Multiscale Simulation Of Laser Ablation And Processing Of Semiconductor Materials

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MULTISCALE SIMULATION OF LASER PROCESSING AND ABLATION OF SEMICONDUCTOR MATERIALS

by

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ABSTRACT

We present a model of laser-solid interactions in silicon based on an empirical potential developed under conditions of strong electronic excitations. The parameters of the interatomic potential depends on the temperature of the electronic subsystem $T_e$, which is directly related to the density of the electron-hole pairs and hence the number of broken bonds. We analyze the dynamics of this potential as a function of electronic temperature $T_e$ and lattice temperature $T_{ion}$. The potential predicts phonon spectra in good agreement with finite-temperature density-functional theory, including the lattice instability induced by the high electronic excitations. For 25fs pulse, a wide range of fluence values is simulated resulting in heterogeneous melting, homogenous melting, and ablation. The results presented demonstrate that phase transitions can usually be described by ordinary thermal processes even when the electronic temperature $T_e$ is much greater than the lattice temperature $T_L$ during the transition. However, the evolution of the system and details of the phase transitions depend strongly on $T_e$ and corresponding density of broken bonds. For high enough laser fluence, homogeneous melting is followed by rapid expansion of the superheated liquid and ablation. Rapid expansion of the superheated liquid occurs partly due to the high pressures generated by a high density of broken bonds. As a result, the system is readily driven into the liquid-vapor coexistence region, which initiates phase explosion. These results strongly indicates that phase explosion, generally thought of as an ordinary thermal process, can occur even under strong non-equilibrium conditions when $T_e >> T_L$. In summary, we present a detailed investigation of laser-solid interactions for femtosecond laser pulses that yield strong far-from-equilibrium conditions.
This Thesis is dedicated to my parents (Mahavir Shokeen and Prem Lata), loving wife (Neha), younger sisters (Namita and Ekta) and daughter (Netanya, who was born during the course of my PhD).
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CHAPTER 1. INTRODUCTION

1.1 Laser ablation and processing of semiconductor materials

For some time now lasers have been used in almost every field of science and technology. Major laser applications include microscopy, spectroscopy, materials processing, photochemistry, micromachining and photochemistry [1-3]. Recent advances in femtosecond laser technology have attracted many semiconductor producers to use femtosecond lasers for cutting high precision semiconductor wafers [4, 5]. Lasers can modify semiconductor surfaces by exciting electrons into anti-bonding states [6]. Another potential use of femtosecond lasers is in developing tools to cut high explosive materials without the danger of detonation [7]. This is possible because of the fact that very little amount of heat energy and mechanical shock is transferred to the surroundings while using femtosecond lasers [8]. It is very interesting and important to understand how materials interact with short pulse lasers to get insight into how processing conditions affect the resulting material structure. Laser irradiation produces intense amount of heat, which can melt the material by thermal or non-thermal processes [9-14]. This ability of lasers to produce extreme high temperatures in short time interval with high monochromaticity and coherency make them very useful in applications like cutting, welding, bending, and brazing. In the semiconductor industry lasers are also used for pulsed-laser annealing [15]. Laser pulses in some applications can be as short as 5fs [16], but for most processing applications pulse widths closer to 100fs [17] are commonly used. In various laser ablation processes like cutting, resistor trimming or high precision drilling, femtosecond pulses have great advantages over conventional nanosecond and picosecond lasers because femtosecond
laser pulses can achieve precise control over the material structure and the laser effect can be confined to a very small volume [18-20]. For example, pulsed laser ablation is able to machine deep, small holes with great precision as shown in Fig.1, where a comparison is shown between the holes drilled by fs and ns laser pulses [21].

![Diagram](https://via.placeholder.it/)

**FIGURE 1:** (a) Comparison of collateral heat damage by three types of laser: continuous wave laser, ns laser, and ps/fs laser [21]. The heat damage to the surroundings is least in the case of ps/fs laser. (b) Comparison of fine hole drilled by fs laser (left) and ns laser (right). It can be seen that hole drilled by fs laser does not show any collateral heat damage while the hole drilled by ns laser show large amount of collateral damage.

Various laser parameters coupled with material’s physical properties defines the nature of physical phenomenon and processes involved in laser-solid interaction. Pulse duration, wavelength, and intensity of the laser are the most important laser parameters. The fluence (F) is
the incident energy per unit area. When material is exposed to a femtosecond laser pulse, the various resulting physical processes like excitation, melting or ablation occur at different time scales [11] as shown in Fig. 2. Excitation of electrons takes place during the pulse itself followed by melting and ablation with timescales in range of picoseconds and nanoseconds respectively.

In metals, free electrons absorb photonic energy and are excited to higher energy levels. In semiconductors, photons with energy larger than the band gap excite electrons from the valence band to empty conduction-band states. Excited electrons transfer energy to the lattice by emitting phonons. The dissipation of the energy is quite complex and involves a wide range of time scales. Over very short timescales (10-100/fs), electron-electron scattering leads to a local equilibrium carrier distribution with extremely high electronic temperature $T_e$. Excited electrons can rapidly emit LO phonons (~200/fs), but complete transfer of energy from the excited electrons to the lattice takes at least few picoseconds [22, 23]. This timescale plays an extremely important role in determining whether the resulting processes will be thermal or non-thermal in nature [24]. When the pulse duration is larger than the equilibration time as in the case of nano second pulses, the phase changes involved can be considered as thermal processes involving quasi-equilibrium thermodynamic states [12] as in the heterogeneous or homogenous melting [25]. For these longer pulses the electron-phonon coupling raises the lattice temperature and ordinary thermal melting occurs. In contrast, for pulse duration less than the equilibration time as in femtosecond lasers, a strong non-equilibrium state between electrons and phonons is produced which results in processes like melting to occur below the thermodynamic melting temperature of the material. These processes are generally referred as non-thermal processes.
FIGURE 2: Typical time scales and intensity ranges of the processes occurring during and after a solid material interact with a 100fs laser pulse [11]. Excitation occurs at a femtosecond timescale which is also the duration of the pulse. Melting occurs on a picosecond time scale and ablation can last up to few nanoseconds.

The possibility of non-thermal processes has been explored experimentally. For very short pulses (~100fs) [12], time–resolved experiments show that lattice destabilization caused by high densities of electron-hole pairs is the dominant mechanism for melting [26, 27]. There have been numerous molecular dynamics (MD) simulation studies of laser-solid interactions [28-34]. The basic approach is to locally heat the material and observe melting and ablation processes. Electronic structure calculations have been used for silicon [35-37], indium antimonide [14],

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germanium [38, 39] and gallium arsenide [27, 40, 41] to elucidate the lattice destabilization during laser excitation.

Currently, the available theoretical tools are not able to explain the detailed structural evolution and relevant timescales involved in the laser-solid interactions in semiconductors when transitions occur in a strong-nonequilibrium state characterized by a high density of electron-hole pairs. In this case, phase transitions may not be representative of ordinary thermal transitions, which have been widely studied using MD simulation. The commonly used approaches for these studies are based on finite temperature density-functional theory (DFT) [37, 42]. Studies using finite-temperature DFT are limited to short length (10–20 Å) and timescales (~5 ps). Hence, direct modeling of the processes of annealing, melting, or ablation is not currently feasible using DFT. However, at present, there are no real atomic-scale computational studies available which can capture the lattice destabilization effect. To capture effect of lattice destabilization, we need to develop empirical potentials whose parameters depend on the electronic temperature $T_e$. This is the main motivation in developing our multiscale model for laser-solid interactions.

1.2 Previous computational and experimental studies

There have been numerous molecular dynamics (MD) simulation studies of laser-solid interactions [28-34]. The basic approach is to locally heat the material and observe melting and ablation processes. For example, Lorazo et al. [12] used molecular dynamics simulation coupled to a Monte-Carlo model for the electronic carriers to elucidate the thermodynamic pathways of transitions, including solidification, melting and ablation in silicon. Similar approaches have been used to study the effect of laser on metal surfaces [28, 29, 31, 32, 43-45]. For metals a
microscopic approach has been used to study the transient behavior of electrons and phonons [11, 46, 47], which has considered the temporal evolution of electrons and phonons distribution functions. MD studies have also been used to elucidate the complex dynamics that results in the formation of nanobumps on metal surfaces [45, 48]. However, these molecular dynamics studies have considered only the regime where melting and ablation occurs due to thermal heating of the lattice, and not due to destabilization of lattice due to high densities of electron-hole pairs.

Electronic structure calculations based primarily on density-functional theory have been used extensively in recent years to study lattice destabilization during laser excitation in silicon [37, 42, 49-51], silica [52], graphite [53-57], diamond [55] and GaAs [49]. For example, in the case of silicon, finite-temperature DFT simulation have shown that weakening of the covalent bonds occurs after strong electronic excitation, resulting in destabilization of the lattice [37, 42, 51]. While electronic-structure methods can elucidate many critical aspects of non-thermal melting, applications are limited to short length (10~20 Å) and time (~5ps) scales. As a result it is still a challenge to relate electronic-structure studies of non-thermal melting to experimental observations.

Laser ablation and materials processing phenomenon can be observed through many experimental techniques, which includes x-ray diffraction [9, 58], ellipsometry [27, 59] and shadowgraphs [60]. The development of new time-resolved experimental techniques presents an important opportunity to elucidate the relationship between non-thermal melting and materials evolution at longer length and time scales. Several groups have directly observed the rapid production of liquid by non-thermal transitions, and in-situ x-ray diffraction has provided direct
visualization of the atomic motion in indium antimonide [61]. However, there are many unanswered fundamental questions relating to the details of the structural evolution and the relevant time scales under conditions of high electronic excitation. For example, one interesting possibility is that a regime exists where thermal melting transitions occur at a temperature lower than the ordinary melting transition due to softening of the lattice [41].

There are theories present to understand the laser-solid interaction by applying continuum-level heat flow equations for the electrons and phonons. For metals, two-temperature model (TTM) has been used to describe the phenomenon of transfer of energy from the hot electrons to cold lattice [44]. The two-temperature model describes the laser-solid interactions well when the laser pulse duration is comparable to thermalization time. But for ultra-short pulses this model is not valid anymore because the time-scales are extremely different. In TTM, the lattice temperature ($T_L$) and electronic temperature ($T_e$) reaches equilibrium using coupled differential equations as given below:

\begin{align}
    C_e(T_e) \frac{\partial T_e}{\partial t} &= \nabla [\kappa_e(T_e)\nabla T_e] G(T_e - T_L) + S(z,t) \tag{1} \\
    C_L(T_L) \frac{\partial T_L}{\partial t} &= \nabla [\kappa_L(T_L)\nabla T_L] G(T_L - T_e) \tag{2}
\end{align}

Recently, coupled atomistic–continuum models of laser–solid interactions are developed, in which the Eq. 1 describes electrons and the atoms are treated with molecular dynamics including a coupling term with the electrons [28-34]. For example, Ivanov and Zhigilei [31, 32] have shown that either heterogeneous or homogeneous melting can occur depending on the pulse duration and fluence.
To summarize, at present the available theoretical tools are unable to completely resolve the questions of structural evolution and relevant timescales involved in laser-solid interactions. Approaches based on finite temperature density functional theory (DFT) \([42, 62]\) and tight-binding have shown that electronic excitation in silicon leads to melting and a resultant liquid with properties quite distinct from ordinary liquid silicon. Recently it has been shown that electronic excitation in silicon can lead to lattice instabilities as exhibited by transverse acoustic (TA) phonon modes with imaginary frequencies \([51]\). However, DFT approaches are limited in their ability to directly model annealing, melting or ablation because of it is limited to shorter length and time scales. Instead molecular dynamics simulation with empirical potentials is often applied to study laser processing and ablation. However empirical potentials have not been developed to capture the effect of lattice instabilities due to electronic excitations.

1.3 Presented study

As described in the previous section, none of the previously available methods are able to completely describe the matter evolution under far-from-equilibrium conditions. The author presents in this dissertation a complete multiscale model for laser-solid interaction in silicon appropriate for far-from-equilibrium conditions. An empirical potential was developed for silicon whose parameters depends on the temperature of the electronic subsystem \(T_e\), which is directly related to the electron-hole pair density and the density of broken covalent bonds. The parameters of the potential are obtained from fitting to a huge dataset obtained from calculations using finite temperature density functional theory (DFT).
The thermodynamics and kinetics of phase transitions predicted by the potential was analyzed as a function of $T_e$ and lattice temperature $T_{\text{ion}}$. The phonon spectra predicted by this potential is in good agreement with finite-temperature density-functional theory. The melting temperature is predicted as a function of $T_e$ and it is concluded that it strongly decreases with increase in $T_e$. In short, the empirical potential was found to include the fundamental physics predicted by the finite temperature density functional theory (DFT) calculations of melting transitions under strong non-equilibrium conditions $T_e >> T_L$.

A complete model for laser-solid interactions was developed for silicon. The time evolution of the carrier density, local electronic temperature, and electronic energy is modeled using a finite-difference approach. The electronic and ionic subsystems are coupled using an inhomogeneous Langevin thermostat using the same approach as described in Refs. [63, 64].

Finally using the complete model, a 25fs laser pulse and a wide range of fluence values has been simulated to elucidate heterogeneous melting, homogenous melting and ablation. We found that phase transitions can usually be described by ordinary thermal processes even when the electronic temperature $T_e$ is extremely high. It was determined that the high density of broken bonds plays an important role in the detailed evolution of the system.

### 1.4 Organization of Dissertation

The main focus of the dissertation is to present a model of laser-solid interaction in silicon. Various chapters in the dissertation are based on the author’s publications resulting from
the research work done during the course of his doctoral studies at University of Central Florida under the supervision of Dr. Patrick Schelling.

In the first chapter of the dissertation, which is the current chapter, the author is discussing the basic physics involved in laser-solid interactions. The details of previously done studies by various scientists in this field have been listed in this chapter. The motivation and approach of research done by author based on finite temperature density functional theory and molecular dynamics has also been highlighted in this chapter.

In the second chapter the author is presenting the details of the empirical potential developed for silicon under conditions of strong electronic excitations. The parameters of the potential are smooth functions of electronic temperature \( T_e \), determined by fitting to data obtained from finite temperature DFT calculations using ABINIT code. This potential is then used to describe the dynamics of silicon irradiated with high intensity short pulse lasers.

The third chapter contains the results, which describes the thermodynamics and kinetics of silicon under conditions of strong electronic excitations. It’s shown in this chapter that laser-induced softening of the lattice can lead to lattice cooling for very short time scales (~100 fs), the effect which has never been recognized before. The thermodynamics of the potential has been analyzed as a function of electronic temperature \( T_e \) and lattice temperature \( T_{ion} \).

In the fourth chapter describes the results showing the role of electronic-excitation effects in the melting and ablation of laser-excited silicon. The results are obtained for a 25fs pulse and a wide range of fluence values are considered resulting in three different regimes representing heterogeneous melting, homogenous melting and ablation. A detailed investigation of laser-solid
interactions for femtosecond laser pulses is presented in this chapter, concluding the author’s research in far-from-equilibrium conditions generated by laser-solid interactions.

The fifth chapter describes different computational methodologies to study thermodiffusion of hydrogen in palladium. The results are obtained using three different methodologies: 1) Direct simulation approach, 2) Green-Kubo formulae, and 3) Constrained-dynamics approach. The heat of transport and reduced heat of transport do not show strong dependence on temperature. The hydrogen is found to be traveling from low temperature to the high temperature end of the system, which is not the case found in experimental studies.
CHAPTER 2. AN EMPIRICAL POTENTIAL FOR SILICON UNDER CONDITIONS OF STRONG ELECTRONIC EXCITATIONS

2.1 Introduction to previous studies

The use of laser pulses for processing of materials has become quite widespread and the recent advances in laser studies have enabled the generation of ultrashort laser pulses (less than 100fs). These ultrashort pulses have very high energies to destabilize the lattice and generate extremely high local charge carrier densities (~ $10^{22}$ cm$^{-3}$). Many groups have observed rapid production of liquid by non-thermal phase transitions. For example, in situ x-ray diffraction has been used to directly visualize the atomic motion in indium antimonide [61]. However, there are many questions unanswered about matter evolution and the respective time scales. For example, there is a possibility that gradual transition from thermal transitions to purely non-thermal transitions can be absorbed as there exits a regime where melting transitions occur at a temperature lower than the ordinary thermal melting due to lattice softening.

Currently, there are no theoretical tools available which can completely describe the phase transitions corresponding to laser-solid interactions. Approaches based on finite-temperature density functional theory (DFT) (Refs. [37] and [42]) and tight-binding [50] show that due to electronic excitations in silicon, the covalent bonds get weaken and the crystal can melt to a liquid which has properties quite distinct from the ordinary liquid silicon. The difference observed between the two liquids was mainly the higher coordination number and a huge reduction of covalent bonding effects in laser melted silicon.
2.1.1 Approaches based on finite-temperature density functional theory

Hohenberg and Kohn showed that in an external potential $v_{ext}(\mathbf{r})$, there exists a functional of the density $F[n(\mathbf{r})]$ such that the energy $E = \int v_{ext}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + F[n(\mathbf{r})]$ has a minimum value when $n(\mathbf{r})$ equal to the ground state electron density $[65, 66]$. This problem was mapped by Kohn and Sham, onto a system of non-interacting electrons moving in an average potential, with the density given in terms of the single particle wave functions as $n(\mathbf{r}) = \sum_{\lambda} \psi_{\lambda}^*(\mathbf{r}) \psi_{\lambda}(\mathbf{r})$. This approach is the basis of modern density functional theory (DFT). Mermin showed that similar approach can be applied to finite temperatures too $[67]$. While the basic formalism for the finite-temperature DFT is well established, the applications still very limited. This approach is basically to minimize the free energy expression given by:

$$\Omega[n(\mathbf{r})] = T[n(\mathbf{r})] + E_{HXC}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r})n(\mathbf{r})d^3\mathbf{r} + E_{II} - T_e S$$  \hspace{1cm} (3)

Where, $E_{II}$ is the classic coulomb energy of the ions, $T_e$ is the electronic temperature and the electronic term is given by $S = k_B \sum_{\lambda} \left[ f_{\lambda} \log f_{\lambda} + (1 - f_{\lambda}) \log(1 - f_{\lambda}) \right]$. Where $f_{\lambda}$ are the occupancies of the single particle states. Mermin also showed that Fermi-Dirac occupation statistics corresponds to the minimum of the free energy functional. For dynamics, the forces are computed from derivatives of the above equation and $\Omega$ is a constant of motion in microcanonical MD simulation $[67-70]$. Recently it has been shown that electronic excitation in silicon can lead to lattice instabilities as exhibited by transverse acoustic (TA) phonon modes with imaginary frequencies $[51]$. Electronic-structure calculations are extensively used in recent years to study lattice destabilization during laser excitation in silicon $[37, 42, 49-51]$, silica $[52]$, graphite $[53-57]$, diamond $[55]$ and GaAs $[49]$. While electronic-structure methods can elucidate
many critical aspects of non-thermal melting, applications are limited to short length (10~20 Å) and time (~5ps) scales

2.1.2 Tight-binding molecular dynamics approach

From many years, the tight-binding molecular dynamics (TBMD) approach has been used to study the properties of silicon with cold electrons [71] as well as the hot excited electrons produced by laser induced excitations [50]. TBMD has also been used to study the laser-induce fragmentation of small silicon clusters [72], but due to lack of experimental data on small Si clusters to compare, these studies are not reliable enough to describe the properties of laser-excited silicon. Its found using constant pressure TB simulations that the nonthermal melting due to electronic excitations also induces a volume expansion opposed to a volume contraction in the ordinary thermal melting of silicon [73]. TBMD studies has an advantage over ab initio DFT calculations that role of hot-carrier diffusion can be easily incorporated in these studies as recently done for laser-induced graphitization of diamond [74]. However, it is still limited in length and time scales from empirical potentials and there is no direct coupling of electrons and phonons in these studies.

2.2 DFT database for potential

We performed finite temperature DFT calculations to get a dataset, which can be used for fitting to get the parameters of the empirical potential. ABINIT code [75] was used for these calculations. The conditions for the calculations were kept similar to the conditions presented in reference [51]. In particular, local-density approximation was used, with the 3s, 3p, 3d orbitals
included for the valence electrons. An 8X8X8 Monkhorst–Pack mesh [76] of k-points was used and the energy cutoff for the plane-wave expansion was taken to be 544 eV. Four different types of lattices (diamond, fcc, bcc, and simple-cubic) were used for calculations at seven different volumes each. Calculations were performed for 48 different electronic temperatures between $k_B T_e = 0$ and $k_B T_e = 2.50$ eV, with starting at $k_B T_e = 0.2$ eV and increments of 0.05 eV. The cohesive free energy was calculated for each case and it is shown that for the diamond lattice the results are in good agreement with prior DFT calculations [37, 42, 51]. We also calculated the TA mode frequencies $\omega_{TA}$ at the X-point using DFT. The results are in good agreement with the previous DFT results, which show that electronic excitation in silicon can lead to lattice instabilities as exhibited by transverse acoustic (TA) phonon modes with imaginary frequencies [51]. The computed phonon dispersion curves are also in good agreement with the experimental values [77].

### 2.3 Potential details

We used a recently published modified Tersoff formalism (called the MOD potential [78]) as a starting point for the empirical potential. Although there are many other potential available for silicon [79-86] but the MOD potential has been shown to provide an excellent description of the phase behavior and kinetics of silicon [78, 87]. The total energy $\Phi$ is given as:

$$\Phi = \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij})$$

(4)

$$\phi_{ij}(r_{ij}) = f_c(r_{ij})[A \exp(-\lambda_1 r_{ij}) - b_{ij} B \exp(-\lambda_2 r_{ij})]$$

(5)
\[
\begin{align*}
\beta_{ij} &= \left(1 + \xi_{ij}^{\eta}\right)^{-\delta} \\
\xi_{ij} &= \sum_{k \neq l,j} \bar{f}_c(r_{ij}) g(\theta_{ijk}) \exp\left[\alpha(r_{ij} - r_{ik})^\beta\right]
\end{align*}
\]

Where, \(r_{ij}\) is the interatomic separation and \(\theta_{ijk}\) is the bond angle between \(ij\) and \(ik\). The function \(g(\theta)\) has been modified from the Tersoff model, and is given for the MOD potential by:

\[
g(\theta) = c_1 + g_o(\theta) g_a(\theta) \tag{8}
\]

\[
g_o(\theta) = \frac{c_2(h - \cos \theta)^2}{c_3 + (h - \cos \theta)^2} \tag{9}
\]

\[
g_a(\theta) = 1 + c_4 \exp[\alpha(h - \cos \theta)^2] \tag{10}
\]

The cutoff function \(f_c(r)\) has been modified from the original Tersoff potential. For \(r \leq R_1\), \(f_c(r) = 1\), and for \(r \geq R_2 = 0\), \(f_c(r) = 0\). In this region \(R_1 < r < R_2\), the cutoff function is given by:

\[
f_c(r) = \frac{1}{2} + \frac{9}{16} \cos\left(\pi \frac{r}{R_2 - R_1}\right) - \frac{1}{16} \cos\left(3\pi \frac{r}{R_2 - R_1}\right) \tag{11}
\]

For \(k_B T_e = 0\)eV, we used the original formulation of MOD potential except with larger cut-offs (\(R_1 = 3.1\) Å and \(R_2 = 3.4\) Å) and \(\alpha = 1.90\) chosen to give a melting temperature \(T_m = 1688\) K close to experiment. For finite electronic temperatures, the parameters were fit to reproduce the DFT cohesive free energies for the diamond, fcc, bcc and simple cubic structures at several different volumes. A detailed procedure as described in Ref. [88] was used to fit the temperature-dependent empirical potential to the \textit{ab initio} DFT results. We kept some parameters fixed because they were found to not be critical for our studies. Because the potential for \(k_B T_e = 0\)eV was not fit to the DFT values, we fit instead to changes in the free energy curves as a function of \(k_B T_e\). The DFT energies were shifted to give the experimental value \(F_{\text{coh}} = 4.63\)eV in the
equilibrium structure. In Table 1 we present the parameters of the potential determined by the fitting. Initially, the fitting was done only for few values of $T_e$, but later a wide range of electronic temperatures was considered, starting from $k_B T_e = 0.2\,\text{eV}$ to $k_B T_e = 2.5\,\text{eV}$ with an increment of 0.05eV. The constant $F_0$ shown in Table 1 is added to the empirical potential to take into account the fact that the free energy of an isolated silicon atom will also depend on electronic temperature. Fig. 3 shows the comparison of the cohesive free energies calculated by DFT and the empirical potential. These values are determined at two different values $k_B T_e = 0$ and $k_B T_e = 2.15\,\text{eV}$. It can be seen from Fig. 3 that the diamond phase becomes less stable with respect to the other phases as the electronic temperature increases. This effect is due to the broken covalent bonds and softening of the lattice from high electronic excitations. Structures with larger coordination numbers like fcc, bcc and sc becomes more stable than diamond structure with increase in $T_e$. 
**TABLE 1:** Parameters used for the empirical potential for different values of $T_e$ are given in table. The notation follows Ref. [78]. Parameters not given in the table are unchanged from the original potential. The constant term $F_0$ is the free-energy of an isolated silicon atom at finite $T_e$. We also include the phonon frequency at the X-point (in cm$^{-1}$) with the lattice parameter $a=5.429$ Å and the DFT value in parenthesis for comparison.

<table>
<thead>
<tr>
<th>$k_B T_e$ (eV)</th>
<th>0.50</th>
<th>1.30</th>
<th>2.15</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (eV)</td>
<td>2944.0685</td>
<td>2179.9844</td>
<td>1827.4731</td>
<td>1761.6812</td>
</tr>
<tr>
<td>B (eV)</td>
<td>92.3232</td>
<td>53.8369</td>
<td>35.7868</td>
<td>31.8686</td>
</tr>
<tr>
<td>$\lambda_2$ (Å$^{-1}$)</td>
<td>1.223828</td>
<td>0.769646</td>
<td>0.370933</td>
<td>0.243576</td>
</tr>
<tr>
<td>$\eta X \delta$</td>
<td>0.610977</td>
<td>0.785708</td>
<td>0.867687</td>
<td>0.906381</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1.679913</td>
<td>1.328494</td>
<td>1.081435</td>
<td>1.027233</td>
</tr>
<tr>
<td>$c_1$</td>
<td>0.214947</td>
<td>0.637945</td>
<td>1.068782</td>
<td>1.155003</td>
</tr>
<tr>
<td>$c_2$</td>
<td>533198.46</td>
<td>172192.94</td>
<td>164461.57</td>
<td>160964.28</td>
</tr>
<tr>
<td>$c_4$</td>
<td>1.090</td>
<td>1.234</td>
<td>1.387</td>
<td>1.450</td>
</tr>
<tr>
<td>$F_0$ (eV)</td>
<td>0.0002</td>
<td>0.13748</td>
<td>0.8928</td>
<td>1.3400</td>
</tr>
<tr>
<td>$\omega_{TA}(X)$</td>
<td>235 (135)</td>
<td>63 (69)</td>
<td>-101 (-97)</td>
<td>-124 (-108)</td>
</tr>
</tbody>
</table>
FIGURE 3: Cohesive free energy per Si atoms determined by the finite-temperature DFT and the fit empirical potential at two values of $T_e$. The DFT results are indicated by symbols (diamonds: diamond; triangle: simple-cubic; squares: bcc; and circles: fcc), and the empirical potential is shown by lines (solid line: diamond, dotted line: simple-cubic; dashed line: bcc; and broken line: fcc).

Fig. 4 shows the dependence of the $T_{ion} = 0$K bulk modulus on electronic temperature $T_e$. The bulk modulus values are calculated from empirical potential and DFT. To obtain the value from DFT we fit the free energy vs. volume data to Birch-Murnaghan equation of state. Bulk modulus values computed using empirical potential show good agreement with DFT values, with both predicting that the bulk modulus decreases with increase in $k_B T_e$. Fig. 5 shows the
dependence of the lattice parameter of diamond structure from empirical potential and DFT on electronic temperature $T_e$. The lattice parameter from DFT is lower than empirical potential because of the fact that DFT underestimates the lattice parameter even at $k_B T_e = 0$. Finally, as $k_B T_e$ increases, the equilibrium volume of the crystal expands.

**FIGURE 4:** Bulk modulus of the diamond structure computed for the empirical potential and DFT. Red squares represent values obtained from the empirical potential and black circle represent values obtained from DFT.
FIGURE 5: Lattice parameter of the diamond structure computed for the empirical potential and DFT. Red squares represent values obtained from the empirical potential and black circle represent values obtained from DFT.

FIGURE 6: For electronic excitations $k_B T_e = 1.3\text{eV}$, $k_B T_e = 2.15\text{eV}$ and $k_B T_e = 2.5\text{eV}$, the ionic temperature $T_{ion}$ is plotted as a function of simulation time. Melting is observed for $k_B T_e = 2.15\text{eV}$ and $k_B T_e = 2.5\text{eV}$ cases but there is no melting for $k_B T_e = 1.3\text{eV}$. 
To see the effect of strong electronic excitations on ionic temperature with time, we simulated the effect of intense laser pulse by using the empirical potential corresponding to an excitation. We started with an 8x8x8 cell consisting of 4096 silicon atoms and equilibrated it at $T_{\text{ion}}=300K$ for 11.05ps. After equilibration, we instantaneously change the empirical potential to correspond to strong excitation and continue the simulation at constant energy and volume. We kept the constant volume boundary conditions for our calculations so that direct comparison can be made to existing DFT results with similar boundary conditions [37, 42]. These references use finite temperature DFT method which was also used to obtain the fitting database for our empirical potential.

As a result of strong electronic excitation, the ionic temperature evolves away from the starting temperature $T_{\text{ion}}=300K$. The evolution of the ionic temperature $T_{\text{ion}}$ can be seen in Fig. 6. For very strong excitations, $k_B T_e = 2.15eV$ and $k_B T_e = 2.5eV$, we find that the lattice melts and the ionic temperature increases dramatically in first 100fs. The final ionic temperature was found to be $T_{\text{ion}}=580K$ for $k_B T_e = 2.15eV$, which is significantly lower than the previously found value $T=1700K$ using DFT [37, 42]. This difference can be explained by the fact that the MOD potential over predicts the energy difference between diamond and the higher coordinated structures like fcc and bcc. Since, the fits at finite $T_e$ are done to reproduce the changes with $T_e$, we have a similar errors at all values of $T_e$. Therefore, a smaller change in energy is predicted (less than $\sim 0.1eV$ per atom) when structural transitions take place from low coordinated structures to highly-coordinated liquid, and hence increase in $T_{\text{ion}}$ is somewhat smaller than what is predicted by finite-temperature DFT. For $k_B T_e = 2.5eV$, we find that the final $T_{\text{ion}}=950K$. For $k_B T_e = 1.30eV$, we find that the system does not melt and that $T_{\text{ion}}$ instead of increasing, actually
decreases from the initial value of $T_{ion}=300K$ to $T_{ion}=230K$. This shows that there is no lattice instability for $k_B T_e = 1.30eV$. Instead a significant softening of the phonon modes is seen in this case. As a result of lattice softening, the atomic displacements are larger, but the average kinetic energy decreases due to weaker restoring forces. We believe that the system is still highly excited and under high stress, and hence the temperature will rise to higher values in a constant pressure simulation.

**FIGURE 7:** Radial distribution function of excited and ordinary liquid Si plotted together. The solid red line represents the radial distribution function of melted silicon after excitation at $k_B T_e = 2.15$ eV. The black dotted line represents the radial distribution function of ordinary liquid silicon when there is no excitation $k_B T_e = 0$ and ionic temperature is kept at $T_{ion}=1700K$. 
FIGURE 8: Solid red line represents the radial distribution function of melted silicon after excitation at $k_B T_e = 2.15$ eV and ionic temperature $T_{\text{ion}}=1700$K. Black dotted line represents the radial distribution function of ordinary liquid silicon when there is no excitation $k_B T_e = 0$ and ionic temperature is kept at $T_{\text{ion}}=1700$K.

We characterized the liquid and find that the structure of liquid silicon that results from strong electronic excitation is quite distinct from ordinary liquid silicon. Fig. 7 shows the radial distribution function $g(r)$ for the $k_B T_e = 2.15$ eV and $T_{\text{ion}}=640$K case compared to radial distribution function of ordinary liquid silicon without any electronic excitation and $T_{\text{ion}}=1700$K. In the excited Si, the first peak occurs at 2.55 Å, while in ordinary liquid silicon the first peak is observed at 2.42 Å. We see a sharp minimum 3.13 Å, which is quite different from the DFT predictions [37, 42] of excited silicon. By setting this minimum as cutoff we find the coordination number of the liquid, which came out to be 5.31. When the ionic temperature of the excited liquid is increased from $T_{\text{ion}}=640$ to $T_{\text{ion}}=1700$K, this sharp minimum largely goes away.
as shown in the Fig. 8. For this case, using 4.0 Å as the cutoff, the coordination number comes around 12.71, which is quite close to the DFT value ranging from 11 to 13 [37, 42]. We conclude that the structure of liquid silicon with strong electronic excitations is quite different from the ordinary liquid silicon. Moreover, the predictions of the empirical potential are in reasonably good agreement with predictions of finite-temperature DFT simulations.

In Summary, we have developed an empirical potential for silicon whose parameters depends on the electronic temperature $T_e$. We elucidated some aspects of melting in conditions of strong electronic excitations and found that melting temperature decreases with increasing $T_e$. This dependence of melting temperature on $T_e$ will be discussed in more details in next temperature. For liquid resulting from the excitation, we find a distinct structure compared to ordinary liquid silicon.
CHAPTER 3. THERMODYNAMICS AND KINETICS OF SILICON UNDER CONDITIONS OF STRONG ELECTRONIC EXCITATION

3.1 Introduction

The empirical potential for silicon described in chapter 2 is explored in detail in this chapter. The thermodynamics of the potential is analyzed as a function of electronic temperature $T_e$ and lattice temperature $T_{ion}$. Rather than using parameters for the potential that are only determined at few values of $T_e$, the parameters of the potential were determined as smooth functions of the electronic temperature $T_e$, with dependence obtained by fitting to finite temperature density functional theory simulations.

3.2 Approach

The empirical potential parameters were fit to finite-temperature DFT calculations for electronic temperature range between $k_B T_e=0.2\text{eV}$ and $k_B T_e=2.5\text{eV}$ with increments of $0.05\text{eV}$, so we obtained a smooth dependency on $k_B T_e$. The $k_B T_e$ dependence is then fit to a polynomial of order 6. For example, $A(T_e)$ the parameter which represents the strength of the repulsive interaction (in eV) depends on $T_e$ in the form

$$A(T_e) = \sum_{n=0}^{6} a_n (k_B T_e)^n$$  \hspace{1cm} (12)

The coefficients of parameters are given in Table 2. For the parameter $a_0$ in each case, we use the original modified Tersoff potential (MOD) parameters [78]. The parameter $\alpha$ is chosen to be 1.9 for the $k_B T_e=0$ case to give the melting temperature close to experimental value $T_m=1688\text{K}$. The
constant $F_0$ is added to take into account the fact that the free energy of an isolated silicon atom will also depend on $k_B T_e$.

**TABLE 2**: Expansion coefficients for the power-series representation of the dependence of the potential parameters on $k_B T_e$. The notation follows ref. [78]. The physical dimensions of the expansion coefficients are not given. However, the dimension of the potential parameters is given in the left column, and the dimensions of the expansion coefficients can be inferred.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
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<td>$A(eV)$</td>
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<td>-2228.6</td>
<td>2188.300</td>
<td>-1079.8</td>
<td>297.01</td>
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</tr>
<tr>
<td>$B(eV)$</td>
<td>121.0047</td>
<td>-15.679</td>
<td>0171.11</td>
<td>237.28</td>
<td>-145.08</td>
<td>42.934</td>
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<td>$\lambda_d(\AA^{-1})$</td>
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<td>-0.7608</td>
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</tr>
<tr>
<td>$\eta\chi\delta$</td>
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<td>0.6076</td>
<td>-0.4737</td>
<td>0.1070</td>
<td>0.0128</td>
<td>-0.0055</td>
</tr>
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<td>$\alpha$</td>
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<td>-0.1281</td>
<td>0.0291</td>
<td>0.0735</td>
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<td>$c_1$</td>
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<td>0.8593</td>
<td>-0.8428</td>
<td>0.7992</td>
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</tr>
<tr>
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<td>0.2325</td>
<td>-0.6229</td>
<td>0.6668</td>
<td>-0.2421</td>
<td>0.0299</td>
</tr>
</tbody>
</table>
FIGURE 9: Cohesive free energy $\Delta F_{\text{coh}}$ computed with respect to the diamond phase as a function of $k_B T_e$ for the fcc (dotted line), bcc (dashed line) and simple-cubic (solid line) phases. Each curve is determined at an atomic value $\Omega_{\text{at}}=20.0 \ \text{Å}^3$. For comparison, DFT values of same quantities are also shown at few values of $k_B T_e$ for different phases, simple-cubic (circles), bcc (squares), and fcc (diamonds). The negative value of $\Delta F_{\text{coh}}$ represents that diamond phase is more stable than other phases while positive value of $\Delta F_{\text{coh}}$ represents that other phase is more stable than diamond phase. For small values of $k_B T_e$, diamond phase is more stable while at higher values of $k_B T_e$, diamond phase is no longer stable and other phase become more stable.

We saw in last chapter that the dependence of the lattice parameter and bulk modulus on $k_B T_e$ predicted by the potential is in very good agreement with the finite-temperature DFT calculations. Here in Fig. 9 we plot the cohesive energy per atom $\Delta F_{\text{coh}}$ of the various phases (fcc, bcc and simple-cubic) relative to the diamond phase. These values are calculated at atomic volume $\Omega_{\text{at}}=20.0 \ \text{Å}^3$. It is evident from the Fig. 9 that when there is no excitation $k_B T_e=0\text{eV}$, the cohesive energy of diamond phase is much larger than that of the other phases ($\Delta F_{\text{coh}}$ is negative),
which is expected since the diamond phase is the stable phase of silicon in ground state conditions. The empirical potential over predicts the energy difference between diamond phase and other phases at $k_B T_e=0$. As we fit the energy differences with respect to $k_B T_e$ instead of fitting to absolute values of $\Delta F_{coh}$, the general dependence on $k_B T_e$ is very well reproduced in Fig. 9. The value of $\Delta F_{coh}$ for the fcc, bcc and simple-cubic phases tend to increase as $k_B T_e$ increases, becoming zero at some point and then eventually becoming positive, indicating that diamond is the least stable crystalline phase at high $k_B T_e$ values. For the empirical potential at $k_B T_e=1.75$eV, the simple-cubic phase becomes energetically more favorable than the diamond phase. By contrast, we see that in the DFT calculations the simple-cubic phase become stable than diamond at $k_B T_e=1.25$eV. This difference in empirical potential and DFT is due to the initial disagreement in the MOD potential at $k_B T_e=0$ for the relative energies of the different phases. For higher values of $k_B T_e$, at around $k_B T_e = 2.5$eV, the difference between various phases becomes extremely small which is consistent with the finite temperature DFT predictions. From the cohesive free energy curves we can predict the structural evolution of silicon with increase in $k_B T_e$. In particular, when the values of $k_B T_e$ increase, the diamond phase becomes destabilized with respect to other crystalline phases. The higher-coordinated phases become more favorable than the open diamond structure, which requires strong directional bonding. This trend is also followed by the liquid phase as seen in the previous chapter, where liquid formed in conditions of strong electronic excitation is more highly coordinated than the ordinary liquid silicon, which still retains mainly four-fold coordinated atoms.

The cohesive free-energy differences between various phases predicted by empirical potential and finite-temperature DFT have important consequences when silicon interacts with a
laser pulse. When a laser pulse is incident on a silicon surface, the system experiences a rapid increase in electronic energy $k_B T_e$, which can make the diamond phase unstable before the atoms are significantly displaced. As a result of this lattice instability, the lattice temperature increases very rapidly in first 100fs, which is shown in Fig. 6 in Chapter 2. The increase in $T_{ion}$ predicted by the empirical potential is somewhat smaller than what is seen in the finite-temperature DFT results because the empirical potential predicts a smaller $\Delta F_{coh}$ (when $\Delta F_{coh}$ is positive) in comparison to the finite-temperature DFT results.

**FIGURE 10:** Phonon frequencies computed by the empirical potential for the $\Gamma$-point LO/TO (solid line), and $X$-point LA/LO (dotted line), TO (dot-dashed line), and TA (dashed line) branches in the diamond lattice with $\Omega_m=20.0 \text{ Å}^3$ as a function of the electronic temperature $k_B T_e$. The finite-temperature DFT results are also shown for the $\Gamma$-point LO/TO (circles), and $X$-point LA/LO (diamonds), TO (triangles), and TA (squares). Negative frequencies in the TA branch correspond to instabilities.
Another way to get an insight into the destabilization of the diamond phase is to determine the dependence of the phonon frequencies on $k_B T_e$ [51]. The softening of the transverse acoustic (TA) phonon branch shows the destabilization of diamond lattice due the electronic excitation. At very high electronic excitation due to a laser pulse, the TA branch becomes unstable and the restoring force that stabilizes the diamond lattice vanishes. As a result, a phase transition from diamond to a highly-coordinated liquid phase occurs. For $\Omega_{at}=20.0$ Å³, we computed the phonon frequencies as a function of electronic energy $k_B T_e$ for the diamond lattice using ABINIT code and following the same method used by Recoules [51]. In this method density functional perturbation theory (DFPT) [89, 90] is used to quantify the effect of electronic excitation on potential energy surface. The effects of electronic excitations are incorporated using the Fermi-Dirac distribution [89, 90]. These frequencies are plotted as function of $k_B T_e$ as shown in Fig. 10. TA phonon frequencies computed using the empirical potential are in good agreement with the finite-temperature DFT calculations. The agreement with finite-temperature DFT calculations is even better for higher values of $k_B T_e$ than for $k_B T_e=0$ where the MOD potential is used with minor changes in cutoffs and alpha parameter. The interatomic bonds are weakened with increase in $k_B T_e$, which was also seen from the bulk modulus variation with $k_B T_e$ [41]. At about $k_B T_e=1.45eV$, the TA zone-edge phonons becomes unstable as can be seen by negative frequencies in Fig. 10. Although, the TA mode instability occurs at a lower value of $k_B T_e$ for empirical potential than finite temperature DFT, the results demonstrate that the empirical potential predicts the right trends and qualitative behavior. The next section explores the thermodynamics and kinetics of potential for finite values of $T_{ion}$, which is an important aspect of a complete model for laser-solid interactions.
3.3 Thermodynamics and kinetics for finite ionic temperature

In this section, we will explore the various aspects of equilibrium thermodynamics and kinetics of the empirical potential. The interatomic bonds are greatly altered when $k_B T_e$ becomes high due to large electron-hole excitations produced by laser pulse. As a result, the thermodynamic properties are strongly dependent on $k_B T_e$. Generally, when we talk about equilibrium thermodynamics the ionic temperature $T_{ion}$ should be equal to electronic temperature $T_e$. However, in our calculations, we have the freedom to fix the $T_{ion}$ and $T_e$ independently because $T_e$ only determines the nature of the interatomic potential. Hence, the simulations reported here represent the dependence of the thermodynamics and kinetic properties of the potential as a function of $T_e$. However, it may be very difficult to verify the results experimentally. Nevertheless, it has previously been shown that equilibrium thermodynamic properties can often be relevant to developing an understanding of strong nonequilibrium physics, including in studies of laser ablation of silicon [12].

3.3.1 Lattice thermal expansion

In Fig. 11, zero-pressure lattice parameters are plotted as a function of lattice temperature $T_{ion}$ and electronic energy $k_B T_e$. These results are obtained for diamond lattice using Parrinello-Rahman algorithm [91] at constant pressure (P=0). The lattice parameter increases with increasing in $k_B T_e$ due to the bond-weakening effect at higher values of $k_B T_e$. With increase in $k_B T_e$, the dependence of lattice parameter on $T_{ion}$ exhibits an interesting behavior, which is shown in Fig. 11. The values of lattice parameters in Fig. 11 are given up to the point where the lattice melts, which occurs when $T_{ion}$ becomes larger than the melting temperature $T_m$ of the crystal at that particular $k_B T_e$. To get a deeper insight into the thermal expansion behavior, we
plot the thermal coefficient of thermal expansion $\alpha_L$ (at $T_{\text{ion}} = 150K$) as a function of $k_B T_e$ in Fig. 12. We can see that for $k_B T_e$ less than 1.0eV, $\alpha_L$ is very weakly dependent on $k_B T_e$. After $k_B T_e = 1$eV, the $\alpha_L$ decreases very sharply and eventually becoming highly negative around $k_B T_e = 1.5$eV. After $k_B T_e = 1.5$eV, $\alpha_L$ starts increasing again and approaches zero around $k_B T_e = 2.25$eV. We can conclude that after the initial rapid expansion due to laser excitation, thermal expansion of the crystal follows rather complex behavior.

**FIGURE 11:** Lattice parameter $a$ plotted as function of ionic temperature $T_{\text{ion}}$ at several values of $k_B T_e$. The curves gets terminated when the crystal get melted which happens when $T_{\text{ion}}$ is greater than $T_m$ that particular value of $k_B T_e$. Where, $T_m$ is the melting temperature at the particular value of $k_B T_e$. 
FIGURE 12: Thermal expansion coefficient $\alpha_L$ plotted as a function of $k_B T_e$ determined at $T_{ion}=150K$. $\alpha_L$ depends weakly in the beginning but then strong decrease and later again starts increasing following a complex behavior after $k_B T_e = 1.0eV$.

3.3.2 Melting transition

To determine the melting temperature $T_m$ from the empirical potential, we simulated liquid-solid coexistence at zero pressure [85, 87, 92]. The system consisted of a 6x6x40 diamond lattice with 11520 atoms. The system was first equilibrated for 5.52ps at a constant temperature, which was set at the estimated melting temperature for the potential. After equilibrating the crystal, half of the atoms in the crystal were fixed in the place while heating the remaining half to a very high temperature of 3000K for 10.52ps. This results in melting half crystal while other half remains perfect diamond crystal. These simulations were done at constant volume conditions. After this the system was cooled to the estimated melting temperature and again equilibrated at that temperature for 11.05ps. During the last step, the fixed atoms were released and the system cell length along the z direction, which is the direction perpendicular to the
liquid-solid interface, was allowed to vary to establish a zero stress condition. The dimensions in the plane of interface were kept fixed at the predicted zero-stress lattice parameters of the crystal. Because the last simulation step is a constant-energy simulation, the system will always evolve toward the coexistence point due to the latent heat of melting. To obtain an accurate value of $T_m$, the temperature was time-averaged for $1\text{ns}$ once the equilibrium was achieved. To remove the inaccuracy of estimated melting temperature in the first step, we used the final value of $T_m$ as the starting point for the next similar run, repeating the cycle 2-3 times. These iterative steps are important because they help in determining the correct choice of lattice parameter in the xy-plane. After 2-3 similar iterations, an accurate value of melting temperature for the potential was obtained.

The results for melting temperature as a function of $k_B T_c$ are shown in Fig. 13. It is evident from the Fig. 13 that the melting temperature decreases sharply with increasing $k_B T_c$. This result is expected due the bond-weakening effect in diamond lattice with increasing $k_B T_c$. For values above $k_B T_c=1.5\text{eV}$, we were unable to stabilize the diamond phase, which might indicate the presence of other crystalline phases. For $k_B T_c=1.5\text{eV}$, melting point was found to be around 300K which indicates that only a slight in increase in lattice temperature should melt the crystal.
FIGURE 13: The melting temperature $T_m$ computed using the empirical potential plotted as a function of $k_B T_e$. The values of $T_m$, at various $k_B T_e$ values, are computed using simulations of liquid-solid coexistence at zero pressure.

3.3.3 Melting kinetics

To determine the melting kinetics of the potential, we used an approach similar similar to the melting calculations described in the previous section. The only difference was in the last step, which was a constant temperature run now instead of a constant energy run near the coexistence point. The final simulation step at constant temperature near coexistence point results in either melting or solidification. The interface velocity is plotted as function of temperature $T_{ion}$ in Fig. 14 for a few different values of the electronic temperature $T_e$. We plotted the interface velocity as a function of the difference between the lattice temperature and the melting temperature, $T_{ion} - T_m$. Negative values of the interface velocity indicates melting, while positive interface velocity indicates crystallization. Three values of $k_B T_e$ are considered for these
calculations $k_B T_c = 0$, $k_B T_c = 0.5 \text{eV}$ and $k_B T_c = 1.25 \text{eV}$. We see from Fig.14 that the rate of melting is similar for all three cases of $k_B T_c$ considered. However, while the rate of crystallization is similar for $k_B T_c = 0$ and $k_B T_c = 0.5 \text{eV}$, for $k_B T_c = 1.25 \text{eV}$ the rate of crystallization is very low. The dependence of the melting or crystallization kinetics on $k_B T_c$ depends upon two factors. First, the driving force for crystallization is lower for high $k_B T_c$ because of the fact that the diamond lattice becomes less stable at high $k_B T_c$. Second, the diffusion in liquid depends on $T_{ion}$. Schelling [87] has reported the kinetics of melting for the MOD potential in detail for $T_c = 0$. In Fig. 14, experimental results from references [85, 93] are also shown for comparison. The empirical potential for $k_B T_c = 0$ is not exactly same as MOD potential as we have changed the cutoffs and value of $\alpha$ parameter. So, the kinetics predicted by the present potential here is little different than the MOD potential but both are in fairly good agreement with the experimental measurements of the interface velocity.
FIGURE 14: Interface velocity of a liquid-crystal system plotted as a function of $T - T_m$, where $T_m$ is the melting temperature. For temperatures below $T_m$, the interface velocity is positive which indicates crystallization. For temperatures higher than the $T_m$, the interface velocity is negative which indicates melting. Three values of $k_B T_e$ are considered $k_B T_e=0$ (circles), $k_B T_e=0.5eV$ (squares) and $k_B T_e=1.25eV$ (diamonds). The experimental values of interface velocities are also given (triangles) from Ref. [93, 94] to compare the results to $k_B T_e=0$ case.

3.3.4 Liquid self-diffusion

In previous chapter, we showed that the structure of liquid produced due to high values of $k_B T_e$ is significantly different form the ordinary liquid silicon at $k_B T_e=0$. The liquid structure calculations from the empirical potential were in good agreement with the finite-temperature DFT calculations. We calculated the values of self-diffusion constants for three different values of $k_B T_e$ at zero-pressure coexistence point for each $k_B T_e$. The three values of $k_B T_e$ considered are $k_B T_e=0$, $k_B T_e=0.5eV$ and $k_B T_e=1.25eV$. The system consisted of 4096 atoms, which in the beginning are heated at a temperature of 3000K for 10.5ps to make sure the crystal is totally
melted. Then the system is cooled to the coexistence point, and statistics for the mean-squared displacement $r^2_{av}$ are determined as a function of time. The results of $r^2_{av}$ computed as a function of time are shown in Fig. 15 for $k_B T_e=0$, $k_B T_e=0.5eV$ and $k_B T_e=1.25eV$. To determine the values of diffusion constant $D$, Einstein relation $r^2_{av} = 6Dt$ is used. The diffusion constants $D$ for different values of $k_B T_e$ are given in Table 3. The result at $k_B T_e=0$ is quite comparable to the experimental value of $D$ of $10^{-4} \text{cm}^2/\text{s}$ [95, 96]. The value of diffusion constant predicted by MOD potential is larger than the value $D = 6.94 \times 10^{-5} \text{cm}^2/\text{s}$ predicted by Stillinger-Weber potential [79]. We see from Table 3 that the value of $D$ decreases with increasing $k_B T_e$. This result seems counterintuitive at first sight because the interatomic forces are reduced with increases in $k_B T_e$, so it might be expected that diffusion would be easier at higher values of $k_B T_e$. However, these values of $D$ are calculated at the $T_{ion}$ equal to the melting temperature at that value of $k_B T_e$, which strongly decreases with increase in $k_B T_e$. The values of $T_m$ at each $k_B T_e$ are also given in Table 3.

**TABLE 3:** Diffusion Coefficients $D$ calculated for the empirical potential for three different values of the electronic energy $k_B T_e=0$, $k_B T_e=0.5eV$ and $k_B T_e=1.25eV$. The values of $D$ are calculated at the melting temperature $T_m$ at the particular value of $k_B T_e$. The values of $T_m$ corresponding to each $k_B T_e$ are also given in the table.

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<th>$k_B T_e$</th>
<th>$T_m$ (K)</th>
<th>$D \times 10^4$ ($\text{cm}^2/\text{s}$)</th>
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<tr>
<td>0</td>
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<td>1.57</td>
</tr>
<tr>
<td>0.5</td>
<td>1292</td>
<td>1.12</td>
</tr>
<tr>
<td>1.25</td>
<td>594</td>
<td>0.21</td>
</tr>
</tbody>
</table>
FIGURE 15: Mean square displacement $r_{av}^2$ computed at the coexistence point as a function of simulation time for liquid silicon. The values are calculated for three different values of electronic energies $k_B T_e = 0$, $k_B T_e = 0.5eV$ and $k_B T_e = 1.25eV$.

3.3.5 Annealing amorphous Si

We explored the possibility of annealing at an interface of amorphous silicon (a-Si) and crystalline silicon (c-Si) by generating strong electronic excitation. This process has been used to produce high-quality polycrystalline films from a-Si by melting and subsequent crystal growth [97]. We explored the potential for direct annealing of a-Si without creating liquid phase. This technique of forming crystalline silicon directly from a-Si without creating any liquid phase has been studied experimentally [15]. To generate the a-Si and c-Si interface we first equilibrated a diamond lattice of dimensions 6x6x40 and 11520 atoms for 11.04ps at ionic temperature $T_{ion} = 1700K$. Then to create a liquid we heat half of the system at temperature $T_{ion} = 3000K$, while
keeping rest half atoms fixed at their positions. Then we anneal the system from $T_{\text{ion}} = 1700\text{K}$ to $T_{\text{ion}} = 0$ at a rate of $3\text{ K/ps}$. The system dimensions in the plane of the interface are kept fixed during the annealing process while the long dimension of the cell perpendicular to the interface is allowed to change and maintain a zero stress condition. At the end of the annealing process we get a $0.43\text{nm}$ thick layer of a-Si, which contains around 2300 atoms. It was found that around 88% of the atoms in the a-Si are four-fold coordinated and the rest 12% are found to be five-fold coordinated atom. The quality of the a-Si region is comparable to the previous study using the same potential by Schelling [87].

The a-Si/c-Si interface obtained from the above calculations is then annealed using the empirical potential at three different values of electronic energy $k_B T_e = 0$, $k_B T_e = 0.5\text{eV}$ and $k_B T_e = 1.25$. The annealing was studied at constant temperature for $1.66\text{ns}$ of simulation time. At $T_{\text{ion}} = 300\text{K}$ and $T_{\text{ion}} = 600\text{K}$, no crystal growth was seen for $k_B T_e = 0$. However, complete annealing of the a-Si region into crystalline silicon is seen for $T_{\text{ion}} = 900\text{K}$ after $0.83\text{ns}$. The growth velocity is found to be $2.62\text{m/s}$ for this case. The experimental studies show much slower annealing than the annealing seen using empirical potential [15]. For $k_B T_e = 0.5\text{eV}$, we did not see any crystalline silicon growth up to $T_{\text{ion}} = 700\text{K}$ but it is possible that the crystalline growth might occur near melting point corresponding to the $k_B T_e = 0.5\text{eV}$, which is $1292\text{K}$. For $k_B T_e = 1.25\text{eV}$, we did not see any evidence of crystallization, and in fact an $0.5\text{nm}$ increase is seen in the a-Si region at $T_{\text{ion}} = 400\text{K}$. Thus, it seems that for very high values of $k_B T_e$, silicon will not crystallize without forming a liquid phase.
3.4 Conclusions

In summary, we have developed an empirical potential for silicon whose parameters depend on electronic temperature $T_e$. The parameters are smooth functions of electronic energy $k_B T_e$. The phonon spectra obtained from empirical potential is in good agreement with the finite-temperature DFT calculations. The unstable TA modes provide strong evidence of diamond lattice destabilization at higher values of electronic excitation. The melting temperature is found to be strongly decreasing with increase in $k_B T_e$, which shows that even slight increase in lattice temperature can result in melting of the crystal. The diffusion constant for liquid silicon is calculated for different values of electronic excitations and the kinetics of the crystal growth at higher $k_B T_e$ is found to be much slower than under ordinary conditions. We did not succeed in directly annealing a-Si to form crystalline silicon without forming a liquid phase first. However, crystalline silicon can possibly be formed at low values of $k_B T_e$ closer to melting point $T_m$ at that particular value of $k_B T_e$. It might also be possible that liquid silicon does form in laser-annealing experiments, but a temperature far below the ordinary melting temperature of $T_m=1683K$. It can be concluded that the production of crystalline silicon is very difficult for higher values of $k_B T_e$ because the diamond crystalline silicon is very less stable under high excitation conditions.
CHAPTER 4. ROLE OF ELECTRONIC-EXCITATION EFFECTS IN THE MELTING AND ABLATION OF LASER-EXCITED SILICON

4.1 Introduction

The ability of femtosecond lasers to interact with precise targets without transferring heat to the surroundings has made them widely used in various materials processing techniques like laser ablation for micromachining applications [98] and laser annealing of amorphous solids [15]. To further enable applications of lasers in materials processing, it is of great importance to understand how matter evolves under the far-from-equilibrium conditions generated by high intensity lasers. In this chapter we are going to see the nature of melting and ablation processes involved in laser-solid interaction. These pathways and mechanisms in laser-solid interaction depend mainly on three laser parameters, the laser pulse duration $\tau_L$, wavelength $\lambda$ and fluence $F$.

High electronic excitation leads to two types of processes thermal or nonthermal in nature. Although, there has been some lack of scientific clarity in the meaning of ‘thermal’ and ‘nonthermal’ processes. For our calculations, we define a ‘thermal’ phase transition to be any case that can be understood within the standard thermodynamic description of phase transitions. For example, in a thermal transition, a well-defined melting temperature exists, and the transition should occur with a discontinuous change in density and the evolution of latent heat. However, we also include in this definition of thermal phase transitions those processes that occur before equilibration between the lattice and electronic subsystems. In this picture, the relevant phase diagram depends on the degree of electronic excitation. We define nonthermal transitions to be any phase transition that does not fit into the standard thermodynamic picture. For example, in a
nonthermal transition, it would not be possible to define a phase diagram that can be understood in terms an underlying free energy function.

Many authors have studied melting and ablation in conditions of high overheating characteristic of laser-solid interactions using Molecular-dynamics (MD) simulations [13, 14, 99, 100]. For example, the conditions of heterogeneous and homogeneous melting were established in Ref. [14]. The mechanism for laser ablation of silicon was elucidated using MD simulation in Refs. [12, 99, 100]. In Ref. [13, 100], it was shown that phase explosion occurs as the result of rapid expansion and cooling of a superheated liquid that results in the system evolving into the liquid-vapor coexistence region. The most important contribution of Ref. [13, 100] was to establish the value of tracking thermodynamic parameters during the evolution of the material after laser excitation. In particular, by tracking the local density, temperature, and pressure after laser excitation, it was demonstrated that the particular mechanism of ablation depends sensitively on both the intensity and time of the laser pulse. For short pulses ($\tau_L = 100$fs), the system continuously attains a superheated liquid state, and adiabatic expansion results in cooling into the liquid-vapor coexistence region. At that point, phase explosion occurs with the homogeneous formation of vapor bubbles within the superheat liquid. By contrast, it was found that for very long pulses ($\tau_L = 100$ps) or very high excitation conditions, the superheated liquid might never enter the liquid-vapor coexistence region. In that case, ablation occurs not by the nucleation of vapor bubbles in the superheated liquid, but rather by the homogeneous expansion into the vacuum of the superheated fluid [13, 100].
It has been shown that under conditions of very strong electronic excitations ultrafast (e.g. sub picosecond) transitions occur [101]. There are some experimental studies present which indicates ultrafast ablation processes for Si, Ti, Au, and Al [102]. In the Coulomb-explosion mechanism of ablation, high excitation conditions result in a redistribution of charge and breaking of chemical bonds. For example, in Ref. [103], it was found for laser fluence in the range of 1-9 J/cm² that Si⁺ and Si²⁺ ions comprised a significant portion of the ablated material, thereby leading the authors to conclude that Coulomb explosion was the dominant mechanism.

As discussed in first chapter, the study of ultrafast processes using MD simulation has been limited by the fact that empirical potentials are not parameterized to describe conditions of strong electronic excitation. Here we describe a complete model in which interatomic interactions are based on empirical potential whose parameters depends on electronic temperature Tₑ, as discussed in previous chapters. In the model, the time evolution of the carrier density, local electronic temperature, and electronic energy is modeled using finite difference approach. The electronic and ionic subsystems are coupled using an inhomogeneous Langevin thermostat similar to the approach used in Refs. [63, 64]. The model is used to simulate the interaction of a silicon slab with an intense femtosecond laser pulse. Several different values of the incident laser F are simulated corresponding to the regimes of heterogeneous melting, homogeneous melting, and ablation. The results in next few sections show that electronic excitations play important role in modeling laser-solid interactions, but there is a less of a clear distinction between thermal and non-thermal transitions than is often thought. In fact, we find that the standard thermodynamic picture of phase transitions applies to most cases. Hence, by our
definition presented above, we fined most instances to be representative of ‘thermal phase transitions.

In the last two chapters we described the empirical potential for silicon whose parameters are smooth functions of the electronic energy $k_B T_e$. The dependence was determined by fitting to finite-temperature DFT calculations [104] for different crystal structures (diamond, fcc, bcc and simple-cubic) at different values of electronic energy $k_B T_e$ and atomic volumes. The parameters were kept similar to MOD potential [78, 87] for the $k_B T_e=0$ case, except higher cutoffs and the $\alpha$ parameter which were adjusted to get the melting temperature closer the experimental value. In the past, a similar approach has been applied to develop an empirical potential for tungsten [105]. The thermodynamics and kinetics of the empirical potential for silicon [106] have been thoroughly studied in chapter 3. In particular, we determined the melting temperature $T_m$ decreases towards zero as we increase the $k_B T_e$, which suggests that the lattice instability due to high excitation strongly impacts the thermodynamics. In short, the empirical potential developed for silicon includes fundamental physics predicted by finite-temperature DFT calculations under strong nonequilibrium conditions with $T_e >> T_L$, generated by femtosecond lasers.

4.2 Simulation Methodology

The femtosecond laser pulse creates strong electronic excitations with a high density of electron-hole pairs in the lattice. To simulate this effect, we need to couple the atomic scale model to a model for the time evolution of the electronic subsystem. For our purpose, we used the finite-temperature approach for the evolution of the electronic subsystem. In particular, the
electronic temperature $T_e$, energy $U$, and carrier density $N$ is given local values averaged over cells. The size of each cell is chosen to be larger than the lattice parameter, so that several atoms are contained in a single cell. In our calculations, the values of $T_e$, $U$ and $N$ are averaged over a volume containing approximately 180 silicon atoms for bulk silicon at room temperature. The volume of each cell is kept fixed during the simulation.

The laser is implemented with a Gaussian pulse shape incident on one side of the slab. The time-dependence of the incident intensity $I(t)$ is given by,

$$I(t) = I_o \exp \left[ -\frac{(t - t_0)^2}{2\tau_L^2} \right]$$  \hfill (13)

The laser pulse width is taken to be $\tau_L = 25\text{fs}$. The laser intensity is maximum at $t=t_0$. If the simulation begins at $t = 0$, we take $t_0 = 50\text{fs}$. The laser fluence $F$ is found by integrating $I(t)$ over the entire duration of the pulse. In particular,

$$F = \int_{-\infty}^{\infty} I(t)dt = I_o \tau_L \sqrt{2\pi}$$  \hfill (14)

In each case, the laser wavelength is assumed to be $\lambda = 530\text{nm}$. This choice is reflected in the parameters used to describe the absorption of the laser energy by the Si slab. The intensity of the laser in the system is attenuated with depth in the system due to one- and two-photon absorption, and also due to free-carrier absorption. The attenuation is described by the non-linear equation,

$$\frac{dI}{dx} = -\alpha I - \beta I^2 - \Theta NI$$  \hfill (15)
Where, $\alpha$ is the optical absorption coefficient for the valence to conduction band excitation, $\beta$ is the two-photon adsorption coefficient, $N$ is the carrier density, and $\Theta$ describes adsorption due to free carriers. In table 4, the parameters are shown which characterize the laser pulses used in the present study taken from Ref. [107]. The two photon adsorption and adsorption by free carriers will be relatively unimportant for low intensity cases. For low intensity cases, the adsorption occurs over a length scale of $\alpha^{-1} = 10^3$nm. As our slab thickness is only 16nm, most of the incident pulse passes through the surface without exciting electron-hole pairs. As a result of which, the adsorption is extremely uniform over the entire slab. For all the cases we studied, even at higher laser intensities, when two-photon and free carrier adsorption become relevant, the adsorption still remains uniform throughout the slab.

To describe the formation and evolution of plasmas in laser-excited silicon, we follow the theory developed in Ref. [107], to develop model for electronic subsystem. Some aspects of the present treatment are somewhat different, but as we will see the details of the carrier dynamics do not have a large effect on the present simulation results mainly because the system size we used is smaller than the length scale where the adsorption occurs. Therefore, the electronic excitation is fairly uniform across the entire silicon slab during entire course of simulation, and diffusion of the excited carriers and holes does not play a major role. The electron-hole current density is given by the expression:

$$ \vec{J} = -D_0 \vec{VN} \quad (16) $$

Where, $D_0$ is the diffusion constant. The terms related to the dependence of the band gap energy on temperature and densities are neglected in the above equation. We have also neglected a term related to the gradient of the electronic temperature $T_e$. In fact, there is a difference in the
physical interpretation of $T_e$ between the current work and what is presented in Ref. [107]. The time scale diffusion across the silicon slab is in the range of 0.10 to 0.20 ps. Thus, the diffusion is quite fast for this system size, and we do not expect that the neglected terms from the above equation will have any important effect. Finally, we assume, as is commonly assumed including in Ref. [99], that N represents the electron $N_e$ and hole density $N_h$. Hence, local charge neutrality, represented by $N_e = N_h = N$ in each simulation cell, is maintained. The electron-hole balance equation is given by,

$$\frac{\partial N}{\partial t} + \nabla \cdot \vec{j} = G + R \quad (17)$$

Where, $G$ and $R$ are the generation and recombination rates. The recombination rate is given by equation,

$$R = -\gamma A N^3 + \delta N \quad (18)$$

Where, the first term accounts for Auger recombination and the second term represents impact ionization. The generation rate is given by two terms to represent one- and two- photon absorption

$$G = \frac{(1 - \Gamma) \alpha I}{\hbar \omega_o} + \frac{(1 - \Gamma)^2 \beta I^2}{2\hbar \omega_o} \quad (19)$$

Where, $I$ is the laser intensity, $\hbar \omega_o$ is the photon energy, and $\Gamma$ is the reflectivity. While the dynamics for the carrier transport and recombination are treated throughout the simulation as described above, there is a very little importance beyond the initial phase of the simulation during excitation by the laser during the first $\sim 50$fs. The reason of this is that the primary role played by the excited carrier density $N$ is to increase the absorption of the incident radiation via
the free-carrier absorption term in Eq. [15]. The recombination term R is quite slow, as a result of which very few carriers recombine during the laser pulse.

The evolution of the electronic energy plays a more significant role in the dynamics since it will be linked to the temperature-dependent interatomic potential. In principle, the electronic energy is connected to the carrier density. However, the simulations here do not make a rigorous connection. The evolution of the energy density $u$ of the electron-hole pairs is given by the equation,

$$\frac{\partial u}{\partial t} + \vec{\nabla} \cdot \vec{W} = S_u - L_u$$  (20)

The energy source term $S_u$ is due to the interactions with the laser, both to create electron-hole pairs and to further excite free carriers. The source term is given by,

$$S_u = (1 - \Gamma)(\alpha + \theta N)I + (1 - \Gamma)^2 \beta I^2$$  (21)

The loss term $L_u$ describes the loss of the electronic energy to the lattice. This term will be determined by coupling the electrons at temperature $T_e$ to lattice using Langevin dynamics as described below. The heat current $\vec{W}$ is given by,

$$\vec{W} = -(\kappa_e + \kappa_h)T_e$$  (22)

In the above expression of heat current, we have neglected the convective term related to the carrier current density $\vec{J}$ that was included in the Ref. [107]. In the presented study, we take the value of thermal conductivity as $\kappa = \kappa_e + \kappa_h$, which is large enough to assure that the electronic temperature $T_e$ rapidly equilibrate across the entire silicon slab and hence the neglect of the convective term in the above equation doesn’t have any appreciable effect on the simulations.
results. For the value of $\kappa$, we assume that the Wiedemann Franz law is valid, and hence $\kappa$ is given by,

$$\kappa = LT_e \sigma$$  \hfill (23)

Where, $L = 2.44 \times 10^{-8} \text{W} \Omega^{-2}$ and $\sigma$ is the electronic conductivity. We use $\sigma = 17.5 \times 10^3 \text{cm}^{-1}$, which is computed using DFT calculations [108].

The local energy density $u_i$ is directly related to the electronic temperature $T_{e,i}$ and excited carrier density $N_i$ in the cell $i$. In fact, $u_i$ represents the energy density that corresponds to the local density of excited carriers $N_i$ described by Fermi-Dirac distribution at temperature $T_{e,i}$.

The local temperature $T_{e,i}$ is related to the free energy $\Omega_i(T_{e,i})$ and energy $U_i(T_e)$ in the $i$ using,

$$U_i(T_{e,i}) = \left[-T \frac{\partial \Omega_i}{\partial T} \right]_{T>T_{e,i}} + \Omega_i(T_{e,i}) - \Omega_{0,i}$$  \hfill (24)

Where, $\Omega_{0,i}$ is the energy of the system with no electronic excitation and hence $k_B T_{e,i} = 0$. The energy $U_i$ is given in terms of the energy density $u_i$ by,

$$U_i = V_i u_i$$  \hfill (25)

Where $V_i$ is the volume of the computational cell $i$. When the energy $U_i^n$ and electronic temperature $T_{e,i}^n$ in the cell $i$ is given at the integration time step $n$, then the algorithm first determines the new energy $U_i^{n+1}$ using Eq. [20]. Then using Eq. [24], the change in the energy $U_i^{n+1} - U_i^n$ is related to the change in free energy and temperature using,

$$U_i^{n+1} - U_i^n = \Omega_i(T_{e,i}^{n+1}) - \Omega_i(T_{e,i}^n) - T_{e,i}^{n+1} \left[ \frac{\partial \Omega_i}{\partial T} \right]_{T=T_{e,i}^{n+1}} + T_{e,i}^n \left[ \frac{\partial \Omega_i}{\partial T} \right]_{T=T_{e,i}^n}$$  \hfill (26)

Expanding $\Omega_i(T_{e,i}^{n+1})$ and $\left[ \frac{\partial \Omega_i}{\partial T} \right]_{T=T_{e,i}^{n+1}}$ about their respective values at temperature $T_{e,i}^n$ corresponding to time step $n$, we obtain,
\[ U_i^{n+1} - U_i^n = -\frac{1}{2} \left[ (T_{e,i}^{n+1})^2 - (T_{e,i}^n)^2 \right] \frac{\partial^2 \Omega_i}{\partial T^2} \bigg|_{T=T_{e,i}^n} \]  

(27)

Then if \( U_i^{n+1} - U_i^n \) is given, we can obtain an expression to determine \( T_{e,i}^{n+1} \) from \( T_{e,i}^n \),

\[ (T_{e,i}^{n+1})^2 = (T_{e,i}^n)^2 - \frac{2[U_i^{n+1} - U_i^n]}{[\partial^2 \Omega_i/\partial T^2]_{T=T_{e,i}^n}} \]  

(28)

The term \( \partial^2 \Omega_i/\partial T^2 \) is related to the specific heat capacity (per silicon atom) of the electronic subsystem \( c_{V,i}(T_{e,i}) \). In particular,

\[ c_{V,i}(T_{e,i}) = -\frac{T_{e,i}}{N_i} \left[ \frac{\partial^2 \Omega_i}{\partial T^2} \right]_{T=T_{e,i}} \]  

(29)

Where \( N_i \) is the number of silicon atoms in cell \( i \). We use for \( c(T_e) \) a polynomial that is fit to the finite-temperature DFT results for the free-energy \( \Omega(T_e) \) for diamond-structure silicon. In particular, we use equation,

\[ c_{V}(T_e) = k_B[0.5593(k_B T_e) + 3.1537(k_B T_e)^2 - 2.3270(k_B T_e)^3 + 0.4990(k_B T_e)^4] \]  

(30)

Where, the values of \( k_B T_e \) are in units of eV. In fig. 16, the plot of \( c_{V}(T_e) \) from \( k_B T_e = 0 \) to \( k_B T_e = 2.15 \) eV is shown, which represents the range of values for \( k_B T_e \) where the empirical potential was fit. For low values of \( k_B T_e \), the specific heat is small due to the fact that only a very low density of electron-hole pairs is excited. As \( k_B T_e \) increases and becomes comparable to the bandgap energy of silicon, the specific heat becomes comparable to \( k_B \), indicating that a very high density of electron-hole pairs are excited. The function \( c_{V}(T_e) \) results in an accurate determination of \( T_e \) resulting from a femtosecond laser pulse which interacts with the silicon lattice before the lattice loses its diamond structure.
The atomic system evolves according to Langevin dynamics integrated using the velocity-Verlet algorithm. For the interactions, we use the total free energy determined by the empirical potential $\Omega_{\text{tot}}$, which depends on the coordinates of all the atoms and the value of the electronic temperature $T_e$ in each of the computational cells. In this approach, the force on atom $k$ which is in all computational cell $i$ with a local temperature $T_{e,i}$ is given by,

$$\vec{F}_k = -\vec{\nabla}_k \Omega_{\text{tot}} - \gamma \vec{v}_k + \vec{\eta}_{R,k}$$

(31)

Where, $\gamma$ is a parameter representing electronic friction and $\vec{v}_k$ is the velocity of atom $k$. In most of the simulation results reported here, we use a value $\gamma = 1.536$ eV ps/nm$^2$. As the value of $\gamma$ controls the time scale for equilibrium between the lattice and electronic subsystems, we also have explored the dependence of our results on this parameter. The energy $\Omega_{\text{tot}}$ is determined from the empirical potential fit in Refs. [41, 106] to the electronic free energy determined from finite-temperature DFT calculations. Finally, the term $\vec{\eta}_{R,k}$ is a stochastic force that depends on the electronic temperature $T_{e,i}$ of the computational cell $i$ where the atom $k$ is located. In particular, the stochastic force is governed by a Gaussian probability distribution with the strength given by the ensemble-averaged value,

$$\langle \vec{\eta}_{R,k} \cdot \vec{\eta}_{R,k} \rangle = \frac{6\gamma k_B T_{e,i}}{\Delta t}$$

(32)

Where, $\Delta t$ is the MD timestep. The damping force and the stochastic force tend to drive the lattice temperature $T_{L,i}$ to equilibrium with the electronic temperature $T_{e,i}$ in each cell $i$. Thus, after laser excitation, the Langevin dynamics tends to increase the lattice temperature to represent electron-phonon interactions. Finally, as energy is transferred from the excited charge
carriers to the lattice, the electronic temperature should decrease. We therefore write the loss
term \( L_{u,i} \) from Eq. for cell \( i \),

\[
L_{u,i} = -\frac{1}{V_i} \sum_k \left[ \gamma v_k^2 - \vec{u}_{R,k} \cdot \vec{v}_k \right]
\]  \hspace{1cm} (33)

Where the sum is over all atoms \( k \) that are within the cell \( i \). While implementation of the above
equation tends to result in cooling of the electronic system and hence a decrease in \( T_{e,i} \), in
principle it can also describe local heating of the electronic subsystem when \( T_{L,i} > T_{e,i} \). The
method described above results in equilibration of the system, with \( T_{L,i} \) and \( T_{e,i} \) approaching a
common equilibrium value.

During the course of a simulation, the local temperatures for the electronic subsystem \( T_{e,i} \)
and lattice subsystem \( T_{L,i} \) for each cell \( i \) are determined at each MD time step. The value of \( T_{e,i} \) is
found by integrating changes in the internal energy \( U_i \) using the local heat capacity of the
electronic subsystem. For most of the simulation, the system is in a far-from-equilibrium state. In
particular, after the laser pulse, \( T_{e,i} \) is much greater than \( T_{L,i} \) in each cell \( i \). Due to electron-
phonon interactions resulting from the Langevin dynamics, \( T_{L,i} \) only approaches \( T_{e,i} \) on a time
scale of about 10ps. Consequently, for most of the MD simulation, the temperatures \( T_{e,i} \) and \( T_{L,i} \)
do not exactly represent the equilibrium thermodynamic parameters in the usual sense. Moreover,
in many cases the system is evolving as a strongly overheated liquid, and hence is in a strong
nonequilibrium state. However, the calculation of \( T_{e,i} \) and \( T_{L,i} \) is straightforward, and tracking the
time evolution of \( T_{e,i} \) and \( T_{L,i} \) provides important insight into the evolution of the system after
laser excitation, including transition from solid to liquid and vapor phases.
**TABLE 4:** Model parameters used to describe the interaction of the incident laser beam with the solid and also the subsequent dynamics of the charge carriers.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.530$\mu$m</td>
</tr>
<tr>
<td>$\tau_L$</td>
<td>25fs</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>$1.009 \times 10^4$ cm$^{-1}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>2.0 cm/GW</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>$5.0 \times 10^{-18}$ cm$^2$</td>
</tr>
<tr>
<td>$\delta$</td>
<td>$6.8 \times 10^{-13}$ s$^{-1}$</td>
</tr>
<tr>
<td>$\gamma_A$</td>
<td>$3.8 \times 10^{-31}$ cm$^6$/s</td>
</tr>
<tr>
<td>$D_0$</td>
<td>18.0 cm$^2$/s</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>0.37</td>
</tr>
</tbody>
</table>

**FIGURE 16:** Electronic specific heat capacity per atom $c_V$ in units of $k_B$ is plotted as a function of electronic energy $k_B T_e$ computed using finite temperature DFT [41, 106]. The filled square points represents the finite-temperature DFT results and the curve represents the fit curve given by Eq. [30].
4.3 Results

We chose a silicon slab with two (100)-type surfaces to simulate the interaction of silicon with femtosecond laser pulses. There are studies available both from experiment [109] and computation [110], which show that these surfaces reconstruct into the (2 x 1) dimer reconstruction. In these simulations we did not use the reconstructed surfaces from the beginning but rather allowed the surfaces to reconstruct on their own. The inclusion of reconstructed surfaces is not significant for these calculations because the amount of energy involved in reconstruction is very small in comparison to the energy input by the simulated laser pulse. The slab included 6 x 6 x 30 non-primitive diamond silicon unit cells with a total of 8640 Si atoms. As the lattice parameter of diamond Si at T=0K is 0.5429nm, the surfaces of the slab had dimensions 3.257nm x 3.257nm and the thickness of the slab was 16.287nm in the beginning of the simulation. The dimension of the supercell along perpendicular to the surface was kept 32.574nm, twice of the thickness of the slab to create large enough vacuum region for any expansion and ablation of system during the simulation. The simulation supercell dimensions were held fixed throughout the calculations. The MD timestep was chosen to be 0.014fs; this is very small compared to the MD time step used in typical calculations. This smaller timestep is chosen because of the fast electronic dynamics and the relatively high energies and temperatures involved in laser-solid interactions.

For a laser of pulse width \( \tau_L = 25 \text{fs} \), several different values of incident laser fluence were considered for simulation. A complete summary of simulation parameters and results that have been analyzed, including the laser fluence \( F \), maximum value of \( T_{e,\text{max}} \), and the final value of the lattice temperature \( T_{L,\text{final}} \) averaged over the simulation volume have been given in Table 5. A
wide range of incident fluence is considered which spans regimes where heterogeneous melting, homogeneous melting, and ablation are observed depending on the level of excitations occurring at a particular fluence. The final lattice temperature $T_L$ as a function of fluence $F$ is shown in Fig. 17, which also indicates the nature of transition due to increasing value of laser fluence. It can be seen from Fig. 17 that for very low values of fluence ($F \leq 0.30 \text{ J/cm}^2$), melting does not occur. With increasing fluence, heterogeneous melting is observed for the range $0.30 \text{J/cm}^2 \leq F \leq 0.35 \text{J/cm}^2$. For higher values of fluence $F \geq 0.35 \text{ J/cm}^2$, homogenous melting takes place, with the entire slab melting at once rather than melting starting at surfaces as was the case in heterogeneous melting. Finally, for even higher values of fluence $F \geq 0.65 \text{ j/cm}^2$, ablation is observed.

We can predict the values of threshold fluence for melting $F_m$, and for ablation $F_a$ using Fig. 17. The results are discussed in detail in next few sections. It can be seen from Fig. 17 that the heterogeneous melting and lower part of the homogeneous melting regime have a nearly constant value of lattice temperature $T_L$, which is very close to the melting point $T_m \sim 1600\text{K}$. This indicates the presence of a latent heat of melting because the energy generated by the incident laser beam is not initially translated into increases values of $T_L$. For higher fluence, $F \sim 0.4\text{J/cm}^2$, the value of lattice temperature $T_L$ starts to increase with increasing fluence. This indicates that the laser pulse has generated enough energy to completely melt the crystal with excess of energy going to increase the lattice temperature $T_L$. This heating of crystal due to excess of energy can ultimately result in ablation of the material. The various regimes homogeneous melting, homogeneous melting and ablation are discussed in greater details in the next few sections.
**TABLE 5:** List of model parameters used to describe the interaction of femtosecond laser beam with the solid silicon slab. A range of fluence is considered to describe the subsequent dynamics of the charge carriers that produces three different regimes: Heterogeneous melting, Homogenous melting and Ablation.

<table>
<thead>
<tr>
<th>Fluence (J/cm$^2$)</th>
<th>$T_{e,\text{max}}$ (K)</th>
<th>$T_{L,\text{final}}$ (K)</th>
<th>Melting</th>
<th>Ablation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.251</td>
<td>7367</td>
<td>1462</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>0.282</td>
<td>7648</td>
<td>1641</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>0.313</td>
<td>8509</td>
<td>1734</td>
<td>Heterogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.344</td>
<td>8753</td>
<td>1786</td>
<td>Heterogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.376</td>
<td>9692</td>
<td>1611</td>
<td>Homogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.407</td>
<td>10070</td>
<td>1731</td>
<td>Homogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.470</td>
<td>11380</td>
<td>2749</td>
<td>Homogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.532</td>
<td>12359</td>
<td>3709</td>
<td>Homogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.564</td>
<td>13052</td>
<td>4137</td>
<td>Homogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.627</td>
<td>14206</td>
<td>5134</td>
<td>Homogeneous</td>
<td>None</td>
</tr>
<tr>
<td>0.689</td>
<td>15337</td>
<td>6201</td>
<td>Homogeneous</td>
<td>Phase explosion</td>
</tr>
<tr>
<td>0.720</td>
<td>15902</td>
<td>6618</td>
<td>Homogeneous</td>
<td>Phase explosion</td>
</tr>
<tr>
<td>0.752</td>
<td>16484</td>
<td>7416</td>
<td>Homogeneous</td>
<td>Phase explosion</td>
</tr>
<tr>
<td>0.846</td>
<td>18308</td>
<td>9609</td>
<td>Homogeneous</td>
<td>Homogenous</td>
</tr>
<tr>
<td>1.033</td>
<td>20844</td>
<td>13111</td>
<td>Homogeneous</td>
<td>Homogenous</td>
</tr>
</tbody>
</table>
FIGURE 17: The final lattice temperature $T_L$ after 50ps of structure evolution is plotted as a function of laser fluence $F$. The symbols represent the transition observed after the simulation. Black circles represent no melting region, Red squares represent heterogeneous melting, green diamonds represents homogenous melting and blue triangles represent ablation. This analysis allows us to determine the approximate threshold fluence values for melting and ablation.

4.3.1 Near melting threshold

We start with the lowest values of fluence to analyze the evolution of the system with time. For $F=0.251$ J/cm$^2$, we did not see any melting in the system. The final temperature of the lattice temperature was found to be $T_L = 1462K$, which is well below the melting temperature of silicon $T_m=1688K$. The maximum value of electronic temperature reached in this case was $T_{e,\text{max}} = 7367K$. For a little higher value of fluence $F = 0.282$ J/cm$^2$, the system is driven very close to melting transition but still no melting is observed. The results for $F = 0.282$ J/cm$^2$ are shown in
Figures 17-19. The simulation slab is divided into various slices and to determine the electronic temperature in each slice we averaged the values of $T_{e,i}$ over several cells comprising a slice. For all the results reported here the system is rather thin compared to the optical absorption length $1/\alpha$. The thickness of the silicon slab is around 16.3nm, which is very small in comparison to the optical absorption length $1/\alpha = 10^3 \text{nm}$. Also, the electronic thermal conductivity is large enough to equilibrate $T_{e,i}$ rapidly over the entire system. Because of these two factors the $T_{e,i}$ is quite uniform over the entire simulation cell.

The evolution of the local electronic temperature $T_{e,i}$ is shown in Fig.18 for $F = 0.282 \text{J/cm}^2$. During the first 100 fs the $T_{e,i}$ increases rapidly to its maximum value $T_e = 7648 \text{K}$. After initial excitation, $T_{e,i}$ start decreasing and the lattice temperature starts increasing, with energy is transferred from the electronic subsystem to the ionic subsystem via electron-phonon interactions. The equilibration time at which lattice temperature $T_L$ becomes equal to electronic temperature $T_e$ is about 10 ps.

We analyzed the time evolution of both local lattice temperature $T_{L,i}$ and local electronic temperature $T_{e,i}$. Fig. 19 shows the time evolution of the local lattice temperature $T_{L,i}$. The kinetic energy $K_i$ of the $N_i$ atoms in each cell $i$ is computed at each MD step. The local lattice temperature $T_{L,i}$ is determined by using equipartition theorem and given by,

$$T_{L,i} = \frac{2K_i}{3N_i k_B} \quad (34)$$

The lattice temperature $T_{L,i}$ does not change much during the laser pulse and remains constant at about $T_{L,i} \sim 250 \text{K}$. As the energy is transferred from electronic subsystem to lattice, $T_{L,i}$ starts
increasing and electronic subsystem cools. The $T_{L,i}$ and $T_{e,i}$ are fairly uniform over the entire system with the possible exception of surface atoms, which can show large temperature fluctuations. This large fluctuation in few surface atoms is possible because there are often very few atoms are found in cells at the surface and also due to the fact that surface reconstructions occur that release energy which might result in temperature fluctuations of surface atoms. The system approaches equilibrium after around 10-20ps and the $T_{L,i}$ stabilizes close to $T_{e,i}$.

The evolution of the lattice temperature $T_L$ of the entire system is shown in Fig. 20. The total lattice temperature $T_L$ is found from the total kinetic energy $K$ of the $N$ atoms in the entire simulation cell using,

$$ T_L = \frac{2K}{3Nk_B} \quad (35) $$

We also include the time-evolution of the melting temperature $T_m$ in Fig. 20. As we have seen in previous chapters that melting temperature $T_m$ decreases with increase in $T_e$. We use the correspondence between $T_m$ and $T_e$ determined in previous chapters and reference [41, 106] to generate the estimated $T_m$ as a function of simulation time. For the value of electronic temperature $T_e$, the electronic temperature of the middle slice in the slab is used. It should be noted that $T_e$ is fairly uniform across the entire system. From Fig. 20, it can be seen that the lattice temperature $T_L$ is comparable to the melting temperature $T_m$. Although the lattice temperature becomes greater than melting temperature $T_L > T_m$, no melting is observed in our simulation of 50ps. It is certain that melting will occur at a longer time, but it might take a very long simulation run to observe the melting. In other words, we can say that the degree of overheating is very low for such a small value of fluence ($F=0.282 \text{ J/cm}^2$), which results in very low velocity of liquid-solid interface. To be precise, for a 50ps simulation, the melt velocity
should have a value of at least 10 m/s in order to melt a single layer of the crystal. Refs. [41, 87, 106] show that about 100K of overheating is required to get a liquid-solid interface velocity of around 10 m/s. The overheating is less that 100K for this case as can be seen from Fig. 20, which likely explains why no melting is observed after 50 ps. However, since lattice temperature $T_L$ is very close to melting temperature $T_m$, we take this case to represent the melting threshold, $F_m = 0.282 \text{ J/cm}^2$. Similarly, the other thresholds can be determined which are shown in next few sections.

**FIGURE 18:** Local electronic temperature profile for various simulation times. The fluence value for these results was $F=0.282 \text{ J/cm}^2$. In the first 100fs when the laser is on, the value of electronic temperature increases very rapidly to a maximum value. High excitations result in strong modifications in the interatomic potential. $T_e$ then starts decreasing with time and lattice temperature $T_L$ starts increasing. The system doesn’t melt for this value of fluence.
FIGURE 19: Local lattice temperature profile for various simulation times. The fluence value for these results was F=0.282 J/cm². In the first 100fs when the laser is on, the value of lattice temperature doesn’t change at all because energy transfer has not started yet. T_L then starts increasing with time and electronic temperature T_e starts decreasing after the energy is transferred from electron to lattice through phonon emissions. The system doesn’t melt for this value of fluence.

FIGURE 20: The evolution of lattice temperature T_L plotted as a function of time. The fluence value for these results is F=0.282 J/cm². The melting temperature T_m is also plotted as a function of time. T_m decreases with increase in electronic temperature T_e, this dependence is used to determine the T_m as function of simulation time.
4.3.2 Heterogeneous melting regime

When the fluence $F$ increase, the excitation level is more and the local electronic temperature $T_e$ increases very rapidly to a maximum value then starts decreasing by transferring energy to the lattice. As a result of which the lattice temperature $T_L$ increases above the melting point $T_m$. As long as the overheating is more than the required for melting, but not too large so then homogeneous nucleation occurs, then melting initiates at the surface and then continues at solid-liquid interface. The progress of solid-liquid interface can be determined as a function of time. For the fluence value $F = 0.344 \ J/cm^2$, snapshots of our system silicon slab are shown in Fig. 21 at various simulation times. The green spheres in Fig. 21 and all such figures in next sections represent the crystalline silicon consisting of four-fold coordinated atoms. Red spheres represents atoms with any other coordination number. When essentially all of the atoms are four-fold coordinated, the structure is crystalline silicon. By contrast, when melting occurs, the coordination number tends to exhibit more atoms that are not four-fold coordinated. Generally, liquid silicon exhibits higher coordination number in comparison to the crystal [42, 111].

Fig. 21 shows that for the fluence $F = 0.344 \ J/cm^2$, there is no sign of melting in first 5ps of excitation. After 10ps of excitation, a few layers of atoms are melted at the surface and a liquid-solid interface is formed at the both surfaces. The liquid layers on both surfaces then keep growing steadily into the crystal over the entire 50ps simulation time. Because the density of ordinary liquid silicon is greater than that of crystalline silicon, the melting process is accompanied by a gradual decrease in the slab volume, which is evident from Fig. 21. We determined the velocity of the liquid-solid interface using the results from Fig. 21. For the fluence $F=0.344 \ J/cm^2$, the interface velocity is found to be 80m/s. For simulations with $F=0.313$
$J/cm^2$, the interface velocity is found to be 34m/s. The magnitude of the interface velocity depends on amount of overheating in the lattice. Higher values of the laser fluence results in more overheating and hence larger interface velocities. Fig. 22 shows the computed values of $T_L$ and $T_m$ as a function of time for fluence $F=0.344 J/cm^2$. A significant amount of overheating is seen in this case. In particular, at a time near 13.8ps, $T_L - T_m = 572K$, which is high enough to melt the crystal with melting initiated at the surfaces. This type of melting is known as heterogeneous melting. As the system continues to melt with simulation time, the lattice temperature $T_L$ gradually decreases. At the end of the simulation, the overheating $T_L - T_m = 250K$, which is far higher than what we simulated in our previous studies [106]. In particular, in Ref. [106] the maximum overheating simulated was $T_L - T_m = 100K$, which resulted in an interface velocity of 15m/s. Therefore, we can conclude that increasing the amount of overheating leads to extremely fast interface velocities before homogenous melting in observed.

The large excitation results in very high electronic temperature $T_e$ and strong suppression of the melting temperature $T_m$. The maximum value of electronic temperature achieved is $T_e = 8753K$ for the incident fluence $F=0.344 J/cm^2$. It can be seen from Fig. 22 that just after the laser excitation, the melting temperature is strongly suppressed to $T_m = 1000K$. For the time interval 5ps to 10ps, the melting temperature strongly decreases because of very high electronic temperatures in that interval. The lattice temperature $T_L$ is well above than $T_m$ but the amount of overheating during this interval is sufficient only to gradually initiate heterogeneous melting at surfaces. The clear evidence of melting is observed after 12ps of laser excitation, when the electronic temperature $T_e$ has decreased to $T_e = 3000K$. This degree of electronic excitation is sufficient only to decrease the melting temperature by about 100K from the equilibrium value of
We can conclude that excitation with fluence $F=0.344\,\text{J/cm}^2$ results in an ordinary thermal phase transition accompanied by some bond-weakening effects. Within this regime of heterogeneous melting, bond weakening due to electronic excitations is a small effect. We will see the homogeneous melting regime in next section.

**FIGURE 21:** For fluence $F = 0.344 \, \text{J/cm}^2$, the snapshots of the evolution of the atomic structure after laser excitation are given at different simulation times. Green spheres represent the crystalline silicon with four-fold coordinated atoms. Red spheres represent the melting silicon with all other coordination numbers. The times after laser excitation, from left to right are 5ps, 10ps, 20ps, 30ps and 47ps.
FIGURE 22: For fluence $F = 0.344 \text{ J/cm}^2$, evolution of $T_L$ and $T_m$ is plotted as a function of simulation time. Within first 100 fs of the laser excitation, the electronic temperature increases very strongly, as a result of which the melting temperature $T_m$ strongly suppressed. When the lattice starts heating and $T_L$ increases, the system becomes strongly overheated resulting in heterogeneous melting as shown in Fig. 21.

4.3.3 Homogenous melting regime

For higher value of fluence, around $F = 0.375 \text{ J/cm}^2$ and higher, amount of overheating is large enough to initiate homogeneous melting. Similar results have been obtained in previous molecular dynamics studies of metals [14] and semiconductors including silicon [12, 100]. We find homogeneous melting occurs when the fluence $F$ is at least about $0.375 \text{ J/cm}^2$. The snapshots of evolution of the structure after laser excitation with fluence $F = 0.532 \text{ J/cm}^2$ are given in Fig. 23. Evidence of disordering can be seen after 2ps of simulation time. After 5ps of
laser excitation, the system is totally melted homogeneously with no evidence of melting starting at the surface, which would be evidence of heterogeneous melting. The melting transition results in a decrease of the volume occupied by the slab, as the density of liquid Si is higher than that of crystalline silicon. After further evolution of the system, the lattice temperature $T_L$ continues to increase, which consequently increases the volume of the slab due to thermal expansion. No ablation is observed in this case because the temperature is not high enough to start any ablation at $F = 0.532$ J/cm$^2$.

The evolution of the lattice temperature $T_L$ and melting temperature $T_m$ at $F = 0.532$ J/cm$^2$ is shown in Fig. 24. The electronic temperature $T_e$ reaches its maximum value $T_{e,\text{max}} = 12,359$K after around 100fs. This high rise in $T_e$ results in major changes in the interatomic potential and consequently a strong decrease in melting temperature. After the laser excitation, firstly, the melting temperature $T_m$ decreases to about $T_m = 646$K and then starts rising again as $T_e$ decreases. As a result of the strong suppression of $T_m$, the homogenous melting process actually occurs when $T_L$ is below the ordinary melting temperature of silicon. However, the lattice temperature $T_L$ is greater than the reduced temperature $T_m$ after about 1.3ps, and the system is completely melted when $T_L = 1488$K after about 4.8ps. At the time homogenous melting occurs, the system is strongly overheated, with the magnitude of overheating given approximately by $T_L - T_m = 544$K. The lattice subsystem continues to heat after melting due to the electron-phonon interactions and consequently the system slab expands by a small amount. The equilibrium between lattice temperature $T_L$ and electronic temperature $T_e$ is achieved after about 30ps with an equilibrium temperature of about 3700K. No ablation is seen in this case, Simulations with the slightly higher value of fluence $F = 0.626$ J/cm$^2$ shows that a few atoms
leave the liquid, but no sign of any large-scale ablation is seen. This value of fluence is still slightly less than the ablation threshold fluence $F_a$ as will be shown in the next section.

**FIGURE 23:** For fluence $F = 0.532 \ J/cm^2$, the snapshots of the evolution of the atomic structure after laser excitation are given at different simulation times. Green spheres represent the crystalline silicon with four-fold coordinated atom and red spheres represent the melted silicon with all other coordination numbers except 4. Few traces of homogenous melting is observed after 2ps. After 5 ps, the system is totally melted homogeneously with no signs of melting starting at surfaces, which was the case seen in heterogeneous melting. Melting also results in contraction of the slab volume due high density of liquid silicon than crystalline silicon.
4.3.4 Ablation regime

Large-scale ablation of silicon is observed for fluence values of $F = 0.689 \text{ J/cm}^2$ and higher. The initial homogenous melting in these cases is followed by ablation of the material. As the slab used in these cases is very thin, the entire 16.29nm-thick slab becomes vaporized. The evolution of the structure for $F = 0.720 \text{ J/cm}^2$ is shown in Fig. 25 at various simulation times. Initial evidence of melting after laser excitation is observed after 1ps. Complete homogeneous melting of the entire slab is observed after 2-3ps. Homogeneous melting in this case is different from the homogeneous melting observed with fluence values less than the ablation threshold. In
particular, for fluence values higher than the ablation threshold, strong expansion is seen instead of the contraction seen in the cases where fluence was less than the ablation threshold. The rapid expansion appears to be an important mechanism for initiating ablation via phase explosion as discussed below.

For fluence $F = 0.720 \, \text{J/cm}^2$, the evolution of lattice temperature $T_L$ and melting temperature $T_m$ is shown in Fig. 26. The melting temperature $T_m$ is suppressed below 500K due to the strong electronic excitation. The lattice is rapidly destabilized and the system overheats (i.e. $T_L > T_m$) within the first 1-2ps. The entire system is homogenously melted when the lattice temperature reaches around $T_L = 1000K$, which is much lower than the ordinary melting point of the silicon (1688K). Even though the melting occurs at a lower temperature than the ordinary melting temperature of silicon, there is still evidence that the transition is thermal in nature. In particular, while the melting transition occurs on a picosecond time scale, there is evidence of latent heat and an ordinary thermal transition at very high levels of overheat. A shoulder is seen on the plot of $T_L$ vs. time, where melting is observed between 2ps to 3ps. This indicates that the heat input from the electronic system is going to disorder the system during melting rather than to increase the lattice temperature $T_L$. After melting, the system undergoes rapid expansion and ablation in conditions with $T_e >> T_L$. The evidence of homogeneous nucleation of vapor phase within the superheated liquid is seen within the first 15$ps$, which strongly indicates that the system has entered into the liquid-vapor coexistence region. After further evolution of the system, $T_L$ and $T_e$ equilibrate around 6600K. It can be seen from Fig. 25 that the system has undergone dramatic expansion after 40ps. After 50$ps$ of simulation, the interatomic interactions in the
system are still strongly altered by the electronic excitations. As a result of which the melting temperature is reduced to $T_m = 1000K$.

It can be seen from Fig. 25 that the initial expansion in silicon slab is fairly uniform and the potential vapor bubbles that form are rather small in size. It might be expected that lower fluence conditions might produce more obvious vapor regions because the critical nucleus size should be larger. The evolution of the system for a little lower fluence $F = 0.689 \text{ J/cm}^2$ is shown in Fig. 27. It shows a clear evidence of homogeneous vapor formation especially at a time of about 30ps. The ablation mechanism for this case is very similar to the studies shown in references [12, 100]. The vapor bubbles start nucleating when the lattice temperature reaches in the range of 5000K to 6000K.

The formation of vapor by the phase explosion mechanism is less clear and for extremely high fluence, there is no evidence of phase explosion type ablation. We simulated the conditions for even higher fluence values, $F=0.846 \text{ J/cm}^2$ and $F=1.034 \text{ J/cm}^2$. For both of these highest fluence conditions we simulated, homogeneous expansion of the superheated liquid occurs with no evidence of phase explosion.

For fluence $F = 1.034 \text{ J/cm}^2$, snapshots of the evolution of system are shown in Fig. 28. The system in this case homogeneously expands without forming any well-defined vapor bubbles. The system density reaches to very low values due to expansion and the final system temperature is found to be about $T_L =13000K$, which is well above the critical temperature for silicon. With the help of all the previous cases discussed, we can finally estimate the ablation threshold to be around $F_a = 0.650 \text{ J/cm}^2$. The error in this estimate for the model reported here is
about 0.02 to 0.03 J/cm². We can improve this estimate by doing more simulations around the ablation threshold but a more exact estimate of Fₐ is not a critical prediction for the results reported here. In conclusion, we see that laser excitation produces three different regimes of heterogeneous melting, homogeneous melting and ablation as a function of laser fluence.

**FIGURE 25:** For fluence F = 0.720 J/cm², the snapshots of the evolution of the atomic structure after laser excitation are given at different simulation times. Green spheres represent the crystalline silicon with four-fold coordinated atom and red spheres represent the melted silicon with coordination number different than 4. Rapid homogeneous melting is observed between 2ps to 3ps, followed by the rapid expansion due to strong electronic excitation. Homogenous nucleation of the vapor phase is observed around 15ps, which clearly shows the initiation of ablation process.
FIGURE 26: For fluence $F = 0.720 \text{ J/cm}^2$, evolution of lattice temperature $T_L$ and melting temperature $T_m$ is plotted as a function of simulation time. The strong suppression of melting temperature $T_m$ due to the strong electronic excitation followed by lattice heating results in homogeneous melting. The rapid expansion results in phase explosion as shown in Fig. 25.
FIGURE 27: For fluence $F = 0.689$ J/cm$^2$, the snapshots of the evolution of the atomic structure after laser excitation are given at different simulation times. Green spheres represent the crystalline silicon with four-fold coordinated atom and red spheres represent the melted silicon with coordination number different than 4. The phase explosion is clearly evident after 30ps.
FIGURE 28: For fluence $F = 1.034 \text{ J/cm}^2$, the snapshots of the evolution of the atomic structure after laser excitation are given at different simulation times. Green spheres represent the crystalline silicon with four-fold coordinated atom and red spheres represent the melted silicon with coordination number different than 4. Due to extremely high lattice temperature $T_L$, homogeneous expansion of the superheated fluid occurs without any evidence of phase explosion.
4.4 Discussions and conclusions

The most important conclusion that can be drawn from the simulations reported here is that ordinary phase transition mechanisms still apply even under conditions of strong electronic excitations. Using the definitions we set forth for ‘thermal’ and ‘nonthermal’ phase transitions, we hence find that the phase transitions observed here can be considered as “thermal” phase transitions. However, the bond weakening effect due to strong electronic excitations still play a critical role in the ablation process. For example, strong electronic excitations promotes melting with a suppressed melting temperature and also by causing rapid expansion it drives the system into the liquid-vapor coexistence region thereby promoting phase explosion.

To compare all the simulations representing each of the important regimes studied here, we took snapshots of each simulation at 5ps, and the results are shown in Fig. 29. It’s the summary of structure evolution at different fluence values after 5ps, which shows the relevance of electronic excitations and bond weakening effects on structural evolution of material after laser irradiance. It can be seen from Fig. 29(a) that for low fluence values around $F = 0.344 \text{ J/cm}^2$, no evidence of melting is seen after 5ps of simulation time. In this case, the system is overheated ($T_L > T_m$), but the melting starts at surface slowly and the velocity of liquid-solid interface is very slow due to small overheating. Although the electronic excitations play a role, but overall the effect is fairly insignificant for this case. It is evident from Fig. 29(b) that for higher fluence values around $F=0.532 \text{ J/cm}^2$, rapid homogenous melting occurs to completion after 5ps. The melting of the crystal accompanies contraction in volume occupied by the slab because the density of the liquid silicon is higher than the crystalline silicon. The melting occurs in this case when the lattice temperature $T_L$ is below the ordinary melting temperature $T_m$ of
silicon. This is due to the bond weakening effect of the high electronic excitations, as a result of which the melting temperature gets strongly suppressed. This effect is important for the short time dynamics, but not much significant for longer times. We find from our simulations that the liquid silicon formed in these cases is ordinary silicon with significant contraction from the crystalline state. This is in contrast with the simulation predictions using finite-temperature DFT [37] and empirical potentials [41]. According to these studies, the liquid silicon with a high degree of electronic excitations is characterized by the higher atomic coordination and significant thermal expansion, which is not seen in our simulations. It is evident from the Fig. 29 (c) (F = 0.720 J/cm$^2$), (d) (F = 0.845 J/cm$^2$) and (e) (F = 1.034 J/cm$^2$) that the effects of electronic excitations is extremely important in case of higher fluence values. For these higher fluence cases, after 5ps of evolution, the strong electronic excitations melt the crystal homogenously and rapid expansion occurs due to the bond weakening effects. The rapid expansion results in nucleation of vapor phase and drive the system into liquid-vapor coexistence region, which ultimately leads to ablation by a phase explosion mechanism, as seen in F = 0.720 J/cm$^2$ case. At even higher values of fluence, including F = 0.845 J/cm$^2$ and F = 1.033 J/cm$^2$ cases, the system doesn’t ablates by phase explosion mechanism and instead ablates via homogenous expansion away from the liquid-vapor coexistence region.

Previous Molecular dynamics simulation studies of laser-solid interaction in silicon have also seen that the rapid expansion of the superheated liquid is an important precursor of the ablation by phase explosion mechanism [12, 100]. In particular, these studies also demonstrate that at high enough fluence, the system evolves away from the liquid-vapor coexistence region and phase explosion does not occur. Our results are in good agreement with these findings.
Moreover, we have added an additional aspect of bond weakening due to high excitations, which was not modeled in the previous studies. Bond weakening is an important factor in deriving the system into the liquid-vapor coexistence region and this effect has been successfully modeled in our simulations. People tend to regard the strong electronic excitation as a mechanism that does not relate to any equilibrium phase transition, and hence the phase explosion mechanism would not be seen when the electronic excitation is very high. We showed that it is possible to have strong excitation and phase explosion occurring at the same time.

The best way to see the effect of electronic excitations on phase explosion mechanism is to compare simulations with and without the electronic excitations. We compared the results described above which includes the electronic excitation effect, to the results of a simulation in which the parameters representing the interatomic interactions do not change with increase in electronic energy $k_B T_e$. All other aspects of the model were kept same as described in this chapter, including the heat capacity model and the evolution of the electronic temperature $T_e$ and lattice temperature $T_L$, but did not allow the interatomic parameters to change from the values which were assigned during the $T_e = 0$ (no excitation) case. In short we can say the bond weakening effects were not included in these calculations, which has been the standard approach of previous molecular dynamics studies of laser-solid interactions. The results of such calculations for fluence $F = 0.846 \text{ J/cm}^2$ are shown in Fig. 30. The final lattice temperature $T_L$ for this case is significantly different from the similar simulation for the same fluence but including the bond weakening effect. The final lattice temperature for the results shown in Fig. 30 is found to be about $T_L = 6000 \text{K}$, which is comparable to the $T_L$ for $F = 0.689 \text{ J/cm}^2$ shown in Fig. 27 (when bond weakening effect was included. Although, the lattice temperatures in Fig. 30 and Fig.
are approximately same but there is a significant difference in the evolution of the structure after laser excitation. The snapshots of the structure evolution in Fig. 30 show complete melting but at a longer timescale and also the lattice expansion in Fig. 30 are less dramatic than the Fig. 27. A very little ablation is observed over the entire 55ps simulation in Fig. 30, with only a few atoms entering the vapor phase. There is no evidence of phase explosion seen in Fig. 30, but we cannot rule out the possibility at a longer time scale. In conclusion, from the comparison of Fig. 27 and Fig. 30, we can say that rapid expansion caused by the bond weakening plays an important role in the ablation process including the phase explosion mechanism.

The equilibrium between electronic and lattice subsystems in our model is controlled by the $\gamma$ parameter, which is chosen as $\gamma = 1.536$ eV ps/nm$^2$ for all the calculations described in this chapter. For this value of $\gamma$, the equilibrium between electronic temperature $T_e$ and lattice temperature $T_L$ is achieved on a timescale of $\sim$10ps. This timescale appears reasonable based on carrier dynamics simulations of laser-generated plasmas in silicon [107], which is using parameters based on experimental observations. However, some other studies, including the molecular dynamics studies in references [12, 100] predict much faster equilibration than in our studies. The electron-phonon interactions in these studies transfer energy to lattice on a timescale closer to $\sim$ 1ps. This timescale plays an important role in seeing the consequences of bond weakening effect due to high electronic excitations. The simulations reported here involve phase transitions which occur in far-from-equilibrium conditions as characterized by $T_e >> T_L$. So if we chose the equilibration time (between $T_L$ and $T_e$) around 1ps then the phase transitions will more closely corresponds to the standard picture of equilibrium thermodynamics. In that case, bond weakening might still play a role, but it is clear that the most dramatic effects will be observed
when phase transitions occur while $T_e$ is still significantly higher than $T_L$. We also explored the dependence of equilibration time on $\gamma$ parameter. For this we simulated two additional values of $\gamma$ for fluence $F = 0.720$ J/cm$^2$ case. The evolution of lattice temperature $T_L$ is shown in Fig. 31 for three values of $\gamma = 1.536$ eV ps/nm$^2$, $\gamma = 3.027$ eV ps/nm$^2$ and $\gamma = 15.36$ eV ps/nm$^2$. From Fig. 31 we see that when the $\gamma = 15.36$ eV ps/nm$^2$, the lattice temperature $T_L$ quickly attains a maximum value and then starts decreasing due to expansion and subsequent cooling of the system. The structure evolution for $\gamma = 15.36$ eV ps/nm$^2$ case is shown in Fig. 32. The melting occurs within 1ps, which is similar to the studies in references [12, 100]. After melting, the superheated fluid starts expanding and finally phase explosion occurs by nucleation of vapor phase in the melted silicon. The expansion found in Fig. 32 is similar to the expansion found in Fig. 25 but the driving force for the expansion is rather different. In Fig. 32, for $\gamma = 15.36$ eV ps/nm$^2$, the rapid expansion is mainly due to the extremely high values of lattice temperature $T_L$, whereas in Fig. 25, the expansion is strongly driven by the highly-excited electronic state that persists with $T_e >> T_L$. After 50ps of simulation, there is little apparent difference in the structure between the Fig. 25 and Fig. 32. However, it is clear from Fig. 31 that the first indication of phase explosion, in both cases after 10-15ps of evolution, is initiated at different values of lattice temperature $T_L$. Thus, while the detailed evolution of density and $T_L$ determines whether the system enters the liquid-vapor coexistence region, the comparison here for different values of $\gamma$ do not result in insignificant qualitative differences in the evolution of the structure. This somewhat surprising result merits future investigation.
FIGURE 29: Snapshots of systems evolved after 5ps of simulation time for different laser fluence values. From left to right, the snapshots correspond to (a) F = 0.344 J/cm$^2$ (b) F = 0.532 J/cm$^2$ (a) F = 0.720 J/cm$^2$ (a) F = 0.846 J/cm$^2$ (a) F = 1.034 J/cm$^2$. For the lowest value of fluence F = 0.344 J/cm$^2$, the system is heated above the threshold for heterogeneous melting, but after only 5ps there is no evidence of melting. For the F = 0.344 J/cm$^2$ case, homogeneous melting is evident after 5ps. For even higher fluence values (c), (d) and (e), homogeneous melting is seen with strong expansion after 5ps and ultimately leading to ablations.
FIGURE 30: For fluence $F = 0.846 \text{ J/cm}^2$, the snapshots of the evolution of the atomic structure after laser excitation are given at different simulation times. The parameters describing the interatomic potential here do not depend on $k_B T_c$. Green spheres represent the crystalline silicon with four-fold coordinated atom and red spheres represent the melted silicon with coordination number different than 4.
FIGURE 31: The lattice temperature $T_L$ is plotted as a function of time for different values of the parameter $\gamma$. The dashed black line represents the results for $\gamma = 1.536 \text{eV ps/nm}^2$, solid red line represents results for $\gamma = 3.072 \text{eV ps/nm}^2$ and dotted green line represents the results for $\gamma = 15.36 \text{eV ps/nm}^2$. In each case the fluence is same as $F = 0.720 \text{ J/cm}^2$. The equilibration time between $T_L$ and $T_e$ strongly depends on $\gamma$. 
FIGURE 32: Snapshots of evolution of atomic structure for $F = 0.720$ J/cm$^2$ and $\gamma = 15.36$ eV ps/nm$^2$. The entire slab is melting within 1ps and large-scale ablation can be seen after around 5 to 10ps. Ablation in this case occurs with $T_L \sim T_e$, with strong evidence of the phase-explosion mechanism driving ablation. The dynamics are much faster in this case as compared to other values of $\gamma$ considered in Fig. 31.

The predicted melting fluence of $F_m = 0.282$ J/cm$^2$ is significantly higher than previous experimental observations [112] and theoretical predictions [107]. According to reference [112], the threshold fluence for melting is predicted as $F_m = 0.150$ J/cm$^2$. In reference [107] the value of
F_m is predicted around 0.200 J/cm^2, which is greater than the value predicted in Ref. [112] but less than the melting threshold value predicted by us. For our calculations we have assumed that the parameter α is independent of lattice temperature T_L, so it becomes straightforward to estimate the value of melting threshold F_m. The energy density u due to a pulse of fluence F can be estimated near the surface by u \sim 2.8 \times 10^3 J/cm^3. For the case here where \alpha = 10^4 cm^{-1} and F = 0.282 J/cm^2, we obtain u = 2.8 \times 10^3 J/cm^3. The volume occupied by each atom in bulk silicon with lattice parameter a = 5.43 Å is \Omega_{at} = 2.0 \times 10^{-23} cm^3. Hence, the energy absorbed per silicon atom is about U_a = 0.35eV. Assuming a specific heat per atom of 3k_B, this energy is enough to increase the lattice temperature by about 1350K, which is consistent with the onset of melting. In table 5, we show computed values for U_a/3k_B that are very similar to this simple estimate. Hence, while F_m = 0.282 J/cm^2 is different than the result found in Ref. [112] and the theoretical predictions in Ref. [107], it is consistent with a simple estimate of the melting threshold.

Differences in the value of melting threshold F_m in our calculations and in references [107, 112] is primarily due to the assumption that the parameter α doesn’t depend on temperature and also the pulse width is short in our case \tau_L = 25fs. The temperature independence of parameter α assumed in our calculations is fairly reasonable because for a laser pulse width τ_L = 25fs, there is insufficient time for a large increase in T_L during the laser pulse. In Ref. [107], α depends on lattice temperature T_L according to,

\[ α = 5.02 \times 10^3 \exp(T_L/430^9 K) cm^{-1} \]  (36)

For T_L = 300K, this equation gives the same value of α as reported in table 4. For the pulse width τ_L = 20ps reported in Ref. [107], T_L increases strongly during the pulse resulting in stronger
adsorption near the surface. This nonlinear effect results in strong increases of $T_L$ near the surface and hence a lower value of melting fluence $F_m$. In Ref. [112], the experiments used a pulse width $\tau_L = 100\text{fs}$, which is longer than our simulations and possibly allows the lattice temperature to increase significantly during the pulse resulting in stronger adsorption. In Ref. [112], the incident wavelength of the laser pulse is 620nm, however the dependence of $\alpha$ on wavelength $\lambda$ is fairly weak in this range [113]. These considerations show how threshold fluence values for melting and ablation depend on $\tau_L$ due to strong nonlinear effects. Including the dependence of $\alpha$ on $T_L$ might improve agreement with Refs. [107, 112] for the melting threshold $F_m$. However, the differences might still exist due to the very short pulse width in our simulations.

The similar differences are found in prediction of ablation threshold. The experimental value of ablation threshold is $F_a = 0.300 \text{ J/cm}^2$, while in our simulations this value is predicted to be $F_a = 0.650 \text{ J/cm}^2$. Other molecular dynamics studies [12] report the ablation threshold value as $F_a = 0.225 \text{ J/cm}^2$. Similar to the case of melting threshold $F_m$, the ablation threshold value $F_a$ also depends on how deeply the incident radiation penetrates. In Ref. [12], the wavelength is $\lambda = 266\text{nm}$ and pulse widths simulated are significantly longer than the value $\tau_L = 25\text{fs}$, used in our simulations. Moreover, it was assumed that as the system melts it becomes metallic, resulting in even stronger absorption of the incident light. As a result of these differences, the laser pulse only penetrated to a depth of 5 – 10nm, resulting in a very high energy density near the surface [12]. However, other aspects of system near the threshold for ablation are consistent between the work reported here and in Refs. [12, 112]. In particular, near the threshold for ablation, we find lattice temperature to be around $T_L = 6000\text{K}$, which is in very good agreement with $T_L$ found in
From the time-of-flight spectroscopy measurements in Ref. [112], the temperature of the ejected material was found to be at somewhat lower value $T = 3000$ to $4000K$ near the ablation threshold, significantly less than $T_L$ reported in Ref. [12] and in our studies here. This can be explained due to the cooling of the ejected materials during expansion, also explained in Ref. [12]. Hence, while $F_a$ depends strongly on incident wavelength and nonlinear effects, the temperature and subsequent evolution of the ejected material appear to be fairly consistent in simulation and the experiment.

There are several aspects of the present model that likely require improvement before simulations of larger systems, different wavelengths $\lambda$, or longer durations $\tau_L$ for the laser pulse. In particular, for the simulations reported here, the excitation of the silicon slab was extremely uniform, and the electronic dynamics and electronic heat condition do not play an important role. For larger systems where electronic dynamics are more relevant, the model for carrier dynamics would require improvements. For example, several effects included in the model reported in Ref. [107] were neglected here. However, there is another fundamental consideration that affects the implementation of a more detailed model. In particular, the electronic temperature $T_e$ has a somewhat different meaning in the results reported here and in Ref. [107]. According to Ref. [107], the excitation is accompanied by a quasi-Fermi level for electrons and holes, which gradually equilibrate due to recombination. The electronic temperature $T_e$ alone is therefore not enough to determine the carrier density in Ref. [107]. By contrast, finite-temperature DFT results assume a single Fermi-level, and as a result the density of electrons and holes is directly related to the electronic temperature $T_e$. Hence, it is not clear that application of all the details in Ref. [107] makes sense in the present context. In short, more realistic models will require better
models of the electronic excitation effects and possibly DFT or other theoretical approaches that can more realistically characterize the dynamics of highly excited systems.

In Summary, we have developed a multiscale model to investigate the laser-solid interaction for silicon, femtosecond laser pulses are considered in the studies that yield far-from-equilibrium conditions characterized by $T_e >> T_L$. Our model presents strong evidence of ordinary ‘thermal’ phase transitions, including melting and ablation via phase explosion, that occur before equilibrium between the electronic and lattice subsystems. Rapid expansion of superheated liquid due to bond-weakening effects appears to drive the system strongly into the liquid-vapor coexistence region, thereby promoting phase explosion. In this respect, the previous-investigated ablation and melting mechanisms are still relevant, but the detailed evolution of the system can depend strongly on bond weakening due to electronic excitations.
5.1 Introduction

Thermodiffusion phenomenon in materials has been the focus of many theoretical and experimental studies over a long period of time. The phenomenon of thermodiffusion refers to mass transport that results from a temperature gradient, or alternatively it refers to the heat flux that accompanies a mass flow. Although several attempts have been made to understand the thermodiffusion process in binary systems but still the fundamental understanding at atomic level has not been made. For example, we can consider the example of hydrogen movement in palladium crystal; there is still no clear argument that can predict the direction of hydrogen flow under a temperature gradient in palladium crystal. This system of Pd:H is a special case in these type of studies because hydrogen diffuses very rapidly in this case. According to the simple kinetic theory, the reduced heat of transport $Q^*$, which describe the thermodiffusion driving force, should be comparable to the activation energy $\Delta U_{act}$ for migration [114, 115]. But this argument is contrary to the experimental results where the values of these two parameters are found to very different from each other. Hence, a simple argument or theory is lacking which can completely describe the magnitude and nature of driving force for thermodiffusion. The heat of transport $Q'$ of H, D and T in the Ta-H system has been studied as a function of temperature showing a linear decrease of $Q^*$ with temperature [116]. Molecular dynamics studies have been previously used to study this effect but they have not been able to provide the clear picture because $\Delta U_{act}$ is typically significantly greater than the $k_B T$, as a result of which diffusion does
not occur on a typical MD time scale. Therefore the direct brute-force calculations are not useful for this purpose. By contrast, hydrogen diffuses rapidly in the Pd lattice, and as a result it is possible to apply brute-force techniques to compute the transport parameters relevant for thermodiffusion.

The reduced heat of transport $Q^*$ (defined in the next section) can be determined from various techniques using MD simulations. Gillan used the Green-Kubo method to explore the thermodiffusion phenomenon in Pd:H system [117-119]. Green-Kubo method uses the time-correlation functions of the coupled heat and mass fluxes to compute transport coefficients [120, 121]. However, the Green-Kubo method is not useful for cases where the diffusion does not occur on typical MD time scales. Recently, McDargh and Schelling developed a technique, known as constrained-dynamics approach [122] that uses the worked required to drive an atom through the transition state in the presence of an applied temperature gradient to calculate the driving force for thermodiffusion. This is a useful technique to compute transport parameters for the cases where Green-Kubo fails because of slow hopping events difficult to observe on a MD time scale. However, significant work is needed to firmly establish the theoretical foundation of this technique and also an extensive comparison is being made to results from other existing methods.

We simulated the thermodiffusion of hydrogen in a palladium crystal using ‘direct’ simulation approach by computing the average drift of hydrogen in presence of a temperature gradient. We developed a new approach to calculate the reduced heat of transport $Q^*$ based on the direct observation of hydrogen drift. Results from three different techniques are compared
and are found to give consistent results for $Q^*$. The values of $Q^*$ is found to be negative which suggest the hydrogen travels in direction of low temperature to high temperature. The $Q^*$ parameter is found to be temperature independent in our simulations.

5.2 Theoretical background

The laws of irreversible thermodynamics are used to obtain a general theory to describe matter transport in solids. We considered a two component Pd:H system to explore the phenomenon of thermodiffusion. The first step to describe coupled transport of heat and matter in this system is to define mass fluxes for palladium and hydrogen. The mass flux $\vec{J}_1$ for the Pd is given by,

$$\vec{J}_1 = \sum_{i=1}^{N_1} \vec{v}_i$$  \hspace{1cm} (37)

Where, $N_1$ is the total no. of Pd atoms and the sum is taken over all the $N_1$ Pd atoms. The same kind of equation is used to define the mass flux of hydrogen $\vec{J}_2$, which is given by,

$$\vec{J}_2 = \sum_{i=1}^{N_2} \vec{v}_i$$  \hspace{1cm} (38)

Where, $N_2$ is the total no. of hydrogen atoms in the crystal. The mass fluxes $\vec{J}_1$ and $\vec{J}_2$ are defined relative to the center of mass frame, the relation between two fluxes is given by,

$$m_1\vec{J}_1 + m_2\vec{J}_2 = 0$$  \hspace{1cm} (39)

Where, $m_1$ and $m_2$ are the masses of Pd and hydrogen respectively. Because of the fact that the mass of hydrogen $m_2$ is very small compared to the mass of Pd $m_1$, the hydrogen flux $\vec{J}_2$ will be dominant in the process. As a result of which, it will be useful and sufficient to consider only the
\( \vec{J}_2 \) and energy flux \( \vec{J}_q \). As described in the Ref. [115] the phenomenological equations for mass and energy flux can be written as:

\[
\vec{J}_2 = \frac{\Omega}{k_B T} \left[ L_{22} \vec{X}_2 + L_{2q} \vec{X}_q \right] \quad (40)
\]

\[
\vec{J}_q = \frac{\Omega}{k_B T} \left[ L_{q2} \vec{X}_2 + L_{qq} \vec{X}_q \right] \quad (41)
\]

Where, \( k_B \) is the Boltzmann constant and \( \Omega \) is the system volume. According to the Onsager’s theorem in the absence of a magnetic field the matrix of L coefficients is symmetric, that is,

\[
L_{q2} = L_{2q} \quad (42)
\]

The driving forces for diffusion are defined by,

\[
\vec{X}_2 = \vec{F}_{ext} - T \nabla \left( \frac{\mu_2}{T} \right) \quad (43)
\]

\[
\vec{X}_q = - \frac{1}{T} \nabla T \quad (44)
\]

Where, \( \vec{F}_{ext} \) is the external force applied on hydrogen atoms and \( \mu_2 \) is the chemical potential of the hydrogen. The thermodynamic deriving forces can be alternatively defined as:

\[
\vec{X}’_2 = \vec{X}_2 + h_2 \vec{X}_q \quad (45)
\]

\[
\vec{X}’_q = \vec{X}_q \quad (46)
\]

The corresponding fluxes are given as:

\[
\vec{J}_q' = \vec{J}_q \quad (47)
\]

\[
\vec{J}_q' = \vec{J}_q - h_2 \vec{J}_2 \quad (48)
\]

Where, \( h_2 \) is the partial enthalpy of hydrogen in the palladium lattice. The transport equations are given as:
The transport coefficients for the two descriptions are related as:

\[ L'_{22} = L_{22} \]  
\[ L'_{2q} = L_{2q} - h_2 L_{22} \]  
\[ L'_{qq} = L_{qq} - 2h_2 L_{2q} + h_2^2 L_{22} \]

The heat of transport can be defined as:

\[ L_{2q} = L_{q2} \equiv Q^* L_{22} \]

Using the above equation and equation (??) we get,

\[ L'_{2q} = (Q^* - h_2)L_{22} = Q'' L_{22} \]

Where, \((Q^* - h_2) = Q''\) is known as the reduced heat of transport. Using equations 49 and 50, and definition of \(Q''\) we get,

\[ \vec{J}_2 = -\frac{L_{22} \Omega}{k_B T} (\vec{\nabla}\mu_2)_T + \frac{L_{22} \Omega}{k_B T} \left[ \vec{F}_{ext} - Q'' \frac{\vec{\nabla}T}{T} \right] \]

Here, we have considered \(J'_2 = \vec{J}_2\) and \(L'_{22} = L_{22}\). The gradient term in the above equation \((\vec{\nabla}\mu_2)_T\) represents the gradient of the hydrogen chemical potential due to concentration and pressure gradients. Therefore, from the above equation, we see that in the absence of any concentration and pressure gradients the hydrogen mass flux is given by,

\[ \vec{J}_2 = \frac{L_{22} \Omega}{k_B T} \left[ \vec{F}_{ext} - Q'' \frac{\vec{\nabla}T}{T} \right] \]
We can get the driving force for the thermodiffusion from the above equation as $\vec{F}_{ext} - Q^{\alpha\beta}\frac{\vec{v}_T}{T}$. This force represents the driving force on a single hydrogen atom in Pd crystal with an externally applied force and temperature gradient.

### 5.3 Simulation approach

We used empirical pair potentials described in Ref. [115] for molecular dynamics calculations. The interaction pair potential between Pd atoms (Pd-Pd) is given by,

$$V_{Pd-Pd}(r) = \sum_{s=1}^{6} a_s r^s$$

(58)

The interaction potentials between hydrogen atoms (H-H) and between hydrogen and palladium atoms (Pd-H) are taken to be same, and given by,

$$V_{Pd-H}(r) = V_{H-H}(r) = A exp(-r/\rho)$$

(59)

The parameters and cutoff distances $r_c$ are kept same as given in Ref. [115]. To remove the discontinuity of the potential energy and resulting forces at cutoff distance $r_c$, we shifted each potential to obtain a smooth potential, which is given by,

$$V^{'}_{\alpha\beta}(r) = V_{\alpha\beta}(r) - V_{\alpha\beta}(r = r_c) - (r - r_c) \left[ \frac{dV_{\alpha\beta}}{dr} \right]_{r=r_c}$$

(60)

Where, $\alpha\beta$ pair represents the any particular pair Pd-Pd, Pd-H or H-H. Using $V^{'}_{\alpha\beta}(r)$, the potentials and first derivatives of these potentials approach zero smoothly at cutoff $r_c$. As a consequence of applying this continuity removal method the shape of the potential gets only slightly altered but significant amount of energy shift is seen. Due to the fact that differences in
Pd-H interaction almost cancel each other in calculations of \( Q^{*'} \), the thermodiffusion phenomenon is no significantly affected by the potential smoothing process.

The calculations were performed using three different methods: 1) Direct thermodiffusion simulations, 2) Green-Kubo formulae method and 3) Constrained dynamics approach. For Pd-H system we concentrated more on Green-Kubo formulae as the diffusion process is very fast in this system so Green-Kubo formulae are totally authentic and practical in this case. We considered a system of \( N_1 = 108 \) Pd atoms and \( N_2 = 20 \) hydrogen atoms. The MD timestep for the calculations was kept \( \Delta t = 0.414 \text{fs} \). The goal of the work described here was to determine the possibility of temperature dependence of the heat of transport. Experimental studies of thermodiffusion of hydrogen in metals have previously shown temperature dependence. Moreover, calculations of the thermodiffusion of vacancies in a single-component metal have also found strong temperature dependence. However, insight into the apparent temperature dependence of the heat of transport is still lacking.

### 5.4 Results: Green-Kubo approach

Gillan successfully analyzed the Green-Kubo formulae to obtain the value of reduce heat of transport \( Q^{*''} \), but with a large statistical error. We reproduced the calculation of \( Q^{*''} \) presented in Ref [118] with improved statistical accuracy. We find that in Ref. [118] an inconsistent definition of \( h_2 \) was chosen, which resulted in \( Q^{*''} = 0.04 \text{eV} \). In our calculations we find that with the correct analysis of \( h_2 \), the values of \( Q^{*''} \) from Ref. [118] and from our calculations are in very good agreement. We simulated the same system size as used by Gilan with \( N_1 = 108 \) Pd atoms and \( N_2 = 20 \) hydrogen atoms. We defined the mass flux of hydrogen as given in Eq. 38 in center-of-
mass reference frame. In Ref. [118], the calculations were made by considering mass fluxes in reference frame fixed to the Pd lattice. In those calculations the Pd mass flux was chosen to be zero while the hydrogen flux was given by the equation,

$$\vec{j}_2' = \sum_{i=1}^{N_2} \vec{v}_i - \frac{N_2}{N_1} \sum_{i=1}^{N_1} \vec{v}_i' = \vec{j}_2 - \frac{N_2}{N_1} \vec{j}_1$$  \hspace{1cm} (61)$$

With using Eq. 61 and Eq. 39 we can see that,

$$\vec{j}_2' = \vec{j}_2 \left(1 + \frac{N_2 m_2}{N_1 m_1}\right) \approx (1.0017)\vec{j}_2$$  \hspace{1cm} (62)$$

From the above equation we can see that the mass flux of hydrogen used by Gilan is almost similar to the mass flux of hydrogen in our calculations. Therefore, it can be concluded that for these calculations, it doesn’t matter much whether we define the hydrogen flux in lattice-fixed reference frame or center-of-mass frame.

In center of mass frame, the energy flux has been computed according to the equation given in Ref. [123],

$$\vec{j}_q = \sum_i \vec{v}_i \epsilon_i + \frac{1}{2} \sum_{i<j} \vec{r}_{ij} \left[ \vec{F}_{ij} \cdot (\vec{v}_i + \vec{v}_j) \right]$$  \hspace{1cm} (63)$$

In the above equation the summations are taken over all Pd and H atoms. Where, \(\vec{F}_{ij}\) is the interaction force between \(i\) and \(j\) atoms. \(\epsilon_i\) is the partial energy and is given by,

$$\epsilon_i = \frac{1}{2} m_i \vec{v}_i \cdot \vec{v}_i + \frac{1}{2} \sum_{j \neq i} V_{ij} \left( r_{ij} \right)$$  \hspace{1cm} (64)$$

Where, \(r_{ij}\) is the distance between \(i\) and \(j\) atoms and \(V_{ij}\) is the interaction pair potential between \(i\) and \(j\) atoms. The same approach of dividing the potential energy equally between two interacting
particles has been used in Ref. [118] and Eq. 64 is completely valid as long as the interactions between particles are relatively short-ranged. The energy flux represented by Eq. 63 includes both heat conduction and mass transport. The heat flux \( \mathbf{\dot{J}}_q \) is calculated using Eq. 48 with the inclusion of correct definition of partial enthalpy of hydrogen \( h_2 \).

The partial energies \( u_1 \) and \( u_2 \), and partial enthalpies \( h_1 \) and \( h_2 \) of Pd and hydrogen respectively, are calculated using the similar approach as used in Ref. [123]. The partial energy \( u_1 \) for Pd is given by,

\[
u_1 = \frac{1}{N_1} \sum_{i=1}^{N_1} \langle \epsilon_i \rangle \tag{65}\]

Where, \( \epsilon_i \) is the partial energy defined by Eq. 64. The summation is taken over all the \( N_1 \) Pd atoms. The partial energy of \( N_2 \) hydrogen atoms is determined using similar equation and is given by,

\[
u_2 = \frac{1}{N_2} \sum_{i=1}^{N_2} \langle \epsilon_i \rangle \tag{66}\]

The total internal energy of the system is calculated by linear combination of the partial energies of hydrogen and Pd and is given by,

\[U = N_1 u_1 + N_2 u_2 \tag{67}\]

The partial enthalpy \( h_1 \) for Pd is defined using the equation given by,

\[h_1 = u_1 + p_1 \Omega \tag{68}\]

Similarly, the partial enthalpy \( h_2 \) for hydrogen atom is given by,

\[h_2 = u_2 + p_2 \Omega \tag{69}\]
The total enthalpy \( H \) of the system is given by the linear combination of \( h_1 \) and \( h_2 \),

\[
H = N_1 h_1 + N_2 h_2
\]  
\( \text{(70)} \)

From Refs. [123, 124], We used the stress tensor to determine the pressure terms \( p_1 \) and \( p_2 \). The elements of the stress tensor \( \pi_{\mu\nu} \) for a pair potential are given by,

\[
\pi_{\mu\nu} \varOmega = \sum_i m_i v_{i,\mu} v_{i,\nu} + \frac{1}{2} \sum_i \sum_{j \neq i} (F_{ij,\mu} r_{ij,\nu})
\]  
\( \text{(71)} \)

Where, \( \mu \) and \( \nu \) represents components in Cartesian coordinates. Therefore, \( v_{i,\mu} \) is a component of the velocity vector \( \vec{v}_i \) for particle \( i \). In the same manner \( F_{ij,\mu} \) is the component of \( F_{ij} \), which is the force on particle \( i \) due to particle \( j \) and \( r_{ij,\nu} \) is the component of \( r_{ij} \), which is the relative position of particle \( i \) with respect to particle \( j \). The total pressure \( p \) is proportional to the trace of the stress tensor given by,

\[
p \varOmega = \frac{1}{3} \sum_{\mu=1}^{3} \langle \pi_{\mu\mu} \rangle
\]  
\( \text{(72)} \)

With using Eq. 71, the above equation can also be written as:

\[
p \varOmega = \frac{1}{3} \left[ \sum_i m_i \langle \vec{v}_i \cdot \vec{v}_i \rangle + \frac{1}{2} \sum_i \sum_{j \neq i} \langle \vec{F}_{ij} \cdot \vec{r}_{ij} \rangle \right]
\]  
\( \text{(73)} \)

As described earlier that the contributions due to the pairwise interactions are equally distributed between the particles, with the application of this correction in the above equation we get,

\[
\langle p_i \rangle \varOmega = \frac{1}{3} m_i \langle \vec{v}_i \cdot \vec{v}_i \rangle + \frac{1}{6} \sum_{j \neq i} \langle \vec{F}_{ij} \cdot \vec{r}_{ij} \rangle
\]  
\( \text{(74)} \)

The partial pressures \( p_1 \) and \( p_2 \) due to Pd and hydrogen respectively are given by,
The total pressure can be determined as,

$$ p = N_1 p_1 + N_2 p_2 $$  \hspace{1cm} (77)

The relation between total enthalpy, total internal energy and total pressure is given by,

$$ H = N_1 h_1 + N_2 h_2 = N_1 (u_1 + p_1 \Omega) + N_2 (u_2 + p_2 \Omega) = U + p \Omega $$  \hspace{1cm} (78)

The approach described above is the correct method to calculate the partial enthalpies $h_1$ and $h_2$, which were either ignored in most studies or wrongly calculated which leads to wrong calculation of thermal conductivity and other transport parameters. Similar approach has been used to calculate the partial enthalpies in binary liquids [125, 126]. The above approach has also been verified to be in good agreement with Green-Kubo and direct method to calculate thermal conductivity [127]. Schelling calculated the partial thermodynamic quantities for Pd:H for 108 Pd atoms and different number of hydrogen atoms at 980K and fixed system volume.

We integrated the time-correlation functions to get the transport parameters given by,

$$ \zeta_{22}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_2(\tau) \cdot \vec{J}_2(0) \rangle d\tau $$  \hspace{1cm} (79)

$$ \zeta_{2q}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_2(\tau) \cdot \vec{J}_q(0) \rangle d\tau $$  \hspace{1cm} (80)

$$ \zeta_{q2}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_q(\tau) \cdot \vec{J}_2(0) \rangle d\tau $$  \hspace{1cm} (81)
\[
\zeta_{qq}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_q(\tau) \cdot \vec{J}_q(0) \rangle d\tau \quad (82)
\]

In particular,

\[
L_{22} = \lim_{\tau \to \infty} \zeta_{22}(\tau) \quad (83)
\]

\[
L_{2q} = L_{q2} = \lim_{\tau \to \infty} \zeta_{2q}(\tau) = \lim_{\tau \to \infty} \zeta_{q2}(\tau) \quad (84)
\]

\[
L_{qq} = \lim_{\tau \to \infty} \zeta_{qq}(\tau) \quad (85)
\]

The heat of transport is determined using,

\[
Q' = \frac{L_{2q}}{L_{22}} \quad (86)
\]

If we use the heat flux \( \vec{J}_q \) as given in Eq. 48, the relevant correlation function are then given by,

\[
\zeta'_{2q}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_q'(\tau) \cdot \vec{J}_q(0) \rangle d\tau \quad (87)
\]

\[
\zeta'_{q2}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_q(\tau) \cdot \vec{J}_q(0) \rangle d\tau \quad (88)
\]

\[
\zeta'_{qq}(\tau) = \frac{1}{3\Omega} \int_0^\tau \langle \vec{J}_q'(\tau) \cdot \vec{J}_q'(0) \rangle d\tau \quad (89)
\]

The correlation function \( \zeta_{22}(\tau) \) remain same in both cases. The relations among various correlation functions are given by,

\[
\zeta'_{2q}(\tau) = \zeta_{2q}(\tau) - h_2 \zeta_{22}(\tau) \quad (90)
\]

\[
\zeta'_{qq}(\tau) = \zeta_{qq}(\tau) - h_2 \left( \zeta_{2q}(\tau) + \zeta_{q2}(\tau) \right) + h_2^2 \zeta_{22}(\tau) \quad (91)
\]

The reduced heat of transport is given by,

\[
Q'' = \frac{L'_{2q}}{L_{22}} \quad (92)
\]
Where, $l_{2q}'$ is given by $l_{2q}' = \lim_{r \to \infty} \zeta_{2q}'(\tau)$ and also $Q'' = Q^* - h_2$. This way $Q^*$ can be calculated independent of $h_2$ but $Q''$ needs a correct method to calculate $h_2$.

We performed 360 independent equilibrium MD simulations at four different temperatures 580K, 780K, 980K and 1280K. At each temperature, the transport coefficients were calculated. In each run, the system is first equilibrated for 10,000 steps, followed by $2 \times 10^5$ MD steps to determine the time correlation functions. In Ref. [118], the averaging was done over a simulation time of 2.0ns resulting in large statistical errors in determining the value of $Q''$. We did the averaging over a simulation time of 29.8ns, which reduces the statistical errors by almost a factor of 4.

In Table 7, we show the determined values of transport coefficients for 580K, 780K, 980K and 1280K. These values are obtained at an integration time of 2ps within an estimate of the numerical error obtained by using standard deviation method. This integration time of 2ps is chosen because at longer integration times, the estimated error becomes almost equal to the values of the parameters itself, as a result of which the evidence of correlations after 2ps diminishes.

The integrated correlation functions as a function of integration time were calculated for 580K, 780K, 980K and 1280K. For example, Fig. 33 shows the $\zeta_{22}(\tau)$ as a function of integration time at an average temperature of 1280K. The results at 980K are found to be in good agreement to the values reported in Ref. [118], especially for the lower values of integration time. For example, At 980K the value for $L_{22}$ reported in Ref. [118] at $\tau=1.2$ps is 0.029 ps$^{-1}$Å$^{-1}$, while for the same time we found this value as $L_{22}=0.033$ ps$^{-1}$Å$^{-1}$. For 980K, we also obtained the diffusion coefficient at 2ps using Einstein’s relation and the value is found to be $D=3.09$cm$^2$s$^{-1}$ within an
estimated error of 0.31 cm$^2$s$^{-1}$. This is in good agreement with the D=3.09 cm$^2$s$^{-1}$ value reported by Gilan.

Fig. 34 shows the integrated correlated function $\zeta_{2q}(\tau)$ as a function of integration time at an average temperature of 1280K. A strong correlation is seen between the energy flux and hydrogen flux.

**FIGURE 33:** Integrated function $\zeta_{22}(\tau)$ plotted as function of time. The average temperature in this case is 1280K.
FIGURE 34: Integrated function $\zeta_{2\omega}(\tau)$ plotted as function of time. The average temperature in this case is 1280K.

FIGURE 35: Integrated function $\zeta_{2\omega'}(\tau)$ plotted as function of time. The average temperature in this case is 1280K.
FIGURE 36: Integrated functions $\zeta_{qq}(\tau)$ and $\zeta_{qq'}(\tau)$ plotted as function of time. The average temperature in this case is 1280K. Black solid line represents $\zeta_{qq}(\tau)$ and red solid line $\zeta_{qq'}(\tau)$.

FIGURE 37: Arrhenius plot of $L_{22}$ with four different temperatures of 580K, 780K, 980K and 1280K. The slope of the curve is activation energy, and is obtained as -0.2877eV.
FIGURE 38: Arrhenius plot of L_{2q} with four different temperatures of 580K, 780K, 980K and 1280K. The slope of the curve is activation energy, and is obtained as -0.2486eV.

TABLE 6: Computed value of partial thermodynamic quantities, partial energies \( u_1 \) and \( u_2 \), partial enthalpies \( h_1 \) and \( h_2 \) calculated for a system of \( N_1 = 108 \) atoms and different values of \( N_2 \) hydrogen atoms. The volume of the system is kept fixed at \( \Omega = 27 \ a^3 \), where \( a \) is the lattice parameter of the palladium \( a = 4.07\text{Å} \). The system volume does not depend on the no. of hydrogen atoms. The temperature of the system is kept at 980K.

<table>
<thead>
<tr>
<th>( N_1 )</th>
<th>( N_2 )</th>
<th>( u_1 )</th>
<th>( u_2 )</th>
<th>( h_1 )</th>
<th>( h_2 )</th>
<th>( p_1\Omega )</th>
<th>( p_2\Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>108</td>
<td>0</td>
<td>-0.563</td>
<td>-</td>
<td>-0.314</td>
<td>-</td>
<td>0.249</td>
<td>-</td>
</tr>
<tr>
<td>108</td>
<td>1</td>
<td>-0.545</td>
<td>0.833</td>
<td>-0.290</td>
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<td>0.255</td>
<td>1.134</td>
</tr>
<tr>
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<td>10</td>
<td>-0.464</td>
<td>0.832</td>
<td>-0.103</td>
<td>1.999</td>
<td>0.361</td>
<td>1.167</td>
</tr>
<tr>
<td>108</td>
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<td>0.845</td>
<td>-0.015</td>
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<td>0.429</td>
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</tr>
<tr>
<td>108</td>
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</tr>
<tr>
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<tr>
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<td>0.483</td>
<td>1.205</td>
</tr>
</tbody>
</table>
In Table 7, a summary of computed transport parameters is given as a function of temperature. It can be seen that all these parameters show some consistent dependence on temperature but the final calculation of heat of transport $Q^*$ and reduced heat of transport $Q^{*'}$ shows no dependence on temperature. This is due to the fact that $Q^{*'}$ is calculated using the relation $Q^{*'} = \frac{L_2^q}{L_{22}}$, which involves the ratio of these parameters, as a result of which the individual dependence of parameters on temperature cancel out while taking ratio. However, some experimental evidences show that there is some dependence of heat of transport on temperature. Table 8 gives the summary of the heat of transport values with estimated errors at different temperatures. It also shows the values of thermal conductivity calculated using equation given by,

$$\kappa = \frac{L_{qq}}{k_B T^2}$$  \hspace{1cm} (93)

Where, $k_B$ is the Boltzmann constant and $T$ is the average temperature. It seen from table 8 that the thermal conductivity $\kappa$ slightly depends on temperature but no strong dependence is seen. The correct value of partial enthalpy of hydrogen $h_2$ is calculated at each temperature.
**TABLE 7:** Computed values of transport parameters calculated for four different values of temperatures 580K, 780K, 980K and 1280K. The values of parameters are obtained at 2ps. The same potentials are used as was in Gilan paper with the additional smoothing of the potentials as described to remove the discontinuity at the cutoff distance $r_c$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$L_{22}$</th>
<th>$L_{2q}$</th>
<th>$L_{2q}^*$</th>
<th>$L_{qq}$</th>
<th>$L_{qq}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>580K</td>
<td>0.00326</td>
<td>0.00568</td>
<td>-0.00068</td>
<td>0.05806</td>
<td>0.04836</td>
</tr>
<tr>
<td>780K</td>
<td>0.01381</td>
<td>0.02490</td>
<td>-0.00257</td>
<td>0.10739</td>
<td>0.06298</td>
</tr>
<tr>
<td>980K</td>
<td>0.03400</td>
<td>0.06200</td>
<td>-0.00700</td>
<td>0.18600</td>
<td>0.07300</td>
</tr>
<tr>
<td>1280K</td>
<td>0.06713</td>
<td>0.12939</td>
<td>-0.01287</td>
<td>0.32540</td>
<td>0.07849</td>
</tr>
</tbody>
</table>

**TABLE 8:** Computed values of heat of transport, reduced heat of transport, partial enthalpy of hydrogen and thermal conductivity at 580K, 780K, 980K and 1280K. Reduced heat of transport is calculated using $Q'' = Q^* - h_2$ and thermal conductivity is calculated using $\kappa = \frac{L_{qq}'}{k_BT^2}$.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$Q^*$</th>
<th>Error in $Q^*$</th>
<th>$h_2$</th>
<th>$Q^*$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>580K</td>
<td>1.74509</td>
<td>0.002</td>
<td>1.946</td>
<td>-0.20090</td>
<td>2.66895</td>
</tr>
<tr>
<td>780K</td>
<td>1.80292</td>
<td>0.148</td>
<td>1.989</td>
<td>-0.18600</td>
<td>1.92053</td>
</tr>
<tr>
<td>980K</td>
<td>1.82353</td>
<td>0.040</td>
<td>2.038</td>
<td>-0.21400</td>
<td>1.41004</td>
</tr>
<tr>
<td>1280K</td>
<td>1.92731</td>
<td>0.073</td>
<td>2.119</td>
<td>-0.19200</td>
<td>0.88872</td>
</tr>
</tbody>
</table>
5.5 Conclusions and future research

In summary, we have calculated heat of transport of hydrogen in Pd lattice by three different methods: direct thermodiffusion simulations, Green-Kubo formulae and constrained dynamics approach. It is found that the heat of transport doesn’t depend on temperature while experimental results suggest that there is some dependency on temperature. A detailed investigation at lower temperatures is required to further clarify issue of not seeing any temperature dependency by simulation results. The value of reduced heat of transport $Q^*$ found from all the three methods is consistently negative and lies in the range of $-0.20\text{eV}$ to $-0.30\text{eV}$. It can be seen from the direct simulations result that hydrogen travel in the direction of increasing local temperature, which is a good validation of results from Green-Kubo and constrained-dynamics methods. The disagreement of results from Ref. [118] is found totally due to the use of incorrect definition of the $h_2$ there. The results reported here are not in good agreement with experimental value $0.065\text{eV}$ in the temperature range of $670\text{K}$ to $830\text{K}$ [128], which suggests that the empirical potential for Pd:H system used here may not accurately reproduce the interaction. This suggests that hydrogen tends to diffuse from the hot end to the cold end. It may also be that thermoelectric effects result in another driving force for hydrogen thermodiffusion. The apparent lack of temperature dependence is also in disagreement with experiment. It may be that temperature dependence seen in experiment is due to quantum-mechanical effects, which are not accounted for in the simulations described here.
LIST OF REFERENCES


