 9) as compared to the remaining atoms (Figure 6.8.b). For the atoms with large coordination, as expected we find a broadening of the distribution of d-states. The average Ag-Ag bond lengths for each atom in the NP range from 2.78 Å to 2.89 Å (Figure 6.8.c). Note that these four Ag atoms also have the largest Ag-Ag bond lengths (~2.85 Å to 2.89 Å).
Figure 6.7 a) Total and partial electronic DOS of Ag\textsubscript{34}. The latter corresponds to the contribution of s and d states b) Total and partial electronic DOS of Cu\textsubscript{34} c) Comparison between the partial (d-states) DOS of Ag\textsubscript{34} and that of Ag bulk d) Comparison between the partial (d-states) DOS of Cu\textsubscript{34} and that of Cu bulk and e) Total electronic DOS of Ag\textsubscript{34} and Cu\textsubscript{34}. The figures incorporated are the geometric structure of these single-element NPs.
Figure 6.8 The Ag$_{34}$ NP

a) Position of the center of the d-states of each atom

b) Coordination distribution and

c) Average Ag-Ag bond lengths
For Cu$_{34}$, we plot in Figures 6.9.a-c the position of the center of the d-states, coordination distribution and the average Cu-Cu bond lengths. We find the position of the center of the d-states (Figure 6.9.a) to be distinctive for the atoms with large coordination. Note that for most of the atoms whose coordination ranges from 6 to 9 (Figure 6.9.b), the position of the center of the d-states ranges from -1.98 eV to -2.33 eV (Figure 6.9.a), while that of the five highly coordinated atoms (from 11 to 13) it sits at -3 eV. The position of the center of the d-states of highly coordinated atom is shifted towards higher binding energy (about 1eV) with respect to that of the low-coordinated atoms. These highly coordinated atoms also present broadening of the band relative to that for the bulk counterpart and those with low coordination. The average Cu-Cu bond lengths in the NP range from 2.46 Å to 2.62 Å (Figure 6.9.c). Among the five atoms with the highest coordination, only three have the shortest average Cu-Cu bond length (2.46 Å), while for that the other two, and is 2.54 Å and 2.60 Å, respectively. Note that those atoms with the highest coordination and the shortest Cu-Cu bond lengths sit at the core of the NPs; hence they are over-coordinated. We infer that if the number of highly coordinated atoms with short bond lengths is large in the NP, their properties may assume control over the overall properties of the NP. As we shall see, the same principle seems to hold across the spectrum of their bi-metallic cousins.

Now we examine the changes in the electronic DOS induced by the increase in Cu to Ag ratio. In Figure 6.10.a-f, we plot the total electronic DOS of the six sample NPs. For purposes of comparison, in each figure we also plot the electronic DOS of the single-element Ag$_{34}$ and Cu$_{34}$ NPs. The considerations that govern the choice of sample will be evident as we proceed.
We start with Ag\textsubscript{32}Cu\textsubscript{2} NP for which Ag to Cu ratio is the largest among the bi-metallic NP family. Figure 6.10.a shows that the presence of only two Cu atoms considerably broadens the total electronic DOS, while as a whole shifts towards higher binding energy. Recall from Figure 6.4.b that the average coordination of the Cu atoms in the NP is 12, while for the Ag atoms it is 7. The average Cu-Cu bond length is 6.3% larger than that of the Cu\textsubscript{34} NP, owing to the fact that the majority of the Cu atom neighbors are Ag. The average Ag-Ag bond length is 2.86 Å, which is about 1% larger than that in Ag\textsubscript{34}. Note also that the average Cu-Ag bond length is 2.77 Å. The average position of the center of the d-states for the Ag atoms is at -4.29 eV, while for the Cu atoms it is at -2.60 eV. The Cu atoms both in Cu\textsubscript{34} and in Ag\textsubscript{32}Cu\textsubscript{2} have the same average coordination. The shift (about 300 meV) towards higher binding energy in the position of the center of the d-states for those in Ag\textsubscript{32}Cu\textsubscript{2} may originate from the presence of large number of Ag neighbors that cause hybridization between Cu and Ag states. As compared to the Ag atoms in Ag\textsubscript{34}, the Ag atoms in Ag\textsubscript{32}Cu\textsubscript{2} present shift (above 700 meV) towards higher binding energy in the position of the center of the d-states. The underlying reason for this large shift is not transparent with examination of the average coordination and the average bond lengths and does not reveal cause for this behavior. It requires local analysis at which the properties of each atom are analyzed. We will summarize the results of this analysis in the following paragraph.

We extend the analysis to examine the characteristics of each atom in the NPs. The position of the center of the d-states of the most of the Ag atoms ranges from -3.88 eV to -4.39 eV (Figure 6.11.a). The exception occurs for the three Ag atoms whose center of the d-states is located at -4.96 eV (atoms #11 and #12) and -5.14 eV (atom #22). These
atoms are highly coordinated (11, two Cu neighbors) and are located in the core of the NP (Figure 6.11.b). The largest coordination for the remaining Ag atoms is 8; most of the atoms so situated have either one Cu neighbor or none. It is attributable that the large shift towards higher binding energy in the average position of the center of the d-states of the NP may partially be controlled by these highly coordinated atom’s electronic characteristics.
Figure 6.9 The Cu$_{34}$ NP a) Position of the center of the d-states of each atom b) Coordination distribution and c) Average Cu-Cu bond lengths
Figure 6.10 The effect of alloying on the total electronic DOS a) $\text{Ag}_{32}\text{Cu}_2$ b) $\text{Ag}_{27}\text{Cu}_7$ c) $\text{Ag}_{17}\text{Cu}_{17}$ d) $\text{Ag}_{10}\text{Cu}_{34}$ e) $\text{Ag}_7\text{Cu}_{27}$ and f) $\text{Ag}_2\text{Cu}_{32}$
We also find that the average Cu-Ag bond lengths for the atoms #11 and #12 is 2.70 Å, while for #22 it is 2.77 Å. There are many other atoms in the NP whose bond lengths are even smaller than those for these particular atoms. However, what makes these atoms different is their high coordination. The individual bond lengths between these three atoms and their neighbors vary broadly between 2.77 Å to 2.99 Å (Figure 6.11.c). The shortest Cu-Ag bond lengths for atoms #11, #12 and #22 are 2.68 Å, 2.67 Å and 2.73 Å, respectively. Although these three atoms have the same coordination number and the elemental environment, the position of the center of the d-states for atom #22 is a bit larger than it is for atoms #11 and #12. A closer look into the bond lengths shows that the average Ag-Ag bond lengths are the same, while the Cu-Ag bond length for atom #22 is slightly larger (at a higher binding energy) than those for the other two. This reflects that atom #22 has less overlap with its Cu neighbors. The shift observed in the center of the d-states of the Ag atoms originates mainly from the high coordination, as observed for some atoms in the two mono-metallic NPs.

The total electronic DOS for Ag_{27}Cu_{7} (Figure 6.10.b) reflects the strong hybridization between the Cu and Ag states. The electronic DOS broadens and presents the appearance of new states both in the higher and lower binding energy regions with respect to that for Ag_{34}. The average coordination for the Cu atoms is 12, with six or four Cu neighbors. The average coordination for the Ag atoms is 7.5, each with large number of Ag neighbors. The broadening of the band with respect to Ag_{34} can be partially explained by larger Ag atom coordination. The average Cu-Cu, Cu-Ag, and Ag-Ag bond lengths are found to be 2.54 Å, 2.71 Å, and 2.92 Å, respectively. The average position of the center of the d-states for the Cu atoms is at -2.31 eV, while for the Ag atoms it is at -
3.79 eV. In comparison to Ag$_{34}$, the center of the d-states is slightly shifted towards higher binding energy.

Figure 6.11 The Ag$_{32}$Cu$_2$ NP a) Position of the center of the d-states of each atom b) Coordination distribution and c) Average Cu-Cu, Cu-Ag and Ag-Ag bond lengths

The center of the d-states for each individual Ag atom ranges from -3.69 eV to -3.91 eV (Figure 6.12.a). The Cu atoms can be classified into two groups: atoms in the chain have the center of the d-states located at a higher binding energy than the atoms in...
the (single) ring. Note that although the Cu atoms are highly coordinated, the position of the center of the d-states does not fall into distinctive levels, as they do in Cu$_{34}$. This originates from the fact that the Cu atoms have only six and four Cu neighbors for the chain and the ring atoms, respectively (Figure 6.12.b). Even though Cu chain atoms have fewer Ag neighbors than do Cu ring atoms, the center of the d-states for the chain atoms is located below that of the ring atoms. This might reflect a stronger overlap between the Cu and Ag states for the chain atoms. Indeed, the analysis of the individual Cu-Ag bond lengths show that for the chain atoms, the Cu-Ag bond length ranges from 2.58 Å to 2.72 Å, while those for the ring atoms range from 2.58 Å to 2.78 Å, indicating that the Cu and Ag states overlap more for the chain atoms. As compared to the Cu-Ag bond lengths in Ag$_{32}$Cu$_2$, those in Ag$_{27}$Cu$_7$ reflect the presence of a larger number of Cu neighbors. Although the Cu atoms are highly coordinated, owing to the large number of Ag neighbors, the Cu-Cu bond length (Figure 6.12.c) is not dramatically shortened, as was the case for some atoms in Cu$_{34}$. 

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Figure 6.12 The Ag$_{27}$Cu$_7$ NP a) Position of the center of the d-states of each atom b) Coordination distribution and c) Average Cu-Cu, Cu-Ag and Ag-Ag bond lengths

The Ag atom coordination ranges from 6 to 9 in this NP. The first group atoms are coordinated 6 with one Cu neighbor. The center of the d-states is at -3.69 eV, which is shifted towards lower binding energy with respect to those for the second group atoms (9 coordinated with three Cu neighbors). The higher coordination of the second group atoms shows broader band than that for the first group; hence the center of the d-sates is located
below (shifted towards higher binding energy) that for the first group. The center of the d-states for the third group atoms (8 coordinated with two Cu neighbors) is at the same position as that for the first group atoms. The average Cu-Ag bond lengths are 2.58 Å, 2.76 Å and 2.71 Å for the first, the second and the third group atoms, respectively. The shortest Cu-Ag bond length for the first group and the largest for the second group atoms may be the reason behind the difference in their center of the d-states owing to the fact that short Cu-Ag bond length signals more overlap between the Cu and Ag states, while the large implies the opposite.

In Figure 6.10.c we present the total electronic DOS of Ag_{17}Cu_{17} that shows shift towards the lower binding energy, indicating the increase in Cu to Ag ratio. The figure shows that there is a splitting in the total electronic DOS into two regions, each of which carriers the characteristics of Cu and Ag, reflecting the hybridization between Cu and Ag states. The Cu atoms can be classified into two groups; the atoms that are 9 coordinated (outer ring atoms) and those with 12 coordinated (chain and inner ring atoms [Figure 6.13.b]). The NP has three Cu rings. Among the highly coordinated atoms, the atoms at the chain have large number of Cu neighbors. The inner ring atoms have less number of Cu neighbors than those of the chain atoms. The average coordination number for the Cu atoms is 10 (Figure 6.4.b), while for the Ag atoms it is 6. Note that the NP has three types of Ag atoms; 5 coordinated (outer Ag ring atom, three Cu neighbors), 6 coordinated (Ag chain atom, six Cu neighbors) and 8 coordinated (inner Ag ring atom, four Cu neighbors). The average center of the d-states of the Cu atoms is at -2.17 eV, which is shifted (700 meV) towards lower binding energy relative to that for Cu bulk atom, indicating that the majority of Cu atoms are less than 12 coordinated. For the Ag atoms,
the position of the center of d-states is located at -3.79 eV, which is also lower (600 meV) than that for the Ag bulk atom (Figure 6.13.a). The average Cu-Cu, Cu-Ag, and Ag-Ag bond lengths are 2.55 Å, 2.71 Å, and 2.98 Å, respectively.

The analysis of each individual atom properties shows that since the NP has highly coordinated Cu atoms, the trend in their center of the d-states is similar to that obtained for Cu$_{34}$. For the highly coordinated Cu chain atoms (12 coordinated with eleven Cu neighbors), the average Cu-Cu bond length is 2.48 Å (3.5% shorter than that in the bulk). The stiffening of this particular bond indicates that there is a local shrinkage in the core of the NP. The average Cu-Ag bond length for the chain atom is also short, 2.51 Å (Figure 6.13.c), reflecting strong overlap between Cu and Ag states. The position of the center of the d-states of the chain atom is at -3.13 eV (Figure 6.13.a), which indicates shift towards higher binding energy with respect to that for Cu bulk atom. This reflects the shrinkage of the Cu-Cu bond lengths owing to the high coordination and the presence of large number of Cu neighbors. The d-band for these atoms broadens as mentioned earlier for Cu$_{34}$. For the inner ring atoms (12 coordinated with eight Cu neighbors), we find the average Cu-Cu bond length to be 1.6% shorter than that for the bulk. The position of the center of the d-states (-2.46 eV) is shifted towards lower binding energy relative to that for Cu bulk atom. The average Cu-Ag bond length is large (2.78 Å), indicating less overlap between Cu and Ag states even though almost half of the neighbors are Ag atoms. For the outer Cu ring atoms, we find the d-states to be centered at -1.83 eV, shifted towards lower binding energy with respect that for the bulk atom, owing to their low coordination.
The Ag atoms in the NP even though have different coordination and elemental environment, the position of the center of the d-states is found to be similar to each other (deviation is at most 200 meV). This indicates that in such composition their properties are not significantly affected by coordination and elemental environment. Their Cu-Ag bond lengths range from 2.67 Å to 2.76 Å, most of which can be understood by examining coordination and the number of foreign atom neighbors. The average Ag-Ag bond length is 1% larger than for the bulk and same for each Ag atom (Figure 6.13.c).

Figure 6.13 The Ag$_{17}$Cu$_{17}$ NP a) Position of the center of the d-states of each atom b) Coordination distribution and c) Average Cu-Cu, Cu-Ag and Ag-Ag bond lengths
The electronic DOS for $\text{Ag}_{10}\text{Cu}_{24}$ is presented in Figure 6.10.d. In comparison to $\text{Ag}_{17}\text{Cu}_{17}$, the DOS carries the characteristics of Cu atoms more than those of Ag. The NP has both high- and low-coordinated Cu atoms ranging from 5 to 14 (Figure 6.14.b). These highly coordinated Cu atoms also occupy the core (either at chain or at the ring); hence have large number of Cu neighbors (ranging from eight to thirteen). Two of the highly coordinated Cu atoms sit at the chain and have the highest number of Cu neighbors. The others with high coordination are located at the inner Cu ring and their neighbors consist of eight Cu atoms. We find the average coordination of the Cu atoms in the NP to be 9, while for the Ag atoms it is 6. The average Cu-Cu, Cu-Ag and Ag-Ag bond lengths are 2.57 Å, 2.77 Å, and 2.96 Å, respectively. The average position of the center of the d-states of the Cu atoms is at -2.31 eV, which is shifted towards lower binding energy relative to that for Cu bulk atom. For the Ag atoms, we find the center of the d-states to be located at -4.18 eV, which is slightly shifted towards lower binding energy with respect to that for Ag bulk atom.

Highly-coordinated Cu chain atoms show similar trend for the position of the center of the d-states obtained those for $\text{Cu}_{34}$ and $\text{Ag}_{17}\text{Cu}_{17}$ NPs. We find the center of the d-states to be shifted towards higher binding energy (Figure 6.14.a); especially for the atom #20 (chain atom). Let us note that this atom is the only Cu atom in the NP with no Ag neighbor. The center of the d-states for the other highly coordinated atoms (with large number of Cu neighbors) also shifted towards higher binding energy. For the atoms #11 and #20 (with the highest position for the center of the d-states), we also find that they have the shortest average Cu-Cu (2.49 Å and 2.47 Å) and Cu-Ag (2.57 Å and N/A) bond lengths, respectively (Figure 6.14.c). As shown for $\text{Cu}_{34}$ and $\text{Ag}_{17}\text{Cu}_{17}$, high coordination
and large number of Cu neighbors for the Cu chain and Cu inner ring atoms are the key factors for the observed distinctive values for the center of the d-states. We also note that the other high coordinated atoms in the NP have either Cu-Cu or Cu-Ag bond lengths to be shortened dramatically.

We find the center of the d-states of the atoms #11 and #20 to be located at -3.36 eV and -3.41 eV (Figure 6.14.a). For the Cu ring atoms, the position of the center of the d-states ranges from -2.66 eV to -2.89 eV. The position of the center of the d-states for the atoms with much lower coordination than 12 ranges from -1.91 eV to -2.26 eV, indicating the shift towards lower binding energy. The position of the center of the d-states for the Ag atoms does not reflect explicit dependence to the coordination and elemental environment. We find the position of the center of the d-states to be close to each other and ranges from -3.96 eV to -4.38 eV. The average Cu-Ag bond length of each individual Ag atom ranges from 2.65 Å to 2.79 Å, most of which can be understood by examining their coordination and the number of foreign atom neighbors. The average Ag-Ag bond lengths are found to be in the range between 2.92 Å and 2.98 Å.

The electronic DOS of Ag$_7$Cu$_{27}$ is plotted in Figure 6.10.e. The increase in Cu to Ag atom ratio causes the band to shift towards lower binding energy. The presence of states at high binding energies (from -4.5 eV to -5 eV) signals the hybridization between Cu and Ag states. The average coordination for the Cu and Ag atoms are 9 and 6, respectively. The average Cu-Cu, Cu-Ag, and Ag-Ag bond lengths are 2.57 Å, 2.75 Å, and 2.96 Å, respectively.
Figure 6.14 The Ag$_{10}$Cu$_{24}$ NP a) Position of the center of the d-states of each atom b) Coordination distribution and c) Average Cu-Cu, Cu-Ag and Ag-Ag bond lengths

The individual Cu atom coordination in the NP ranges from 5 to 14. The highly coordinated Cu atoms have large number of Cu neighbors (ranging from nine to thirteen [Figure 6.15.b]) as they occupy the core. Note that the NP has both Cu rings and a chain and it is not a complete closed shell NP. The chain atoms (#3 and #13) are over-coordinated. An inner Cu ring atom (#2) is the only Cu atom with no Ag neighbor, while the other Cu atoms have at least one Ag neighbor. The coordination of the Ag atoms is either 5 or 6 with large number of Cu neighbors as expected.
In this NP too, the analysis of the position of the center of the d-states for each individual atom provides a clear indication that the variation in the position of the center of the d-states show strong dependence on coordination and immediate elemental environment. We find that the position of the center of the d-states for the Cu atoms is at -2.36 eV, which is much lower than that for Cu bulk atom. For the Ag atoms, the center of the d-states is located at -4.29eV, which is slightly lower than that for Ag bulk atom.
Confirming our results presented above, the Ag atoms are slightly affected by their elemental environment. A closer look into the individual position of the center of the $d$-states for each atom brings up a similar picture obtained on our earlier discussion. The effect of high coordination and large number of Cu neighbors on the position of the center of the $d$-states of the Cu atoms is easily traceable. Similar trends are observed for Cu$_{34}$, Ag$_{17}$Cu$_{17}$ and Ag$_{10}$Cu$_{24}$ NPs. The center of $d$-states for highly coordinated Cu atoms is shifted above 1 eV (towards higher binding energy) with respect to that for the low-coordinated atoms (Figure 6.15.a). The common features of these atoms are their being highly coordinated and have large number of Cu neighbors (Figure 6.15.b). The position of the center of the $d$-states for the Ag atoms is in the range of -4.13 eV to -4.51 eV.

The analysis of the average Cu-Cu and Cu-Ag bond lengths of the highly coordinated atoms with distinctive position of the center of the $d$-states shows that they differ significantly from those of the low-coordinated atoms. The average Cu-Cu bond length for atom #2 (highly coordinated Cu inner ring atom) is 2.47 Å, which is much shorter than that for the bulk (2.57 Å). The average Cu-Cu and Cu-Ag bond lengths for atom #6 (an inner ring atom) are 2.47 Å and 2.59 Å (Figure 6.15.c), respectively. These short bond lengths reflect the high coordination along with the presence of large number of Cu neighbor. The chain atoms (#3 and #13) have relatively large Cu-Cu bond lengths, 2.66 Å and 2.63 Å, respectively. However, their Cu-Ag bond lengths are very short (2.48 Å), indicating strong overlap between Ag and Cu states. The Cu-Cu and Cu-Ag bond lengths for the remaining Cu atoms in the inner ring are 2.53 Å and 2.56 Å, respectively. Owing to the presence of large number of Cu atoms in the NP, these highly coordinated Cu atoms show distinctive features in their electronic structures that can be rationalized.
by examining their coordination and the elemental environment. For instance, the center of the d-states of the atom #3 (chain atom) is at a slightly lower binding energy than that for the atom #2 (ring atom). Examination of their coordination and elemental environment reveal that both are highly coordinated atom. Difference originates from the fact that the ring atom does not have any Ag-atom neighbor, while the chain atom has one Ag-atom neighbor. Let us not forget that the geometric structure of the NPs is also an important factor, and seems especially in this case, contributing to the observed difference. Some of the low-coordinated Cu atoms have short Cu-Cu bond lengths, while their Cu-Ag bond lengths are relatively large, ranging from 2.71 Å to 2.95 Å. The average Cu-Ag bond lengths for the Ag atoms are in the range from 2.66 Å to 2.80 Å, most of which are above 2.70 Å. The average Ag-Ag bond lengths (2.96 Å) are the same for each atom.
The existence of the large Cu to Ag atom ratio in Ag$_2$Cu$_{32}$ brings up a shift in the electronic DOS towards lower binding energy (Figure 6.10.f). In this NP, the average Cu and Ag atom coordination is 8 and 6, respectively. Five of the Cu atoms are highly coordinated (12 to 14) with no Ag neighbor (Figure 6.16.b). The remaining Cu atoms have their coordination ranging from 6 to 9, most of which has zero Ag neighbor (at most two Ag neighbors). Highly coordinated Cu atoms occupy the chain (#27 and #29) and the inner ring (#7, #16 and #18). The Ag atoms are coordinated 5 and 7 with large number of Cu neighbors. The average bond lengths for Cu-Cu, Cu-Ag, and Ag-Ag are 2.54 Å, 2.74 Å.
Å, and 2.95 Å, respectively. The average position of the center of the d-states for the Cu atoms is at -2.25 eV, which is much lower (600 meV) than that for Cu bulk atom. For the Ag atoms, the center of the d-states is located at -4.14 eV, which is slightly lower than that for Ag bulk atom.

The analyses for the individual atom properties confirm that the center of the d-states for highly coordinated atoms is shifted towards higher binding energy with respect to those for the low-coordinated atoms and the bulk atom. We find the highest position of the center of the d-states to be for the inner Cu ring atoms (Figure 6.16.a).

The Cu-Cu bond lengths for highly coordinated atoms are 2.48 Å (for inner ring atoms, #16 and #18), 2.51 Å (for inner ring atom #7), and 2.62 Å (for the chain atoms #27 and #29). Among these atoms, only atom #7 has Ag neighbor. It also has short Cu-Ag bond length (2.56 Å). Note that the remaining Cu atoms have also short Cu-Cu bond lengths ranging from 2.47 Å to 2.49 Å, most of which does not have any Ag neighbors (Figure 16.c). The available Cu-Ag bond lengths range between 2.67 Å and 2.95 Å. The average Cu-Ag bond lengths for the Ag atoms are 2.64 Å (for atom #34) and 2.76 Å (for atom #33). The bond length with an individual neighbor is as small as 2.56 Å, while for some neighbors, the bond length is 2.95 Å (governed by the location of the neighbors in the NP). The average Ag-Ag bond lengths are the same (2.95 Å) for each Ag atom.

6.5 Change in the Position of the Center of d-states

In order to understand the controlling factors for the reactivity of extended and/or finite systems, it is important to examine thoroughly the local contributions. Research in the area has provided many important contributions to the understanding of the
controlling factors for reactivity. A simple but extensively used model was proposed [48], in which reactivity of a metal surface is determined by the coupling of adsorbate states and the substrate (metal) states. The model suggests that there are three parameters that affect surface reactivity: (i) the center of the d band ($\varepsilon_d$); (ii) the filling of surface d-states; (iii) coupling matrix ($V$). The model estimates $\varepsilon_d$ to be the average energy of the entire d-band, which can be obtained from first-principles calculations or using photoemission spectroscopy [257]. The model is based on many simplifications and assumptions, for instance, for bi-metallic systems, it is important to assume that there is no significant charge transfer between the interacting metals. It has been shown that for most of the cases [258] it provides insights into the factors affecting the reactivity of a particular system. The underlying reasons for enhanced or surpassed reactivity of some metal surfaces upon adsorption of particular atoms or molecules were also explained using the d-band model. It was shown especially for hetero structures that the adsorption of a metal atom on substrate made of another metal changes the electronic properties of the metal substrate. This was attributed to the change in the position of the center of d-bands of the substrate atoms [259]. In another study using d-band model, it was shown that, the adsorption properties of single atoms, dimers, and molecules on the metal substrates can be altered in the presence of strain. This modification is attributed to the fact that the position of the center of the d-band of the substrate atoms is shifted towards lower binding energy (in the presence of tensile strain). The shift towards lower binding energy increases the reactivity of the substrate atoms and lowers the adsorption energy [260]. It is also known that the low-coordinated atoms (such as those at step or kinks) are more reactive than highly coordinated ones (those at terraces). Analysis of the low-
coordinated atoms shows that their position of the center of the d-states is at lower binding energy than that for high-coordinated atoms.

Figure 6.17 a) Average position of the center of the d-states for Cu and Ag atoms versus Ag-atom content and b) Percentage change in the average center of the d-states versus Ag-atom content
Following the approach, we examine how different coordination, bond lengths and elemental environment affect the position of the center of the d-states with a view in understanding reactivity of these NPs. In Section 6.4, we have already shown for our sample NPs that highly coordinated Cu atoms with short bond lengths occupying the core and/or the inner rings show features in the center of their d-states dissimilar to those of low-coordinated atoms. In this section, we examine how these local effects emerge in the average center of the d-states (averaged over each atomic species) and what the corresponding effects are in shaping the overall electronic structure of the entire family of NPs. For this purpose, we calculate the average position of the center of the d-states for each atom species in each NP. We compare these average values for both Cu and Ag atoms in each bi-metallic NP with those for the two single-element NPs.

In Figure 6.17.a, the average center of the d-states for both Cu and Ag atoms in each NP is plotted as a function of the Ag-atom content. The figure makes it clear that the center of d-states for the Cu atoms in alloyed NPs deviates up to 500 meV from those in the single-element Cu\textsubscript{34} NP. Recall from Section 6.4 that the center of the d-states of each highly coordinated Cu atom with short bond length deviates above 1eV from those of low-coordinated atoms. Since the number of highly coordinated Cu atoms in a NP are far less numerous than low-coordinated ones, averaging the center of d-states over all the atoms fails to reflect this crucial feature. When we turn to the average center of the d-states for Ag atoms, what strikes us in Figure 6.17.a is how, in some Cu-rich NPs (those with 0 to 10 Ag-atoms, exception of NP with 9 Ag atoms) -- the deviations from the single-element Ag\textsubscript{34} NP are in the neighborhood of 1eV -- much greater than those for some Ag-rich NPs (those with 11 to 27 Ag-atoms). The majority of these are shifts
towards higher binding energy. The two highest shifts (towards lower binding energy) are -- 1.6 eV and 0.9 eV -- for Ag$_{1}$Cu$_{33}$ and Ag$_{6}$Cu$_{28}$, respectively. Because the single Ag atom in the former is accompanied by large number of highly-coordinated Cu atoms, its d-states overlap only with those of Cu. Although there are considerable more Ag atoms in Ag$_{6}$Cu$_{28}$, their distribution within the NP does not allow formation of many Ag-Ag bonds, likewise forcing the d-states of the Ag atoms to overlap with the d-states of the Cu atoms, many of which (as in Ag$_{1}$Cu$_{33}$) are highly coordinated. Notice that (Figure 6.1), the NPs with 0 to 10 Ag atoms do not have completely closed shells and any particular symmetry (except for Ag$_{9}$Cu$_{25}$), while those with 11 to 27 Ag-atoms have completely closed shells and partial symmetry. We also find the deviation of about 1 eV for those NPs with 28 to 34 Ag-atoms (also have no symmetry). The details concerning each atom d-states, coordination distribution, bond lengths for each NP are complied in Appendix D: Chapter 6. The electronic DOS for each NP in the family is summarized in Appendix E: Chapter 6. For each NPs geometric shape, consult Figure 6.1.

Figure 6.17.b summarizes the percentage deviation in the average center of the d-states for Cu and Ag atoms of each bi-metallic NP from those for the single-element NPs. Notice from the figure that the shift in the center of the d-states for Cu atoms is mostly towards lower binding energy, while for Ag atoms the shift is in the opposite direction. In the case of Cu atoms, the majority in each NP are less than 12 coordinated: these low-coordinated atoms cause the d-band to be narrowed, bringing a shift towards lower binding energy. In the case of Ag atoms, the average Ag-atom coordination increases with Ag-atom content: one should thus expect the d-band to be broadened. Again, it must be kept in mind that these average values can give us global view of the electronic
structure. Note that for such finite-sized systems, a distinctive deviation can be introduced by a change in the properties of particular atoms provided their ratio is at least comparable to that of those more closely in line with the average.

6.6 HOMO-LUMO Gaps

Small single-element metal clusters exhibit striking size-dependent variations in their chemical reactivity [261]. The first attempt in examining their chemical reactivity has been to identify the size or the range of sizes at which the metal/insulator transition takes place. A transition from metallic to non-metallic behavior with increasing size is expected when a band structure is established [262]. In order to determine the key magic sizes in this respect, the energy difference between the HOMO and LUMO is considered to be correlative to the band-gap that separates valence and conduction bands. A HOMO-LUMO energy difference close to zero is thus commonly accepted as indicating the transition to metallic state.

For bi-metallic clusters, size alone is no longer the sole parameter in shaping the electronic structure [263]. In the context of the present study, for a fixed-sized NP family, we have calculated the HOMO-LUMO gap for each composition with the aim of revealing the effect of alloying upon metallic to non-metallic transition. The research in this context is limited. Recent DFT calculations [15] for the electronic structure of Pt$_{12-n}$Cu$_n$ NP family showed that the electronic density at HOMO is larger for Cu atoms away from the Pt atoms, while the LUMO is reverse and the delocalization is larger on Cu atoms close to Pt atoms. The authors also reported interplay between structure and global reactivity parameters. They showed that there is an electronic balance between the two
species; hence combination of these atoms could also increase the reactivity of these clusters. They also noted that depending on the composition the cluster can be more nucleophilic (donating an electron pair) or electrophilic (accepting an electron pair).

For our bi-metallic NP family, in Figure 6.18 we plot HOMO-LUMO gap versus Ag-atom content in the NPs. The figure makes it clear that the HOMO-LUMO gap ranges from as low as 0.2 eV to 0.9 eV, revealing a great diversity in the electronic characteristics. For seven NPs, the gap ranges from 0.20 eV to 0.40 eV, for ten NPs the gap is between 0.40 eV to 0.60 eV, while for the remaining (eighteen) NPs, the gap is the highest ranging between 0.60 to 0.90 eV. Interestingly, the highest gap is found for the NP at which Cu to Ag ratio is 1. For this bi-metallic NP family, most of the NPs have large gaps -- a signature of electronic stability -- even though they are made of metal atoms. Mixing of these two metals at the nanoscale, for some compositions in the family leads properties to become far from metallic: the NPs exhibit significantly small gap indicates their high chemical activity, while those with large gap suggest their chemical inactivity.

Notice from the figure that there is not any explicit correlation between Cu to Ag ratio and the magnitude of the gaps; hence the metal to non-metal transition. In a recent study on the PdCo clusters showed that for a fixed size, the metallicity decreases almost monotonically with Co concentration [19]. Although some general ideas derived for metal to non-metal transition, there is more to be examined in the area. Hence, it is worth looking into the underlying reasons behind the transition from metallic to non-metallic behavior for our bi-metallic clusters. We first notice that those NPs with completely closed shells (Figure 6.1) or possessing high symmetry have large HOMO-LUMO gaps.
This can be understood by the fact that high symmetry increases possibility of hybridization owing to the strong overlap of the wave functions. However, those NPs with open shells and low or no symmetry reduce the overlap between wave functions, creating new states close to Fermi level. These low-symmetry NPs have much smaller gaps than those with high symmetry (see Figures 6.1 and 6.18). At this stage of the analysis, the results indicate that large HOMO-LUMO gaps may be attributable to high symmetry.

Figure 6.18  HOMO-LUMO gap versus Ag-atom content in the NPs
6.7 Bond Lengths, Charge Density Distribution, EDOS of Ag\textsubscript{17}Cu\textsubscript{17} NP

In Appendix D: Chapter 6, we summarize the coordination distribution, the distribution of the center of the d-states, and the distribution of the average bond lengths for each atom in each NP. Analysis provides so far, we have pointed out certain correlations that are common for most of the atoms in most of the NPs. It is desirable, though, to go into much deeper detail for each NP. We have calculated the bond lengths between each atom and every one of its neighbors, the charge density distribution within the NP (for revealing binding/bonding strength) and the electronic DOS of each atom. Although we have carried out this comprehensive analysis for every NP in the family, it is not feasible to discuss the results for each NP at this level of details. When there is no perfect mirror symmetry, there is large number of non-equivalent atoms, each of whose range of properties would require discussion. Fortunately, much can be illuminated by focusing on the two NPs posses mirror symmetry. We begin here with a discussion on the properties of Ag\textsubscript{17}Cu\textsubscript{17} NP. This NP is also of interest because it has the highest HOMO-LUMO gap. Ag\textsubscript{17}Cu\textsubscript{17} has total of six rings: three Ag rings (each ring consisting of five atoms) and three Cu (each consisting of five), see Figures 6.19.b-c. As shown in Figure 6.19.a, the Ag atoms form the shell and the Cu atoms are at the core of the NP. Still, compared to Ag\textsubscript{27}Cu\textsubscript{7}, some of the Cu atoms in this NP are somewhat exposed beyond the core (Figure 6.1). The NP also has a chain of two Ag terminal and two Cu core atoms (Figure 6.19.d). Owing to the perfect mirror symmetry, there are only six nonequivalent atoms; three Cu and three Ag. For ease of reference, we classify the rings (pentagons) from the mirror plane as Cu ring\textsubscript{0}, Cu ring\textsubscript{±}, and Ag ring\textsubscript{0}, Ag ring\textsubscript{±} (Figure 6.19.b-c).
We identify the atoms of the chain as Cu 0+, Cu 0-, Ag 0+, and Ag 0- (Figure 6.19.d). The rings classified as ± are equal to each other owing to the mirror symmetry (see Figure 6.19.a). Each ring has only one atom that can identify the atoms in that particular ring and those at the twin ring. Among the nonequivalent atoms, four belong to the rings and two belong to the chain (the elements pair Cu 0+ and Cu 0- are equal to each other as are those of Ag 0+ and Ag 0-). The Cu 0+ and Cu ring0 (inner ring) atoms are 12-coordinated, with eleven and eight Cu neighbors, respectively. The atom in the Cu ring+ is 9-coordinated, with five Cu neighbors. The coordination of the three nonequivalent Ag atoms is 8, 6 and 5 for Ag ring0, Ag 0+ and Ag ring+, respectively. The Ag 0+ atom has six Cu neighbors, the Ag ring0 atom four Cu and the Ag ring+ three Cu neighbors.

Figure 6.19 a) Geometric structure of Ag17Cu17 NP b) Three Ag rings c) Three Cu rings and d) The chain
Figure 6.20 Side view of Ag$_{17}$Cu$_{17}$ NP

In order to reveal the effect of the coordination and the environment on the bond lengths, we calculate the bond lengths between the nonequivalent atoms and the rest of the atoms (Table 6.1). The bond length between the Cu $0^\pm$ and the Cu ring0 (inner ring) atom is found to be 2.49 Å, which is 3.3\% shorter than that for the bulk nearest neighbor distance. The bond length between Cu $0^\pm$ atom and the Cu ring$^+$ is 2.46 Å and it is 4.08 Å with Cu ring$^-$ atoms. The bond length (2.48 Å) between the Cu atoms in the chain is much shorter than in the bulk, reflecting the stiffening of the bonds in the core of the NP. The bond lengths between the atoms in the Cu ring0 are much shorter than those in the Cu ring$^+$. The bond length with the Ag ring atoms are 4.18 Å, 4.23 Å and 5.01 Å for Ag ring$^+$, Ag ring0 and Ag ring$^-$, respectively. We also find the bond length between the Cu chain atom (Cu $0^\pm$) and the Ag chain atom (Ag $0^+$) is 2.51 Å, which is also shorter than the bond length for Cu-Ag dimer. Note that in addition to the stiffening of the bond within the Cu ring atoms, there is also stiffening of the bonds between the atoms in the chain. The shortest Cu-Cu, Cu-Ag and Ag-Ag bond lengths are found to be 2.46 Å, 2.52
Å and for 2.98 Å, respectively. The large contraction of the bond lengths between the atoms in the core of the NP also appear in the vibrational dynamics [88] and in the local electronic DOS (see the discussion below).

In order to further clarify the “localized” stiffening of the bonds between the atoms in the core of the NP, we first calculate the charge density distribution within the NP. We present the charge density distribution between the atoms in the outer Cu ring (Cu ring+), between the outer and the inner Cu rings (Cu ring+ and Cu ring0), and those for the inner Cu ring (Cu ring0), in the Figure 6.21.a, Figure 6.21.b, and Figure 6.21.c, respectively. Note from Figure 6.21.a that the charge density accumulation (red color/black areas) is traceable between the atoms of the outer Cu ring and the Cu chain atom. As noted above the bond length between the Cu chain atoms and the outer ring atoms is as short as 2.46 Å, confirming the observed strong charge accumulation. The charge density distribution presented in Figure 6.21.b shows that there is also accumulation between the inner Cu ring and outer Cu ring atoms. Finally, the Figure 6.21.c exhibits strong charge accumulation within the inner Cu ring atoms, confirming the observed stiffening of the bonds (Table 6.1).

We have also calculated the charge density difference of the NP with the aim of revealing more explicitly the highly charged areas in the NP. The charge density difference is calculated using the following equation:

\[ \Delta \rho (r) = \rho_{Ag_{17}Cu_{17}} (r) - \left( \rho_1 + \ldots, \rho_{17} \right)_{Cu \ atoms} (r) - \left( \rho_1 + \ldots, \rho_{17} \right)_{Ag \ atoms} (r) \]  

(6.4)
where $\rho_{Ag_{17},Cu_{17}}(r)$ is the total charge density of the NP. As shown in the equation, we calculate the charge density of each atom and subtract it from the total charge density of the NP by keeping the positions of the atoms exactly as they were in the NP. In Figure 6.22, we plot the resulting charge density difference. The figure makes it clear that the charge density accumulates in the core of the NP (red area) for which the stiffening of the bonds is the greatest (Table 6.1). This stiffening results from the high coordination of Cu core atoms, each with a large number of Cu neighbors.
Table 6.1 Bond lengths between non-equivalent atoms and each atom in Ag\(_{17}\)Cu\(_{17}\)

<table>
<thead>
<tr>
<th>Cu ring(\uparrow) Type (NN)</th>
<th>d(Å)</th>
<th>Cu ring(0) Type (NN)</th>
<th>d(Å)</th>
<th>Cu(\uparrow) Type (NN)</th>
<th>d(Å)</th>
<th>Ag ring(\uparrow) Type (NN)</th>
<th>d(Å)</th>
<th>Ag ring(0) Type (NN)</th>
<th>d(Å)</th>
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<th>d(Å)</th>
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<td>2.461</td>
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<td>Ag ring(0)</td>
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<td>6.455</td>
<td>Cu ring(\uparrow)</td>
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</table>

* 1, 2 and 3 in parenthesis show the atoms with the shortest, medium and the largest bond lengths, respectively.
Figure 6.21 Charge density distribution for Ag$_{17}$Cu$_{17}$ NP a) between chain and outer Cu ring b) between inner Cu and outer Cu rings and c) within inner Cu ring
Figure 6.22 Charge density difference for Ag$_{17}$Cu$_{17}$ NP; red area represents high charge density (the accumulation of the charge)

In order to trace the differences in coordination, bond lengths and the elemental environment of these nonequivalent atoms in the NP, we examine the partial electronic DOS (PDOS). We have already discussed the total electronic DOS of the NP in the earlier sections, where we showed that most of the contribution comes from the d-states. In Figure 6.23.a-c we summarize the PDOS (d-states) of the three nonequivalent Cu atoms, together with the PDOS of the bulk Cu atom for comparison. Notice from Figure 6.23.a that the PDOS for the chain atom (Cu 0±) shows broadening of the band with respect to that for the bulk atom. The chain atom sits at the core of the NP, is highly coordinated (12) with large number (eleven) of Cu neighbors, and makes short bond lengths (2.46 Å) with its neighbors (Table 6.1). The PDOS for the inner Cu ring atom (Cu
ring0) also shows slight broadening of the band (Figure 6.23.b). Note that the inner ring atom is also highly coordinated, but four of its neighbors are Ag. The bond length between the neighboring Cu atoms in the ring is 2.55 Å, which is slightly shorter than that of the bulk. The short bond length (2.53 Å) between the Cu ring0 and Ag ring± atoms signals strong hybridization between the Cu and Ag states: thus the factors behind band broadening are different for these differently situated Cu atoms. For the chain atom the overlap between the Cu-Cu states originates from the short Cu-Cu bond lengths, which in turn are due to high coordination coupled with a high number of Cu neighbors. The PDOS for the outer Cu ring atoms (Cu ring±) shows a narrowing of the band with respect to that of the bulk (Figure 6.23.c). This is attributable to their lower coordination (9) than that for the bulk atom.

In Figures 6.23.d-f, we present the PDOS for the three nonequivalent Ag atoms. The figures clearly reflect the hybridization between Ag and Cu states. The PDOS of the Ag chain atom (Ag 0+) shows narrowing of the band as compared to that for Ag bulk atom. Note that the Ag chain atom has low coordination (6) and no Ag neighbors. The hybridized states can be understood by the presence of a large number of Cu neighbors. In contrast to the PDOS of the chain atoms, the PDOS of the inner Ag ring atom (Ag ring0) shows broadening of the band, indicating its higher coordination (8). In Figure 6.23.e we also see the Cu-Ag hybridized states, which emerge from the presence of four Cu neighbors. Figure 6.23.f summarizes the electronic DOS of the outer Ag ring atom (Ag ring±). The figure makes it clear that the band is narrowed relative to that for Ag bulk owing to its low coordination (5). Existence of three Cu neighbors in the bonding leads to production of new states.
Recall (from Section 6.4) that the position of the center of the d-states of atoms can vary about 1.5 eV (Figure 6.13.a). The effect of coordination and elemental environment are clearly visible: only highly coordinated atoms show distinctive values for their centers of the d-states. The broadening of the band for the Cu $0^+$ atom relative to that of the bulk is in line with the position of its center of d-states. For the Ag atoms, since the coordination distribution is not broad and there are no highly coordinated Ag atoms with short bond lengths, the centers of their d-states do not show distinctive values. Finally, note that the atoms whose position of the center of the d-states is close to the Fermi level are expected to be chemically active. An examination of the center of the d-states for the Cu atoms can help for pinpointing such selectivity. However, the Cu atoms in the NP are located mostly inside the core of the NP; hence for any reaction to occur, the atoms have to be reachable.
Figure 6.23 The partial electronic DOS of the non-equivalent atoms for a) Cu $0^+$ b) Cu ring0 c) Cu ring$\pm$ d) Ag $0^+$ e) Ag ring0 and f) Ag ring$\pm$
In order to bring these points into focus for the central topic of this study as a whole -- the effects of progressive alloying within this family of NPs -- let us now compare what we have just highlighted concerning the electronic structure of Ag$_{17}$Cu$_{17}$ with that of the one other mirror-symmetrical NP in the family, namely, Ag$_{27}$Cu$_{7}$.

In both cases the Cu atoms are embedded in the core of the NP, but for Ag$_{17}$Cu$_{17}$, some of the Cu atoms are exposed to the surface, not surrounded by the Ag atoms as in the case of Ag$_{27}$Cu$_{7}$. We have shown that the ratio of Cu to Ag in the NP determines the bond hierarchy and affects such properties as dynamics [88]. Here we focus on electronic structure. For each NP, recall that the bond lengths between atoms of the same and different species can be classified from the shortest to the largest as Cu-Cu, Cu-Ag and Ag-Ag. We have also seen that the Cu atoms in NPs are affected by the environment more than are the Ag atoms. The presence of more Cu atoms causes the bond lengths to be stiffened, especially in the core of the NP.

We just showed that for Ag$_{17}$Cu$_{17}$, the bond lengths between the Cu atoms in the core of the NP and their neighbors are stiffened. In order to reveal the effect of the Cu to Ag ratio on the different bond length types, we summarize in Table 6.2, the average shortest Cu-Cu, Cu-Ag and Ag-Ag bond lengths.

For Ag$_{17}$Cu$_{17}$, the shortest Cu-Cu bond length is 2.46 Å, which is 4% shorter than that of the bulk (2.57 Å). For Ag$_{27}$Cu$_{7}$, this bond becomes only 2.52 Å (2% shorter than bulk). Let us note that the ratio between Ag to Cu atoms in the first NP is 1, while it is almost 4 for the second NP. The ratio makes it clear that the more the Cu atoms in the NP, the stiffer the bonds get especially but not merely for the core atoms. We showed above that the core atoms in Ag$_{17}$Cu$_{17}$ are highly coordinated, have large number of Cu
neighbors and make short bonds with their neighbors. This emerged as the broadening of
the bands in their electronic DOS. This bond-length profile does not show up in Ag$_{27}$Cu$_7$
owing to the fact the Cu core atoms, even though they are highly coordinated, have many
Ag neighbors, with the result that their bond lengths are not as short as those for Ag$_{17}$
Cu$_{17}$.

Table 6.2 The shortest Cu-Cu, Cu-Ag and Ag-Ag bond lengths in Ag$_{17}$Cu$_{17}$ and Ag$_{27}$Cu$_7$
NPs

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length (Å)</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag$<em>{17}$Cu$</em>{17}$</td>
<td>Ag$_{27}$Cu$_7$</td>
</tr>
<tr>
<td>Cu-Cu</td>
<td>2.46</td>
<td>2.52</td>
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<tr>
<td>Cu-Ag</td>
<td>2.51</td>
<td>2.58</td>
</tr>
<tr>
<td>Ag-Ag</td>
<td>2.98</td>
<td>2.85</td>
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</table>

As the table makes it clear, the second shortest average bond length type is the
Cu-Ag. We find this bond length in Ag$_{17}$Cu$_{17}$ to be 2.7% shorter than that in Ag$_{27}$Cu$_7$.
The existence of large number of Cu atoms in the former NP causes this bond to stiffen
as do the Cu-Cu bonds. Note that these short bond lengths in the former NP signal high
overlap between the wave functions, leading to stronger hybridization between the states
of Cu-Cu and Cu-Ag. The Ag-Ag bond lengths in these NPs are the largest of all. That is
why we found that the addition of more Ag atoms into the NPs increases monotonically
the NPs’ average bond length. Notice from the table that the average Ag-Ag bond length
in the Ag$_{17}$Cu$_{17}$ NP is 5% larger than that in the Ag$_{27}$Cu$_7$. It is clear that owing to the
perfect core-shell structure, the large numbers of Cu atoms are embedded into the core of
the NP leaving the Ag atoms to occupy the shell; hence decreasing the Ag-atom
coordination. This leads the Ag-Ag bonds to be longer in the case of Ag$_{17}$ Cu$_{17}$ than those in the Ag$_{27}$ Cu$_{7}$ NP.

6.8 Conclusions

Taken together, our electronic structure calculations using DFT for the Ag$_n$Cu$_{54-n}$ NP family reveal the importance of understanding local contributions -- (atomically-resolved) -- to the overall electronic structure of each NP. The number-density analysis for each coordination reflects the core-shell structure of some of these NPs in which Cu atoms occupy the core, while Ag atoms form the shell. As the Ag-content increases in the NPs, the average coordination of both Cu and Ag atoms increases. The increase is sharper for Cu atoms than that for Ag atoms. This originates from the fact that when Ag to Cu ratio increases, the population of Cu atoms increases in the core, and at the same time, forcing the Ag atoms to occupy inner sites of the NPs. The effect of alloying on coordination is also reflected in the bond lengths. The bond lengths between the same and different element species can be ranked from the shortest to the largest in the order of Cu-Cu, Cu-Ag and Ag-Ag. Analysis of average bond length for each NP shows that as one increase Ag-content, the NPs’ average bond length increases monotonically. The individual Cu-Cu, Cu-Ag and Ag-Ag average bond lengths vary slowly with the increase in Ag-content.

We find from the analysis of the excess energy and the second differences in energy that Ag$_{27}$Cu$_{7}$ NP is the energetically most stable NP within the family, in agreement with the earlier study using model potentials [235]. The results also show that the formation energy per atom decreases monotonically as the Ag-content increases,
indicating that an increase in the number of Ag atoms reduces the average bonding strength. This is attributable to the fact that the number of Cu-Cu bonds decreases as these are replaced by Cu-Ag and Ag-Ag bonds, with strengths relatively lower than those of Cu-Cu (owing to the lower cohesive energy of Ag than that of Cu).

As we compare the electronic densities of states (DOSs) of the bi-metallic NPs with those of the two single-element NPs, we find changes to appear in the DOS, as shifts towards either higher or lower binding energies as well as hybridization between the states of Cu and Ag. Analysis of the electronic DOS’s of the bi-metallic NPs shows that the underlying reasons for their characteristics can be understood only by examining each atom’s properties. This originates from the fact that overall properties of such finite-sized systems as those of our family NPs can be governed by just a few atoms whose properties are distinctive. For instance, specifically examination of the position of the center of the d-states for each atom in each NP reveals that highly coordinated Cu atoms occupying the core of the NPs present distinctive features in their position of the center of the d-states. As compared to that of the bulk atoms, their center of the d-states shifts towards higher binding energy. This shift originates from the presence of large number of Cu neighbors, which leads to short bond lengths between the atoms at the core. Strong contraction is observed in the core of the NPs due to finite size. Our charge-density distribution analysis for one of the most symmetric NPs (Ag_{17}Cu_{17}) shows explicit correlation between the accumulation of charge and the stiffening of bond lengths. We find that as compared to the outer Cu ring atoms, there is a stronger charge accumulation among the inner Cu ring atoms. This is in agreement with the scale of bond lengths between the atoms within each ring. From the charge density difference, we confirm that the charge is accumulated at the
core of the NP. The stiffening of the bond lengths between the core atoms reaches up to 4% with respect to that with the bulk, causing the Cu core atoms to be “over-coordinated” -- the “true” coordination of these Cu atoms is actually higher than that of in the bulk. The electronic DOSs of these particular atoms shows a broadening of the band relative to that of a bulk atom: short bond lengths induce strong overlap between the d-orbitals, leading to hybridization between the states. The Ag atoms in the NPs are rarely as highly coordinated as the Cu atoms, owing to the fact that they form the shell. Hence, relatively few highly-coordinated Ag atoms appear only in Ag-rich NPs -- from Ag_{34} to Ag_{28}Cu_{6} -- whose position of the center of the d-states is also shifted towards higher binding energy.

Since the d-band of Cu is much closer to Fermi level than that of Ag, it is to be expected that Cu is more reactive than Ag, as indeed it is known to be. In terms of reactivity of these NPs, our analysis shows that mixing of Ag with Cu does not seem to affect the overall reactivity of Ag atoms. Rather only those NPs with a relatively large number of Cu atoms at the shell (low-coordinated) exhibit chemical reactivity. The HOMO-LUMO gaps of these Cu-rich NPs range from 0.20 eV to 0.40 eV. We infer that the low coordination of Cu atoms in certain particular compositions (entailing corresponding structures) may be the underlying reason for these NPs reactivity. Moreover, the position of the center of the d-states of these low-coordinated Cu atoms shifts towards lower energies (about 1.5 eV), indicating that these atoms can be more reactive than the other Cu atoms (those in the core).

This is an important result, pointing to possibility of site-selective reactivity for these particular compositions. Moreover, these low-coordinated atoms belong to the NPs with no particular symmetry, all but one with incomplete shells that consisting of mixture
of Cu and Ag atoms. Note that this feature is not observed for completely closed shell NPs whose gap is large. For Ag-rich NPs (28 to 33 Ag atoms) with relatively small HOMO-LUMO gaps, the Cu atoms are not exposed in the shell; hence there are no low-coordinated Cu atoms. For these NPs, the underlying reason for their reactivity (small gap) is that these particles, lacking any particular symmetry, have a low level of degeneracy.

The HOMO-LUMO gaps vary between 0.20 eV and 0.88 eV as the composition changes. Our results indicate that the HOMO-LUMO gap can be tunable by alloying. This thus indicates that the electronic structure of these finite-sized systems can be altered strongly with progressive alloying. One of the underlying reasons for the variation in these gaps is structure-oriented: the NPs with high symmetry and/or completely closed shells have large gaps, while the NPs with no/or partial symmetry and/or incomplete closed shells (with Cu atoms) have small gaps. We find $\text{Ag}_{17}\text{Cu}_{17}$ to have the highest gap in the family, while $\text{Ag}_{7}\text{Cu}_{27}$, $\text{Ag}_{8}\text{Cu}_{26}$ and $\text{Ag}_{28}\text{Cu}_{6}$ NPs have the lowest gaps. Structural examination of these NPs shows that $\text{Ag}_{17}\text{Cu}_{17}$ has perfect mirror symmetry and completely closed shell, while $\text{Ag}_{7}\text{Cu}_{27}$, $\text{Ag}_{8}\text{Cu}_{26}$ NPs do not have any particular symmetry, are not closed shell, and have few Cu atoms at the shell. $\text{Ag}_{28}\text{Cu}_{6}$ also has no symmetry. The correlation between the magnitude of the gap and the geometric structure persists throughout the whole family.

In summary, the extensive electronic structure analysis signals that physical and chemical properties of this core-shell NP family can be tunable by controlling the chemical composition and relative sizes of core and shell.
Our results also raise important questions for future research. For instance, what other factors is there causing diversity in the HOMO-LUMO gaps? We infer that it is the low coordination of Cu atoms in particular compositions lead to chemical reactivity. One can further examine whether there is a correlation between the magnitude of the gap and the ratio of these low-coordinated Cu atoms. It is also important to understand the individual contributions of each element in the resulted electronic properties of alloy NPs. For instance, one can study another family of NPs of the same size by varying the impurity identity. This can be done in many classifications: (i) impurity elements that are similar to Cu in view of electronic properties; (ii) alloy consisting of a mixture of two elements with small misfit (iii) magnetic impurities for monitoring the change in magnetic properties with progressive alloying.

One such factor for controlling the HOMO-LUMO gap is reported to be d-s hybridization. Our preliminary analysis provides that d-s hybridization is present for those sample NPs regardless of their gap and their structural characteristics. However, one notes that it may be the strength of this particular hybridization is of the key parameter. Further analysis of examination of hybridization index and the charge-density distributions at HOMO and LUMO (for characterization of orbitals) may provide underlying reason(s) for the observed variation in the gaps.

As established now the properties of these nanostructures converge to those of the bulk as size increases. A study combining several sizes of the same family of these NPs may provide insights into how these electronic properties differ from those of the 34-atom NPs. In particular, what controls the magnitude of the HOMO-LUMO gaps for larger sizes since with increasing size; the composition and the relative atomic positions
will be re-arranged. Are these size affects element dependent? If the answer is yes, what correlations can be driven? At which size the electronic properties become similar to those of the bulk? These and further questions are worth answering in order to gain broader understanding of the properties of these bi-metallic NPs.
We present results for tip-induced extraction of a Cu adatom from Cu mound on Cu(111), and compare the characteristics to that for a similar Ag system. Molecular-dynamics and molecular static simulations were carried out using interaction potentials from the embedded atom method. Molecular-dynamics simulations revealed differences in the modes of extraction for the cases of Ag and Cu systems and their dependence on tip geometry. For the case of a sharp Ag tip, the extraction of a Ag adatom occurs via the pulling mode, while with a blunt Ag tip, the extraction is more complex involving a two-step motion. On the other hand, the relatively stronger Cu-Cu interaction leads to a sliding and/or dragging mode in which the whole three-dimensional cluster is dragged followed by the extraction of the adatom from the cluster. Molecular static simulations provide a detailed analysis of the changes in the energy landscape in the presence of the tip, resulting in a substantial decrease of the energy barrier for an adatom to descend from the mound.
7.1 Introduction

Since its invention by Binning et al [1], STM has become an important tool for imaging structure formations at surfaces [264], yielding valuable results for many surface science problems at the nanometer scale. In recent years, STM is increasingly becoming a manipulation tool by which atoms and molecules are moved around and taken to a desired spatial location [265-268]. The STM tip causes modification in the energy landscape in its vicinity which, in turn, controls the characteristics of the manipulation. Thus, detailed knowledge of the energy landscape in the presence of the tip may help control atomistic processes such as chemical reactions, growth, and nanostructuring, to name a few. The ability of the STM tip had already been used to manipulate laterally [265, 266], and also vertically [267] individual atoms and molecular movements. Recently, the STM has been used to extract atoms from a metal substrate by tip crashing [268]. Of the experimental investigations aiming to shed some light on the basic mechanisms governing single atom and molecule manipulation, the work of Meyer et al [269] is particularly worth mentioning in the present context. From their observation, they classified the manipulation process into two modes: lateral and vertical. In the lateral mode, a particle is moved on the surface to the desired place without losing contact with the substrate, while in the vertical mode, a particle is pulled up from its initial position by the tip and then dropped down on the surface at the desired location. They further divided the lateral manipulation into three distinct sub modes, depending on the tip-particle interaction. They showed that on Cu(211), Pb and Cu atoms can be manipulated by attractive tip-adatom interactions in such a way that the atoms follow the tip discontinu-
ously by hopping from one site to the next (pulling mode). For the case of Pb atoms, manipulation may also proceed through attractive forces but in a continuous way (sliding mode) with tip-particle interaction increasing very strongly. The third mode, which was observed in the case of single CO molecules, is the pushing mode resulting from a repulsive interaction between the tip and the molecule. From the theoretical side, there were few attempts [45, 54, 270] to explain the experimental findings and rationalize the physical phenomena governing manipulation.

Sorensen et al [45] investigated Au adatom diffusion energetics on Au(100), in the presence of a Au tip, and found a lowering of the activation energy. Similarly, using the example of the lateral manipulation of a Cu adatom along a step on Cu(111) with a Cu tip, Kurpick and Rahman [46] showed that while the presence of a tip lowers substantially the diffusion barriers toward the tip, the barrier in the opposite direction increases. In these systems, the phenomenon was explained in terms of the coordination between the tip and surface atoms. The motion of an adatom on metal surfaces in the presence of the tip arises from changes in the potential-energy surface that are controlled by the characteristic of the interatomic potentials which in the above-mentioned systems exhibit a bond-length–bond-order correlation. At particular heights, the adatom gains new bonds with the tip atoms, which makes its motion more favorable toward the tip than away from it. Kurpick and Rahman also show that the qualitative changes in the activation energies do not depend on the details of the tip; however, the shape and form of the tip apex and the height of the tip from the adatom affect quantitatively the energetics. A further theoretical study of vertical and lateral manipulation on flat, stepped, and kinked metal surfaces by Ghosh et al. [270] revealed shifts in the saddle
points and the presence of significant relaxations of the surface and tip atoms, providing more concrete factors behind the energy landscape perturbations introduced by the tip.

Figure 7.1 Atom extraction process a) 3D STM image of a Ag nanocluster deposited by tip-surface contact. Tip is brought close to the protruded part of the cluster and then moved laterally towards a destination on the surface b) STM image acquired after this shows a height reduction of the cluster protrusion and the extracted atom on the surface destination c) Manipulation signal of this event reveals the atomistic details of the atom extraction and d) Drawings demonstrating the two types of tip-height peaks. Image courtesy to Despande et. al. [271]
The issue of pulling, pushing, or sliding of the atoms by the tip has appeared once again in a recent experimental study which established that it is possible to extract individual atoms from a three-dimensional (3D) mound [271]. Figure 7.1.a shows an STM picture taken during the manipulation mode. The figure shows that the tip approaches to the 3D mound from the back (the arrow indicates the motion of tip). The following figure, Figure 7.1.b represents the situation after the tip passes through mound. Figure shows that the tip extracted the atoms from the mound and they are placed at the surface (yellow dots). In Figure 7.1.c, the manipulation signal is plotted as the tip moves on the surface to reveal the atomistic process of the extraction process. The experiment for the first revealed that the STM tip can extract atoms in addition to its ability of manipulation. In order to ensure the reliability of the results, the experiments are repeated for many times and at each sequence the extraction process was achieved. Figure 7.2 represents a sequence of STM images obtained from the STM movies. It shows that at each trial, the STM tip extracts the atoms from the 3D mound.
Figure 7.2 Atom-by-atom extraction sequence. A sequence of STM images from an STM movie shows atom by-atom extraction from a Ag cluster. This series proves the reliability of atom-extraction process. *Image courtesy of Despande et. al, [271]*

Since the local environment (geometrical) of atoms on a 3D mound differs from that on flat, stepped, or kinked surfaces, the modifications to the energy landscape introduced by the presence of a tip may not be readily extrapolated from what has been learned from the earlier studies [45, 54, 270]. In this study, our aim was to simulate the extraction process for the same system as the experiment in order to determine whether in relatively similar conditions the extraction process is possible. Combining the MD (to extract dynamics of extraction process) and MS (to rationalize the findings of MD simulations) simulations, we have reached to the conclusion that indeed for Ag(111) system
A Ag adatom can be extracted from a 3D Ag mound by a Ag tip through the pulling mode, in qualitative agreement with the experimental work of Despande et al [271]. The underlying reason for the extraction process is obtained using the MS simulations in which we scan the energy landscape to determine the perturbation induced to the energy landscape by the tip. The details of the extraction process will be discussed below.

For further understanding of the controlling factors for the extraction process and whether it is element dependent, we have performed the similar calculations for the extraction of a Cu adatom form a 3D mound on Cu(111) surface. Note that these calculations revealed differences in extraction processes both quantitative and qualitative between the Cu and Ag systems. In the case of Cu adatom extraction from Cu mound on Cu(111), the adatom extraction is obtained by sliding mode (which is different from that of a Ag(111) system). In addition to the extraction of single Cu adatom, the calculations also showed that clusters of three to five atoms can be manipulated. These calculations indicate that the extraction mechanism is element dependent and more complex for the case of Cu system.

In this chapter, we will discuss the results of the simulations for extraction processes for both systems. We will then explain the underlying reasons for the observed differences between the two systems. In section 7.2, we describe the model system used in these calculations. In section 7.3 we give the theoretical details employed in this study. Section 7.4 presents the results for both Cu and Ag systems. The first two sub-sections (7.4.1-2) are devoted on discussing the MD simulations and the third sub-section (7.4.3) provides the results of MS simulations. Finally, we present the conclusions in section 7.5.
7.2 Model Systems

The prototype system for manipulation and/or extraction processes is illustrated in Figure 7.3. The model system consists of a tip, an adatom on top of a 3D island, and a substrate. As shown in the figure, the substrate has six atomic layers of fcc(111) each containing 8x10 atoms. The 3D island consists of a two-dimensional (2D) pad containing 25 atoms on top of which there is a three-atom cluster. The adatom (the subject of manipulation and/or extraction) is located in the threefold site on top of this cluster. The tip consists of 35 in the case of sharp tip (single atoms as the tip apex), while it has 34 atoms for the blunt tip (three atoms as the tip apex). In order to determine effect of the size of the system on the calculated parameters, we have repeated the simulations for selected cases using a larger system -- consisting of nine layers with 20x20 atoms per layer. The calculations showed that the results obtained using smaller size is similar to those obtained using a larger size system.

Figure 7.3 a) Model system for the extraction/manipulation b) Possible diffusion mechanism on (111) and c) 3D mound from which adatom is extracted (from A to B)
7.3 Theoretical Methods

In this study, the atoms in the model system interact through an empirical many-body potential obtained from the EAM [50], with parameterization by Voter and Chen (VC) [65]. These potentials have had important success in revealing the characteristics of Cu and Ag surfaces, and have been proven to be reliable for examining the energetics, structure, and dynamics of these transition metals [51]. The first step is to perform MD simulations at relatively low temperature (100 K) to mimic the experimental setup [271]. These simulations are expected to provide the atomistic details of the extraction process. The positions and velocities of the atoms in MD simulations are calculated using a fifth-order predictor corrector method [272]. Each system is first thermalized by performing a simulation under constant number of particles, constant volume, and constant temperature (NVT) conditions for 20 ps (the time step used for these calculations is $1 \times 10^{-15}$ s). After this phase of thermalization of the system, we perform a simulation with constant number of particles, constant volume, and constant total energy (NVE) for 200 ps with the following constraints: (i) the bottom two layers of the substrate are held fixed to avoid an artificial motion of the whole MD cell due to the presence of the tip, (ii) the top two layers of the tip are held fixed to avoid a landing of the tip on the surface due to the attractive forces, (iii) two atoms of the pad are held fixed to avoid an artificial sliding of the island and the mound when the tip is moving laterally, and finally (iv) the tip is given a constant lateral velocity of 5–10 nm/ns ($5 \times 10^{-5} - 10^{-4}$ Å per time step). After each picosecond during the simulation, the position of the adatom, the mound, the pad, the first surface layer, and the tip atoms are stored. These are necessary for making a movie for
the extraction process and provide valuable insights into the atomistic details of the event. From the movies, we have extracted snapshots from the 200 sets of data.

The MS simulations are used to relax the system to its minimum-energy configuration at 0 K. These simulations are performed using a standard CG method [91], which has been shown to yield the same relaxation structures as simulated annealing methods for similar systems (see Ref. 23 in Ref. 14). During the minimization process, the two bottom layer atoms of the substrate and two atoms on the island are kept rigid. All the tip atoms except the ones on the top two layers are allowed to relax to their equilibrium positions for each simulation. Note that from the earlier studies, it is known that the presence of tip modifies significantly the potential-energy surface [45, 54, 270] seen by an adatom on a terrace, near a step edge, or a kinked site. As a result, adatom may diffuse toward (or away from) the tip. The objective of this study is to understand the processes by which an adatom can be extracted from a 3D cluster on Ag(111) or Cu(111). Clearly, the key parameter to extraction process is overcoming of the first barrier that adatom sees in jumping from its equilibrium position (threefold site) to the first threefold site on the wall of the mound, from which the adatom will slide easily down, as the barrier to diffuse is the same as the one on Ag(111) which is about 40 meV. The bottleneck is hence formed by the first barrier equivalent to the Schwoebel barrier found near a step [25]. The presence of the tip is expected to change the landscape of the energetics and a detailed analysis of this barrier for several locations of the tip is needed. The sliding up, back to the original position, is possible and a successful extraction would prevent this process to happen. In other words, extraction would occur when the tip at a certain position would increase the ratio between the barriers to climb up and diffuse
down. These two barriers associated with these two processes can be studied using lateral and vertical manipulation techniques, respectively. For lateral manipulation, for a fixed tip height and lateral position as measured from the adatom initial position, the total energy of the system is calculated as the adatom position is varied laterally. In the case of vertical manipulation, and again for a fixed tip height and lateral position as measured from the adatom initial position, the total energy of the system is calculated as the adatom position is varied vertically.

7.4 Results and Discussion

In this section, we will present a summary of the results of the MD simulations for different tip heights. For every simulation, the position of the adatom is monitored to assess the success of the extraction. The first section is devoted for the Ag adatom extraction from a Ag mound on Ag(111), while the second section discusses the Cu adatom extraction from a Cu mound on Cu(111). To study the physical properties behind a successful tip-induced extraction, we will also present results of MS simulations (third section) in which the tip height and lateral positions were varied. This part is expected to help to rationalize the results obtained using MD simulations.

7.4.1 Tip-induced Extraction of a Ag Atom From a Ag Mound on Ag(111)

We have performed several MD simulations for Ag tip heights (as measured from the initial position of the adatom) between 3.43 Å and 2.43 Å with a step of 0.1 Å. Every simulation is started with the tip apex lateral position of about 3.5 Å away (behind) from
the adatom followed by the tip moving laterally toward the adatom with a constant speed of 5 or 10 nm/ns and the calculation is stopped when the tip is about 5 Å in front of the adatom. The calculations are performed using both the sharp and blunt tips. Note that the MD simulations for different tip heights between 3.43 Å and 2.53 Å did not provide an extraction process. Extraction was observed at the height of 2.43 Å between the sharp tip apex and the adatom. In Figures 7.4.a-f, we present a sequence of snapshots taken at 5, 40, 100, 115, 135, and 175 ps after the start of the simulation (at tip height of 2.43 Å) respectively. In Figure 7.4.a, the apex atom is just behind the adatom whose lateral and vertical positions seem not to be affected by the presence of the tip. In Figure 7.4.b, the apex atom is directly on top of the adatom, while in Figure 7.4.c it is just in front of the adatom. The lateral and vertical positions of the adatom are hence unaffected during these first 100 ps of the simulation. It is when the tip apex atom is about 2 Å laterally in front of the adatom (Figure 7.4.d) that there is a change in the lateral position of the adatom with motion toward the tip. The adatom continues its monotonic motion toward the tip as it moves away from the adatom (Figure 7.4.e) and finally it is extracted from the mound as seen in Figure 7.4.f.
Figure 7.4 Snapshots from MD simulation for Ag adatom extraction from a Ag mound on Ag(111) by sharp tip
Figure 7.5 Snapshots from MD simulation for Ag adatom extraction from a Ag mound on Ag(111) by blunt tip
MD simulation using a blunt Ag tip reveals a mechanism of extraction reflecting the complex nature of the interatomic interaction as reflected below in the changes in the energy landscape. Figure 7.5 shows snapshots from the MD simulation where the tip apex atoms vertical position is 2.63 Å above that of the adatom. These snapshots are taken at 5, 60, 90, 135, 150, and 185 ps after the start of the simulation as shown in Figures 7.5a–f. In Figure 7.5.a, the lateral position of the apex atoms is behind the adatom whose position is not affected by the presence of the tip; the same situation can be seen in Figure 7.5.b when the apex is just above the adatom. As the tip moves laterally away from the adatom, two atoms from the apex are in front of the adatom while the third is behind it, as illustrated in Figure 7.5.c. Notice from figure that the adatom has moved with the tip attempting to overcome the barrier for extraction. In Figure 7.5.d, the adatom is seen to move back to the top of the mound as a result of the failure of the tip to flatten enough the energy landscape for the adatom to be extracted. As the third atom of the apex is now in front of the adatom taking a similar role played by the apex of a sharp tip, the energy landscape is now flat enough for the adatom to be extracted, as seen in Figures 7.5.e–f.

7.4.2 Tip-induced Extraction of a Cu atom From a Cu Mound on Cu(111)

To simulate the extraction process for Cu systems, we have used the same model as for Ag where the tip and the substrate are made of Cu. We performed simulations with a starting height of 2.63 Å and repeated several simulations with decreasing tip height by a step 0.1 Å. For all heights above 2.03 Å, the simulations did not produce any extraction of the adatom. Finally, a simulation at a tip height of 1.93 Å showed a successful
extraction. A detailed analysis of the movie extracted from the simulation revealed that the extraction of the Cu atom from the Cu mound proceeds through a totally different mode than in the case of Ag atom extraction. We noticed that the Cu adatom was always in close contact with the tip during the manipulation phase, suggesting that in this case, the extraction is actually through a sliding (or dragging mode) involving the manipulation of the whole cluster and the adatom indicating very strong interaction between Cu atoms as compared to that between Ag atoms. Indeed, as the tip approaches the adatom as illustrated in Figure 7.6.a (corresponding to 42 ps after the start of the simulation), the cluster and the adatom move collectively toward the tip (see Fig. 7.6.b taken just after 1 ps Figure 7.6.a). From this moment, the tip, the cluster, and the adatom move collectively (Figures 7.6.c-e). Note that the motion of the cluster is not monotonic but rather consists of rotation (c), then a jump (d), and another rotation (e). Finally, when the tip passes the edge of the pad, the adatom is extracted (f).
Figure 7.6 Snapshots from MD simulation for Cu adatom extraction from a Cu mound on Cu(111) by blunt tip.
This remarkable manipulation of the whole cluster plus adatom stimulated us to perform MD simulations for clusters containing three to five atoms and in both 2D and 3D configurations. We show hereafter the cases of 2D trimer and tetramer clusters on Cu(111). From Figures 7.7 and 7.8, we note that once the cluster is in contact with the tip, it travels along with the tip with a motion consisting of a series of a rotation followed by a jump. For the case of a pentamer, once the tip gets in contact with the cluster and starts the sliding motion of the pentamer, the tip apex atom gets extracted and attaches to the pentamer as an adatom with no further motion of the cluster.

![Figure 7.7 Snapshots of MD simulation for Cu trimer manipulation](image)

**Figure 7.7 Snapshots of MD simulation for Cu trimer manipulation**
In order to illustrate further the difference between the Ag and Cu extraction cases illustrated in Figures 7.4 and 7.6, in Figure 7.9 we plot the lateral positions of the adatom and the tip apex versus time for simulations done at 100 K and tip heights of 2.43 Å and 1.93 Å for Ag and Cu, respectively. From Figure 7.9.a, note that the Ag adatom’s lateral position stays almost constant when the tip moves from a position behind the adatom to positions in front of it. When the tip reaches the position of about 2 Å in front of the Ag adatom (for which the barrier for hopping down becomes minimal as discussed earlier), the latter starts moving laterally toward the tip and finally hops down. For the case of Cu, the scenario is much different, as illustrated in Figure 7.9.b. As the tip approaches the
adatom (with lateral separation of about 2.5 Å) the latter moves back toward the tip and
sticks to it (at about 43 ps after the beginning of the simulation). After that, the tip and the
adatom move together for about 6 Å (in the time interval between 43 ps and 118 ps) after
which the adatom is extracted.
Figure 7.9  Lateral position of the adatom and the tip apex as a function of time at 100 K for a) Ag system and b) for Cu system.
7.5 Diffusion Barriers From Molecular Static (MS) Simulations

In order to evaluate the manipulation capabilities of the tip, we first study the energy landscape seen by a diffusing atom in the absence of the tip. In the case of a silver atom hopping down from a Ag mound on Ag(111), in the absence of the tip, the adatom encounters a barrier of 0.3 eV (A to B in Figure 7.10). Once the adatom reaches point B, it could climb up to position A after overcoming the same barrier of 0.3 eV (B to A), as illustrated in Figure 7.10.

Figure 7.10 The two possible adsorption sites on the mound
In the presence of the tip, these two barriers are modified, as seen from the results summarized in Table 7.1. It is actually the difference between these two barriers that should dictate (exponentially) the probability of the adatom extraction by the tip. Indeed, if the barrier from A to B is reduced substantially, while that from B to A is moderately reduced, one can conclude that once the adatom makes it to B, it will continue sliding down. However, if the barrier from B to A is also dramatically reduced, one expects the adatom to have a high probability to go back to its original position (A) after a hop to B.

It is then essential to study the behavior of these two barriers in the presence of the tip. When the adatom hops from A to B, we consider it to be the case of lateral manipulation, while hopping from B to A is classified here as vertical manipulation, as defined earlier. In Table 7.1, we summarize the energy barriers to escape from the mound (lateral manipulation) and return back to the mound (vertical manipulation) as a function of the tip height and shape. Note that for both tip shapes, the difference between these two barriers is relatively high indicating the success of adatom extraction from the mound.

The determination of the change in the barriers involved in the extraction of a Cu atom from a Cu mound using MS simulations was not possible since we found that the whole cluster moves when the tip is close to the adatom. A restriction on the motion of the Cu cluster would significantly alter the energy landscape and hence the extracted barriers for diffusion would be meaningless.

The obvious difference between the strong interactions during manipulation of the Cu systems and the generally gentle ones for Ag systems stems from the fact that Cu and Ag have different cohesive energies and lattice constants. Manipulation of a Cu adatom in the Cu system with a (larger) cohesive energy of 3.49 eV (2.95 eV for Ag) coupled
with a (smaller) lattice constant of 3.615 Å (4.09 Å for Ag) would probe larger gradients during manipulation for tip-adatom distances (of the order of nearest-neighbor separation) than those in the case of a Ag adatom in the Ag system. Consequently, one would expect Cu to be “stiffer” near equilibrium positions than Ag. This argument can be tested as follows: if Cu and Ag would have the same curvature at equilibrium, the phonon spectrum of one could then be extracted using the other with a multiplicative factor equal to the square root of the inverse of the ratio of the masses. Using this relationship, and starting from the Ag vibrational spectrum (with a maximum of the bulk band at about 4.6 THz), one would expect the Cu bulk band to present a maximum at 6.00 THz. In fact, the experimentally measured phonon bulk band for Cu presents a maximum at about 6.8 THz, a shift of about 0.8 THz from the predicted value using the ratio of masses; a positive shift reflects the extra stiffness of the Cu potential as compared to the Ag one.

Table 7.1 The activation energy barriers for Ag adatom jump from the mound on Ag(111) for lateral and vertical manipulation mode

<table>
<thead>
<tr>
<th>Height (interlayer separation) (Å)</th>
<th>Energy barrier (eV) (sharp tip)</th>
<th>Energy barrier (eV) (blunt tip)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lateral manipulation</td>
<td>Vertical manipulation</td>
</tr>
<tr>
<td>2.43 (1.03)</td>
<td>0.032</td>
<td>0.18</td>
</tr>
<tr>
<td>2.63 (1.11)</td>
<td>0.052</td>
<td>0.21</td>
</tr>
<tr>
<td>2.83 (1.20)</td>
<td>0.124</td>
<td>0.24</td>
</tr>
<tr>
<td>3.03 (1.28)</td>
<td>0.190</td>
<td>0.27</td>
</tr>
<tr>
<td>3.23 (1.37)</td>
<td>0.280</td>
<td>0.28</td>
</tr>
<tr>
<td>3.43 (1.45)</td>
<td>0.290</td>
<td>0.30</td>
</tr>
<tr>
<td>3.63 (1.54)</td>
<td>0.300</td>
<td>0.31</td>
</tr>
</tbody>
</table>
We have performed extensive MD simulations of adatom extraction from a mound by a manipulative tip for Ag and Cu systems. Successful extraction was achieved for particular tip heights which depend on the system’s elemental composition. For Ag system, extraction was possible at tip heights of 2.43 Å (for sharp tip), while 2.63 Å for blunt tip. For Cu system, extraction is achieved using a sharp tip at the height of 1.93 Å, above the initial position of the adatom. For Ag system with a sharp tip, the extraction is clearly through a straightforward pulling mode, while for the blunt tip, the three atom apex leads to extraction through two stages, each of which can be reasoned on the basis of the local adatom environment. For Cu, the situation is much more complex as a result of the relatively strong interaction between Cu atoms that allows the tip to induce motion to the whole cluster through a sliding and/or dragging mode. In addition to MD simulations of adatom extraction, we have also performed several simulations in which 2D Cu clusters containing three, four, and five atoms were manipulated through a drag using a sharp tip. We found that for the critical size of five atoms, the tip loses its apex atom to the cluster after the tip attempts to drag this cluster. Detailed analysis of the energy landscape (using MS simulations) shows that in the case of Ag, the tip alters the landscape in such a way that when the tip is in front of the adatom and close to the edge of the mound, the energy for the adatom to hop down over the mound edge decreases very rapidly. Finally, we have traced the qualitative differences between manipulation of Cu and Ag systems to their difference in cohesive energy and lattice constant.
CHAPTER 8: CONCLUSIONS

This dissertation describes the results of a theoretical study providing insights into the importance in understanding atomically-resolved (local) contributions for the dynamics, thermodynamics, and stability of the metal surfaces and the mono- and bi-metallic NPs. By revealing these contributions serves as the basis for the ultimate goal, which is to build understanding how to alter the characteristics of events in order to gain insights into the key factors for constructing functionalized materials with unique features.

Changes in the vibrational properties of the surfaces from those of the bulk are found to be confined mainly to the first-layer atoms. Low frequency end of the spectrum presents an enhancement that yields a lower contribution to the vibrational free energy as compared to that of the bulk. This observed feature is attributed to the softening of the in-plane force-field resulting from the loosening of the bond due to the loss of neighbors of the first layer atoms. Change in coordination of the atoms appears also clearly in their thermodynamical functions. Comparison between the results obtained from DFT and EAM shows that the EAM results are very close to those obtained from DFT for both Cu(100) and Ag(100) surfaces, but for the (100) surfaces of Pd, Pt and Au, the EAM describes very poorly the interactions.

Diffusion of single Cu and Ag adatoms on Cu(100) and Ag(100) showed that there is a relation between the strength of binding and the diffusion barriers. The results also revealed that when one considers drawing conclusive argument for diffusion and
growth, one has to take into account both diffusion mechanisms, namely hopping and exchange. Exchange mechanism is found to be relevant for Cu adatom diffusion on Ag(100) terrace, and for the diffusion at step edges except for Ag adatom diffusion on the step edge of the Cu(100). These results point out the feasibility of alloying of Cu atoms into Ag(100) especially at step edges, while this is much less likely for Ag adatom diffusion on Cu(100). The resulting E-S barriers point that owing to a negative E-S barrier for Cu on Ag(100) and a large (positive) E-S barrier for Ag on Cu(100), these hetero systems may grow the opposite. The former is expected to grow a layer-by-layer manner, while the latter may present formation of mounds on the surface.

Diffusion of single atoms on strained lattices showed that strain can be used to modify diffusion barriers by means of altering the binding energies of the adsorbate relative to the substrate. This is attributed to the fact the strain induces changes into the electronic structure of the substrate atoms. The analysis of the d-band center of the substrate atoms revealed that center of d-band shifts towards either higher or lower binding energies depending on the type of strain. Diffusion barriers increase with increasing tensile strain as a result of the shift of the center of d-band of substrate atoms towards lower binding energy. This yields increase in adsorption energy of the adsorbate thus increases the diffusion barriers. Compressive strain causes the opposite effect – the center of the d-band of the substrate atoms shifts towards higher binding energy causing a decrease in the adsorbate adsorption energy. Although the largest shift in the center of the d-states is obtained for the case of Pd adatoms diffusion on Pd(100), the results revealed that strain effect (especially tensile strain) on the diffusion barriers is less enhanced in this case. The analysis of the elastic response of each surface has shown that the response
to strain is the highest for Cu(100), and the lowest for Pd(100). From these analyses, one can see that the effect of elastic response mostly controls the changes induced to the diffusion barriers. The analysis for adatom diffusion near step edges showed that the E-S barriers can be altered strongly with strain. The change in the height of the E-S barriers originates from the change in terrace diffusion barriers owing to the fact that strain is relieved near step edges by in-plane relaxations. Strong modification of the E-S barriers opens up opportunities for controlling growth mode/morphology. The results revealed that tensile strain decreases the E-S barriers thus leads formation of smooth layers, while compressive strain increases the E-S barriers yielding formation of rough films.

Single atom (Cu or Ag) diffusion via hopping mechanism on the terraces and step edges of Cu(110), Cu(100) and Ag(100) showed that the prefactors are in the range of $10^{-3}$ cm$^2$/s regardless of diffusion mechanism studied. The effect of substrate vibrations is found to be negligible (a factor less than 2 is observed). Compensation effects in vibrational frequencies of the diffusing entity and cancellations in the change of the vibrational free energy are responsible for the quasi-constant value ($10^{-3}$ cm$^2$/s) reported frequently in the literature. The perturbation induced to the substrate by the presence of an adsorbate is found to be localized thus providing the most contribution to the vibrational free energy.

Analyses of the diffusion activation barriers and prefactors for 7-atom cluster diffusion have provided that the prefactors are comparable to those for single atom diffusion. The vibrational contributions of the substrate atoms to the calculation of the prefactors are found to be negligible for both homo and hetero diffusion. The most contribution to the vibrational free energy comes from the cluster itself. Analyses of the
VDOS showed that for Cu$_7$ cluster on Ag(111), the low frequency end of the vibrational spectrum populates as a result of strong interaction among the cluster atoms as compared to those with the substrate. The enhancement at the low frequency of the spectrum causes large vibrational free energy contributions and smaller prefactors than those for Cu$_7$ cluster on Cu(111). Analyses of the atomistic processes obtained from MD simulations have revealed that the diffusion of 7-atom cluster for both homo and hetero cases is governed by the combination of concerted motion and the diffusion of individual atoms. The clusters undergo a shape transition -- short-lived -- during the diffusion, thus it can be concluded that the concerted motion is not the only diffusion mechanism governing the diffusion of compact 7-atom cluster.

Detailed analyses of the structural, vibrational dynamics and thermodynamics of the family of the bi-metallic Ag$_n$Cu$_{34-n}$ NPs revealed the effect of progressive alloying. The increase in the ratio of Ag to Cu atoms is found to increase the average bond lengths. The analyses showed that the overall properties are controlled by the interplay between coordination and the elemental environment. Increase in the number of Cu atoms in the NPs induces systematic stiffening to the force-field thus causes a shift towards high frequencies in the VDOS. Low-frequency end of the spectrum represents linear dependence on the frequency. The vibrational free energy is found to increase as the Cu content increases in the NPs. Change in the mean-square amplitudes and the Debye temperatures of the Cu and Ag atoms in these NPs can be rationalized on the basis of coordination arguments.

The results of the electronic structure calculations for the Ag$_n$Cu$_{34-n}$ NP family revealed the importance of examining the atomically-resolved contributions to the overall
properties. The bond length analysis showed that the hierarchy of the bond lengths from the shortest to the longest is in the order of Cu-Cu, Cu-Ag and Ag-Ag. The formation energy per atom decreases monotonically as the Ag to Cu ratio increases. This shows that increase in the number of Ag atoms reduces the average bonding strength owing to the fact that the number of Cu-Cu bonds decreases as these are replaced by Cu-Ag and Ag-Ag bonds, with strengths relatively lower than those of Cu-Cu. Changes induced to the electronic DOS appear as shifts towards either higher or lower binding energies as well as hybridization between the states of Cu and Ag. Each of which can be rationalized with coordination and the elemental environment arguments.

The analyses have revealed that overall properties of these finite-sized systems can be controlled by just a few atoms whose properties are distinctive. Thus examination of each atom characteristics is the key to the understanding of the properties. Analysis of each individual atom in these NPs showed that Cu atoms occupying the core -- for most of the NPs with high symmetry -- show broadening of the band owing to their being over-coordinated, and have large number of Cu neighbors. These atoms also have their center of d-states shifted towards higher binding energy as compared to that of the bulk atom. The observed broadening feature is also found for Ag atoms but only in few NPs (Ag-rich) owing to the fact most of the Ag atoms are not highly-coordinated thus the overlap of Ag wave functions are not as enhanced as those for Cu atoms. Analyses of the charge density distribution and charge density difference for one of the most symmetric NP (Ag_{17}Cu_{17}) have shown that the core of the NP gets contracted due to finite size thus the highest charge accumulation is observed in the core of the NP.
The analysis shows those NPs with a relatively large number of Cu atoms at the shell (low-coordinated) exhibit chemical reactivity. The HOMO-LUMO gaps of these Cu-rich NPs range from 0.20 eV to 0.40 eV. Since the small gap is signature of activity, for those cases the low coordination of Cu atoms in particular compositions may be the underlying reason for their reactivity. Moreover, the position of the center of the d-states of the low-coordinated Cu atoms shifts towards lower binding energies (about 1.5 eV) indicating that these atoms can be more reactive than the other Cu atoms (those in the core). This is an important result revealing the possibility of site-selective reactivity for these particular compositions. For completely closed shell NPs whose gap is large, this feature is not observed. The HOMO-LUMO gaps vary between 0.20 eV and 0.88 eV as the composition changes reflecting the fact that the HOMO-LUMO gap can be tunable by progressive alloying. Deeper analysis showed that one of the underlying reasons for the variation in these gaps is structure-oriented, and the correlation between the magnitude of the gap and the geometric structure persists throughout the whole family. Thorough analysis of the electronic structure signals that physical and chemical properties of this core-shell NP family can be tunable by controlling the chemical composition and relative sizes of core and shell.

The study combining the MD and MS simulations to reveal the atomistic processes responsible for the extraction of single atoms from mounds, and manipulation of 2D-3D clusters showed that Ag atom extraction from a Ag mound on Ag(111) is through a pulling mode, while the same for Cu system is obtained at relatively lower tip-adatom height, and through a dragging/sliding mode. The underlying reason for the extraction is attributed to the fact that the presence of tip flattens the potential energy
experienced by the diffusing atom. Tip perturbation causes reduction to the edge descent barrier thus allows the adatom to diffuse easily (hence to be extracted). For Cu case, this procedure is bit more complex involving also the manipulation of the cluster underneath the adatom. The observed difference in the extraction processes between these two systems stems from the difference in their cohesive energies and lattice constants indicating that the interactions between the Cu atoms are stronger than those for Ag atoms.
LIST OF PUBLICATIONS


2 Handan Yildirim and T. S. Rahman, Diffusion Barriers for Ag and Cu adatoms on the Terraces and Step Edges on Cu(100) and Ag(100): An Ab-initio Study, Phys. Rev. B 80, 235413 (2009)


8Handan Yildirim, A. Kara, S. Durukanoglu and T.S. Rahman, Calculated Pre-Exponential Factors and Energetics for Adatom Hopping on Terraces and Steps of Cu(100) and Cu(110), Surf. Sci. 600, 484-492 (2006)

9Handan Yildirim and T. S. Rahman, A first-principles study of the effect of lattice strain on diffusion energetics, to be submitted

10Handan Yildirim, A. Kara and T. S. Rahman, Electronic Structure of Ag$_n$Cu$_{34-n}$ Nanoparticle Family, to be submitted

11Handan Yildirim, A. Kara and T. S. Rahman, Multi-Scale Simulation of Multi-atom Diffusion: Application to 7-atom Concerted Motion, to be submitted

12Handan Yildirim, A. Kara and T. S. Rahman, Energetics and Atomistic Process for 2D Cu cluster Diffusion on Ag(111), to be submitted
Starting with the equation for the prefactor using the vibrational free energy:

\[
D_0 = \frac{k_B T}{\hbar} n d^2 \exp \left( \frac{-\Delta F_{vib}}{k_B T} \right)
\]

(A.1)

where \( \Delta F_{vib} = F_{vib}^{\text{hollow}} - F_{vib}^{\text{saddle}} \). The vibrational free energy is expressed as:

\[
F_{vib} = k_B T \sum \ln 2 \sinh \left( \frac{h \nu_i}{2k_B T} \right)
\]

(A.2)

The Vineyard equation for the prefactor is given by the following equation:

\[
D_0 = A \prod_{i=1}^{3N} \frac{V_i^{\text{hollow}}}{V_i^{\text{saddle}}}
\]

(A.3)

at the high temperature limit, where \( k_B T \gg h \nu \) and \( x = \frac{h \nu}{k_B T} \). Applying the condition at high temperature limit as \( \sinh(x) \rightarrow x \) when \( x \rightarrow 0 \), we re-write the equation A.2 for the vibrational free energy as:

\[
F_{vib} = k_B T \sum \ln 2 \sinh \left( \frac{h \nu_i}{2k_B T} \right)
\]

(A.4)

\[
F_{vib} = k_B T \sum \ln \left( \frac{h \nu_i}{k_B T} \right)
\]

(A.5)

Inserting this new equation (A.5) for the vibrational free energy into the equation A.1 for the prefactor, the equation A.1 is re-written as:
We have reached the equation A.12 that is equal to the equation A.3, where A is constant for a given process on a given surface.
## Frequencies of the Normal Modes of Adatom

**Table B.1.** The frequencies of Cu and Ag adatoms on Cu(100) and Ag(100) (in parenthesis) using EAM-FBD, EAM-VC and DFT-GGA (without substrate contribution)

<table>
<thead>
<tr>
<th>Processes</th>
<th>Direction of he mode</th>
<th>Frequencies EAM-FBD (THz)</th>
<th>Frequencies EAM-VC (THz)</th>
<th>Frequencies DFT (GGA) (THz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>Hollow</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$x, y$ 3.28 (2.26)</td>
<td>3.82(2.52)</td>
<td>3.58(2.68)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.71(3.50)</td>
<td>5.04(3.26)</td>
<td>4.80(3.24)</td>
</tr>
<tr>
<td></td>
<td>Saddle</td>
<td>$y$ 2.95(1.99)</td>
<td>3.55(2.36)</td>
<td>3.38(2.43)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 5.30(3.75)</td>
<td>5.68(3.67)</td>
<td>5.18(3.62)</td>
</tr>
<tr>
<td>P2</td>
<td>Hollow</td>
<td>$x$ 3.46(2.35)</td>
<td>3.77(2.47)</td>
<td>3.86(3.03)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y$ 3.50(2.38)</td>
<td>3.81(2.52)</td>
<td>3.69(2.83)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.80(3.53)</td>
<td>5.12(3.33)</td>
<td>4.96(3.35)</td>
</tr>
<tr>
<td></td>
<td>Saddle</td>
<td>$y$ 3.37(2.10)</td>
<td>3.59(2.38)</td>
<td>3.58(2.80)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 5.37(3.80)</td>
<td>5.71(3.68)</td>
<td>5.26(3.54)</td>
</tr>
<tr>
<td>P3</td>
<td>Hollow</td>
<td>$x$ 3.46(2.35)</td>
<td>3.77(2.47)</td>
<td>3.86(3.03)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y$ 3.50(2.38)</td>
<td>3.81(2.52)</td>
<td>3.69(2.83)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.80(3.53)</td>
<td>5.12(3.33)</td>
<td>4.96(3.35)</td>
</tr>
<tr>
<td></td>
<td>Saddle</td>
<td>$y$ 3.17(2.02)</td>
<td>3.43(2.23)</td>
<td>3.56(2.76)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.80(3.50)</td>
<td>5.09(3.31)</td>
<td>5.27(3.54)</td>
</tr>
<tr>
<td>P4</td>
<td>Hollow</td>
<td>$x$ 3.46(2.35)</td>
<td>3.77(2.47)</td>
<td>3.86(3.03)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y$ 3.50(2.38)</td>
<td>3.81(2.52)</td>
<td>3.69(2.83)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.80(3.53)</td>
<td>5.12(3.33)</td>
<td>4.96(3.35)</td>
</tr>
<tr>
<td></td>
<td>Saddle</td>
<td>$y$ 3.30(2.07)</td>
<td>3.53(2.32)</td>
<td>3.27(2.77)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 5.42(3.83)</td>
<td>5.76(3.72)</td>
<td>5.34(3.56)</td>
</tr>
<tr>
<td>P5</td>
<td>Hollow</td>
<td>$x$ 4.24(2.90)</td>
<td>4.59(2.89)</td>
<td>4.31(3.36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y$ 3.02(2.13)</td>
<td>3.30(2.19)</td>
<td>3.46(2.55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.66(3.25)</td>
<td>4.85(3.17)</td>
<td>5.19(2.92)</td>
</tr>
<tr>
<td></td>
<td>Saddle</td>
<td>$y$ 3.28(2.08)</td>
<td>3.08(2.33)</td>
<td>3.59(2.75)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 5.32(3.79)</td>
<td>4.99(3.65)</td>
<td>5.39(3.78)</td>
</tr>
<tr>
<td>P6</td>
<td>Hollow</td>
<td>$x$ 4.24(2.90)</td>
<td>4.59(2.89)</td>
<td>4.31(3.36)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$y$ 3.02(2.13)</td>
<td>3.30(2.19)</td>
<td>3.46(2.55)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$z$ 4.66(3.25)</td>
<td>4.85(3.17)</td>
<td>5.19(2.92)</td>
</tr>
<tr>
<td></td>
<td>Saddle</td>
<td>$x$ 4.32(2.81)</td>
<td>4.33(2.74)</td>
<td>3.67(2.51)</td>
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<td></td>
<td>$z$ 4.91(3.35)</td>
<td>5.29(3.41)</td>
<td>5.50(3.76)</td>
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</table>
Prefactors and Diffusion Coefficients

(Tables B.2 and B.3)

**Table B.2.** Prefactors and diffusion coefficients at two different temperatures for adatom diffusion via hopping on flat and stepped surfaces of Cu(100) using DFT-GGA, EAM-FBD, and EAM-VC. Results in {} refer to DFT-GGA (with substrate contribution), [ ] for DFT-GGA (without substrate contribution), ( ) for EAM-FBD and (( )) for EAM-VC calculations (without substrate contribution).

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<tr>
<th>Processes</th>
<th>(D_\theta(T)) (cm(^2)/s) 300 K</th>
<th>(D_\theta(T)) (cm(^2)/s) 600 K</th>
<th>(D(T)) (cm(^2)/s) 300 K</th>
<th>(D(T)) (cm(^2)/s) 600 K</th>
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<td>P1</td>
<td>{3.00x10(^{-3})}</td>
<td>(2.95x10(^{-3})}</td>
<td>{1.72x10(^{-12})}</td>
<td>{7.06x10(^{-8})}</td>
</tr>
<tr>
<td>P2</td>
<td>{2.30x10(^{-3})}</td>
<td>(2.28x10(^{-3})}</td>
<td>{1.32x10(^{-12})}</td>
<td>{5.46x10(^{-9})}</td>
</tr>
<tr>
<td>P3</td>
<td>{1.32x10(^{-3})}</td>
<td>(1.31x10(^{-3})}</td>
<td>{1.83x10(^{-12})}</td>
<td>{4.87x10(^{-8})}</td>
</tr>
<tr>
<td>P4</td>
<td>{1.24x10(^{-3})}</td>
<td>(1.22x10(^{-3})}</td>
<td>{1.72x10(^{-12})}</td>
<td>{4.56x10(^{-8})}</td>
</tr>
<tr>
<td>P5</td>
<td>{1.24x10(^{-3})}</td>
<td>(1.23x10(^{-3})}</td>
<td>{1.14x10(^{-14})}</td>
<td>{3.72x10(^{-9})}</td>
</tr>
<tr>
<td>P6</td>
<td>{1.26x10(^{-3})}</td>
<td>(1.25x10(^{-3})}</td>
<td>{7.47x10(^{-17})}</td>
<td>{3.04x10(^{-10})}</td>
</tr>
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</table>
Table B.3. Prefactors and diffusion coefficients at two different temperatures for adatom diffusing on flat and stepped surfaces of Ag(100) using DFT-GGA, EAM-FBD and EAM-VC. Results in {} refers to DFT-GGA (with substrate contribution), [ ] for DFT-GGA (without substrate contribution), ( ) for EAM-FBD, and (( )) for EAM-VC calculations (without substrate contribution).

<table>
<thead>
<tr>
<th>Processes</th>
<th>$D_0(T)$ (cm$^2$/s) 300 K</th>
<th>$D_0(T)$ (cm$^2$/s) 600 K</th>
<th>$D(T)$ (cm$^2$/s) 300 K</th>
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<td>[2.24x10$^{-3}$]</td>
<td>[9.68x10$^{-11}$]</td>
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<td></td>
<td>(1.57x10$^{-3}$)</td>
<td>(1.56x10$^{-3}$)</td>
<td>(5.49x10$^{-12}$)</td>
<td>(9.25x10$^{-7}$)</td>
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<td>((2.01x10$^{-3}$))</td>
<td>((1.59x10$^{-11}$))</td>
<td>((1.79x10$^{-7}$))</td>
</tr>
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<td>{1.71x10$^{-3}$}</td>
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<td>{5.57x10$^{-7}$}</td>
</tr>
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<td>(1.04x10$^{-3}$)</td>
<td>(9.59x10$^{-12}$)</td>
<td>(9.98x10$^{-8}$)</td>
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<td>((9.95x10$^{-4}$))</td>
<td>((1.35x10$^{-11}$))</td>
<td>((1.16x10$^{-7}$))</td>
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<td>(1.18x10$^{-3}$)</td>
<td>(1.17x10$^{-3}$)</td>
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APPENDIX C: CHAPTER 5
Average Bond Lengths Distribution as a Function of Elemental Environment

(Tables C.1 to C.7)
### Table C1. For Cu atoms with coordination 12

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<th>0Ag</th>
<th>1Ag</th>
<th>2Ag</th>
<th>3Ag</th>
<th>4Ag</th>
<th>5Ag</th>
<th>6Ag</th>
<th>7Ag</th>
<th>8Ag</th>
<th>9Ag</th>
<th>10Ag</th>
<th>11Ag</th>
<th>12Ag</th>
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</thead>
<tbody>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
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Average Free Energy Contribution as a Function of Elemental Environment

(Values are in meV in Tables C.8 to C.14)
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<td>-53</td>
<td>-43</td>
<td>-55</td>
<td>-45</td>
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Table C.15. Total vibrational free energies of the nanoparticles and percentage contribution from low frequency end of the spectrum for some of the NPs (using Debye frequency of bulk Ag)

<table>
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<tr>
<th>Nanoparticle</th>
<th>$F_{vib}^{\text{total}}$ (eV)</th>
<th>(% contribution from low frequency)</th>
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</thead>
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<td>Ag$_{34}$</td>
<td>-1.8226</td>
<td></td>
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<tr>
<td>Ag$_{33}$Cu$_1$</td>
<td>-1.7802</td>
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<td>Ag$_{32}$Cu$_2$</td>
<td>-1.7529</td>
<td></td>
</tr>
<tr>
<td>Ag$_{31}$Cu$_3$</td>
<td>-1.7345 (73.4%)</td>
<td></td>
</tr>
<tr>
<td>Ag$_{30}$Cu$_4$</td>
<td>-1.7378</td>
<td></td>
</tr>
<tr>
<td>Ag$_{29}$Cu$_5$</td>
<td>-1.6758</td>
<td></td>
</tr>
<tr>
<td>Ag$_{28}$Cu$_6$</td>
<td>-1.6167</td>
<td></td>
</tr>
<tr>
<td>Ag$_{27}$Cu$_7$</td>
<td>-1.6129 (71.4%)</td>
<td></td>
</tr>
<tr>
<td>Ag$_{26}$Cu$_8$</td>
<td>-1.5906</td>
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<tr>
<td>Ag$_{25}$Cu$_9$</td>
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<td>Ag$<em>{24}$Cu$</em>{10}$</td>
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<td></td>
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<tr>
<td>Ag$<em>{22}$Cu$</em>{12}$</td>
<td>-1.5117</td>
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<td>Ag$<em>{21}$Cu$</em>{13}$</td>
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<td>Ag$<em>{20}$Cu$</em>{14}$</td>
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<td>Ag$<em>{18}$Cu$</em>{16}$</td>
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<tr>
<td>Ag$<em>{17}$Cu$</em>{17}$</td>
<td>-1.4351 (65.3%)</td>
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</tr>
<tr>
<td>Ag$<em>{16}$Cu$</em>{18}$</td>
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<td></td>
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<td>Ag$<em>{15}$Cu$</em>{19}$</td>
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<td>Ag$<em>{12}$Cu$</em>{22}$</td>
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<td>Ag$<em>{10}$Cu$</em>{24}$</td>
<td>-1.1530 (53.4%)</td>
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<td>Ag$<em>8$Cu$</em>{26}$</td>
<td>-1.1452</td>
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<tr>
<td>Ag$<em>7$Cu$</em>{27}$</td>
<td>-1.0826 (51.2%)</td>
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<td>-1.0322 (48.6%)</td>
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<td>Cu$_{34}$</td>
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Table C.16. Average Debye temperature $\langle \theta_D \rangle$ of the NPs together with those from constituent Ag and Cu atoms

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<th>$\langle \theta_D \rangle$ of Nanoparticles (K)</th>
<th>$\langle \theta_D \rangle$ of Cu Atoms (K)</th>
<th>$\langle \theta_D \rangle$ of Ag Atoms (K)</th>
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<td>69.6</td>
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<td>70.9</td>
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<td>Ag$_{32}$Cu$_2$</td>
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<td>69.8</td>
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<td>Ag$_{31}$Cu$_3$</td>
<td>71.5</td>
<td>98.1</td>
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<td>Ag$_{30}$Cu$_4$</td>
<td>69.2</td>
<td>85.6</td>
<td>67.0</td>
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<td>71.9</td>
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<td>Ag$_{28}$Cu$_6$</td>
<td>77.5</td>
<td>107.9</td>
<td>71.0</td>
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<td>78.3</td>
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<td>78.7</td>
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<td>97.6</td>
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<td>93.9</td>
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Center of d-band, Coordination and Average Bond Lengths in Each NP

(Figures D.1 to D.35)
Figure D.1. The Ag\textsubscript{34} NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.2. The Ag\textsubscript{33}Cu\textsubscript{1} NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.3. The Ag\textsubscript{32}Cu\textsubscript{2} NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.4. The Ag\textsubscript{31}Cu\textsubscript{3} NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.5. The Ag$_{30}$Cu$_4$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.6. The Ag$_{29}$Cu$_5$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.7. The Ag$_{28}$Cu$_{6}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.8. The Ag$_{27}$Cu$_{7}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.9. The Ag$_{26}$Cu$_8$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.10. The Ag$_{25}$Cu$_9$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.11. The Ag$_{24}$Cu$_{10}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.12. The Ag$_{23}$Cu$_{11}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.13. The Ag$_{22}$Cu$_{12}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number.

Figure D.14. The Ag$_{21}$Cu$_{13}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number.
Figure D.15. The $\text{Ag}_{20}\text{Cu}_{14}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.16. The $\text{Ag}_{19}\text{Cu}_{15}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.17. The Ag$_{18}$Cu$_{16}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.18. The Ag$_{17}$Cu$_{17}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.19. The Ag$_{16}$Cu$_{18}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.20. The Ag$_{15}$Cu$_{19}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
**Figure D.21.** The $\text{Ag}_{14}\text{Cu}_{20}$ NP  

- **a)** The position of the center of the d-band versus atom number  
- **b)** Coordination versus atom number  
- **c)** The average Ag-Ag bond length versus atom number

**Figure D.22.** The $\text{Ag}_{13}\text{Cu}_{21}$ NP  

- **a)** The position of the center of the d-band versus atom number  
- **b)** Coordination versus atom number  
- **c)** The average Ag-Ag bond length versus atom number
Figure D.23. The Ag\textsubscript{12}Cu\textsubscript{22} NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.24. The Ag\textsubscript{11}Cu\textsubscript{23} NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
**Figure D.25.** The Ag$_{10}$Cu$_{24}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

**Figure D.26.** The Ag$_{9}$Cu$_{25}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.27. The Ag$_8$Cu$_{26}$ NP  

a) The position of the center of the d-band versus atom number  
b) Coordination versus atom number  
c) The average Ag-Ag bond length versus atom number

Figure D.28. The Ag$_7$Cu$_{27}$ NP  

a) The position of the center of the d-band versus atom number  
b) Coordination versus atom number  
c) The average Ag-Ag bond length versus atom number
Figure D.29. The Ag$_6$Cu$_{28}$ NP

a) The position of the center of the d-band versus atom number

b) Coordination versus atom number

c) The average Ag-Ag bond length versus atom number

Figure D.30. The Ag$_5$Cu$_{29}$ NP

a) The position of the center of the d-band versus atom number

b) Coordination versus atom number

c) The average Ag-Ag bond length versus atom number
Figure D.31. The Ag₄Cu₃₀ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.32. The Ag₃Cu₃₁ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.33. The Ag$_2$Cu$_{32}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number

Figure D.34. The Ag$_1$Cu$_{33}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Figure D.35. The Cu$_{34}$ NP a) The position of the center of the d-band versus atom number b) Coordination versus atom number and c) The average Ag-Ag bond length versus atom number
Electronic Densities of States (EDOS) of Each NP

(Figures E.1 to E.33)
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1) Surface vibrational thermodynamics from ab initio calculations for fcc(1 0 0), Surface Science, Volume 604, Issues 3-4, 15 February 2010, Pages 308-317

2) Calculated pre-exponential factors and energetics for adatom hopping on terraces and steps of Cu(1 0 0) and Cu(1 1 0), Surface Science, Volume 600, Issue 2, 15 January 2006, Pages 484-492

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Handan Yildirim, Abdelkader Kara and Talat S Rahman

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