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Molecular-dynamics calculation of the vacancy heat of transport

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We apply the recently developed constrained-dynamics method to elucidate the thermodiffusion of vacancies in a single-component material. The derivation and assumptions used in the method are clearly explained. Next, the method is applied to compute the reduced heat of transport $Q_v^* - h_{fv}$ for vacancies in a single-component material. Results from simulations using three different Morse potentials, with one providing an approximate description of Au, and an embedded-atom model potential for Ni are presented. It is found that the reduced heat of transport $Q_v^* - h_{fv}$ may take either positive or negative values depending on the potential parameters and exhibits some dependence on temperature. It is also found that $Q_v^* - h_{fv}$ may be correlated with the activation entropy. The results are discussed in comparison with experimental and previous simulation results. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4886577>]

I. INTRODUCTION

We have recently introduced a new method, termed constrained-dynamics, for computation of the heat of transport of vacancies and interstitial solutes.^{1,2} The method, which is quite different from earlier approaches,^{3–9} was shown to give satisfactory agreement when compared to Green-Kubo calculations,² and generally reasonable values for the heat of transport in comparison to experiment.¹ In Ref. 1, the central equation of the constrained-dynamics approach, in this case for computation of the reduced heat of transport for vacancies, $Q_v^* - h_{fv}$, was found to be

$$Q_v^* - h_{fv} = W_{1 \rightarrow 2} \frac{T}{\Delta T}, \quad (1)$$

where $W_{1 \rightarrow 2}$ is the work done by the constraint force F_c to move the constrained atom from z_1 to z_2 , where z_1 and z_2 represent the positions of the local minima of the integrated work $W(z)$, given by

$$W(z) = \int_{z_1}^z \langle F_c(z') \rangle dz'. \quad (2)$$

Hence, the work in Eq. (1) is given by $W_{1 \rightarrow 2} = W(z_2)$. The quantity $\langle F_c(z') \rangle$ is the time-average of the force required to hold the atom at z' . Generally, the atom is displaced along the direction of the temperature gradient $\vec{\nabla}T$, and the temperature difference ΔT in Eq. (1) is found by integrating the temperature gradient along the path of the constrained atom. Specifically, $\Delta T = T_1 - T_2$, where T_1 is the local temperature at z_1 , and T_2 is the local temperature at z_2 .

Before constrained-dynamics can become a standard approach, it is important to place the method on a more solid

theoretical foundation. In Ref. 2, the predicted value for the heat of transport of hydrogen atoms in a Pd lattice was computed using the constrained-dynamics method and found to be in essentially exact agreement with standard Green-Kubo techniques. This provides some support for the constrained-dynamics approach. While this is encouraging, the limited study in Ref. 2 probably is not sufficient to validate the approach. One challenge is that in the case of vacancy-mediated thermodiffusion, Green-Kubo methods are not practical and it is difficult to directly validate the constrained-dynamics approach. More broadly, there are many problems where the diffusion rate is too slow to directly apply Green-Kubo techniques to validate predictions using the constrained-dynamics approach. Yet it is precisely these problems that constrained-dynamics was developed to address.

In this article, we examine the assumptions made in the derivation of Eq. (1). In particular, we present a more thorough derivation meant to address questions that have arisen after publication of Ref. 1. The method is then used to compute the heat of transport of vacancies in model fcc metals using Morse potentials and an embedded-atom model (EAM) potential for Ni. It is shown that the computed values for the reduced heat of transport $Q_v^* - h_{fv}$ vary in a systematic manner with the parameters of the potentials, and moreover, appear to be correlated with the activation entropy.

II. THEORETICAL BACKGROUND

We consider here specifically the thermodiffusion of vacancies in a single-component material. Here, we present a more thorough discussion than Ref. 1, with the objective of clarifying the relation of the quantities in Eq. (1) with the quantities calculated in the constrained molecular dynamics calculation which we carry out to determine them. We will also demonstrate that the method obeys the laws of

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thermodynamics applied to irreversible processes. In the following, we omit vector notation for simplicity. The vacancy and energy current densities, J_v and J_q , are given by the expressions first presented in Ref. 1

$$J_v = L_{vv}X_v, \quad (3)$$

$$J_q = L_{qq}X_q, \quad (4)$$

where X_v and X_q represent the driving forces for mass and heat transport. The driving forces are given by

$$\begin{aligned} X_v &= -F_{ext} - T\nabla\left(\frac{\mu_v}{T}\right) + Q_v^*\left(-\frac{\nabla T}{T}\right) \\ &= k_B T\left(-\frac{\nabla c_v}{c_v}\right) + (Q_v^* - h_{fv})\left(-\frac{\nabla T}{T}\right), \end{aligned} \quad (5)$$

$$X_q = -\frac{\nabla T}{T}, \quad (6)$$

where F_{ext} is a (coarse-grained) external force, c_v is the vacancy concentration, Q_v^* is the vacancy heat of transport, and h_{fv} is the enthalpy of formation for vacancies. The negative sign for the external force is to indicate that forces are applied to atoms rather than directly to vacancies. In Ref. 10, a thorough discussion of the phenomenological transport equations can be found. With appropriate definitions of the transport coefficients the equation for the vacancy current J_v can be rewritten, taking account of an external force applied to the atoms as

$$J_v = -D_v \nabla n_v + \left(\frac{D_v}{k_B T}\right) n_v \left[-F_{ext} + (Q_v^* - h_{fv}) \left(-\frac{\nabla T}{T}\right) \right], \quad (7)$$

where $D_v = L_{vv}k_B T/n_v$. This equation implicitly defines the reduced heat of transport $Q_v^* - h_{fv} \equiv Q_v'^*$ which we wish to compute. For our purposes, it is important to emphasize that the relations Eqs. (3)–(7) refer to quantities averaged in space and time over scales long compared to the typical dynamic time scales in the system and similarly over spatial distances at least as large as the interatomic distances in the system of interest. In the case at hand, we are concerned with the transport of vacancies which takes place via hopping of atoms (in the direction opposite to that of the vacancy current) over distances of the order of the lattice spacing. These hops are rare events which take place quickly (less than 1 ps) separated by long residence times (nanoseconds or more depending on the hopping barrier and temperature). The time scales on which the macroscopic Eqs. (3)–(7) apply are the latter times. Details of the hopping dynamics have been averaged away in the coarse graining. Similarly, spatial details of the path followed during the hop have been integrated out in the spatial coarse graining, and the smallest relevant spatial scale is the distance Δz along the thermal gradient between metastable positions of the vacancy. Thus when relating microscopic quantities computed in molecular dynamics simulations to the variables in these equations, we can regard the thermal gradient as $\Delta T/\Delta z$ in which Δz is the distance between metastable positions of the vacancies along the direction of the thermal gradient and ΔT is the corresponding difference in the local temperature.

In the molecular dynamics calculations used to implement Eq. (7), a time-varying constraint force $F_c(z)$ is applied to the atom which would otherwise undergo a hop, holding it at a fixed position z along the path between local minima. Effectively, the Hamiltonian of the constrained system for pair-wise interactions with potential energy $\phi(r)$ is

$$H(z) = \sum_{\mu=1}^2 \frac{p_{1,\mu}^2}{2m} + \sum_{i=2}^N \frac{\vec{p}_i \cdot \vec{p}_i}{2m} + \sum_{j=2}^N \phi(r_{1j}) + \sum_{i=j+1}^N \sum_{j=2}^{N-1} \phi(r_{ij}). \quad (8)$$

Here, the constrained atom corresponds to $i=1$, and the index μ represents the Cartesian components. The position vector of atom $i=1$ is then $\vec{r}_1 = x_1 \hat{i} + y_1 \hat{j} + z \hat{k}$. Hence the z -coordinate of the hopping atom is constrained and given by $z_1 = z$. The z -component of the momentum of the hopping atom is zero, $p_{1,3} = 0$. Thus the simulation does not simulate the dynamics of the hop but constrains the hopping atom to move adiabatically from one stable minimum to the next in the presence of a thermal gradient imposed by the boundary conditions on the simulation. The average force imposed over the passage from one stable minimum to the next is

$$F_{ext} = \frac{1}{z_2 - z_1} \int_{z_1}^{z_2} \langle F_c(z') \rangle dz' = \frac{W_{1 \rightarrow 2}}{z_2 - z_1}, \quad (9)$$

where the brackets on $\langle F_c(z') \rangle$ denote a time average in the molecular-dynamics simulation, assumed to be equivalent by the usual ergodicity assumption to a thermal average in an ensemble representing the local thermodynamic equilibrium. Thus F_{ext} is a coarse-grained force, appropriate for inclusion in the macroscopic description of the constrained calculation in Eq. (7). During this molecular dynamics calculation, there is only one vacancy and it is not allowed to flow. Thus there is no spatial gradient in the density and no vacancy current. In these conditions, the macroscopic Eq. (7) becomes

$$0 = \left(\frac{D_v}{k_B T}\right) n_v \left[-F_{ext} + Q_v'^* \left(-\frac{\nabla T}{T}\right) \right]. \quad (10)$$

For the temperature gradient, we take $\nabla T = \frac{T_1 - T_2}{z_1 - z_2}$, and then obtain

$$F_{ext} = -\left(\frac{Q_v'^*}{T}\right) \left(\frac{T_1 - T_2}{z_1 - z_2}\right). \quad (11)$$

Inserting Eq. (9) for F_{ext} , we recover the central equation of the method, Eq. (1). One can regard the integral in Eq. (9) as the work required to slowly return the atom from z_1 to z_2 after a hop as described in the Appendix, where we also show that there is no violation of the second law in the processes that are involved.

In Sec. III, specific technical details are given about the constrained-dynamics method. These were reported in Refs. 1 and 2 but are reproduced here for completeness. Details of the particular empirical potentials used are also given.

III. SIMULATION APPROACH

We report here simulation results using three different Morse-type potentials and an EAM potential for Ni. The Morse potentials take the form

$$V(r) = \epsilon[e^{-2\alpha(r-r_0)} - 2e^{\alpha(r-r_0)}]. \quad (12)$$

In the MD simulations using Morse potentials we express energies in units of ϵ , masses in units of the mass m of the atom simulated, lengths in units of r_0 , and time in units of $r_0\sqrt{m/\epsilon}$. In these units, we chose a time step of $\Delta t^* = 0.001$. We chose three different values of αr_0 . In particular, we consider $\alpha r_0 = 4.55$, $\alpha r_0 = 6.0$, and $\alpha r_0 = 8.0$. The Morse potential has a minimum at $r - r_0 = 0$, where the value is $V(r = r_0) = -\epsilon$. The cutoff for the interactions was taken to be $r_{cut} = 3.0r_0$, which in each case is somewhat greater than twice the lattice parameter at zero reduced pressure $p^* = 0$. The parameterization $\alpha r_0 = 4.55$ was used in the Cherns potential¹² for Au. The Cherns potential for Au was implemented in calculations of the vacancy heat of transport as reported in Refs. 7–9.

Using the Morse potentials described above, we performed simulations at the reduced temperature $T^* = \frac{k_B T}{\epsilon} = 0.15$ and several different fixed volumes. At each volume, the time-averaged pressure was computed. The reduced pressure, p^* , as a function of reduced volume V^* is shown in Fig. 1. The results in Fig. 1 were obtained from 10^4 MD time steps without including the first 10^3 steps of equilibration. We fit the data in Fig. 1 to the Birch-Murnaghan equation of state

$$p^*(V^*) = \frac{3B_0^*}{2} \left[\left(\frac{V_0^*}{V^*} \right)^{7/3} - \left(\frac{V_0^*}{V^*} \right)^{5/3} \right] \times \left[1 + \frac{3}{4}(B_0' - 4) \left[\left(\frac{V_0^*}{V^*} \right)^{2/3} - 1 \right] \right], \quad (13)$$

where B_0^* is the reduced bulk modulus at zero pressure, B_0' is the pressure derivative of the bulk modulus, V^* is the reduced system volume per atom, and V_0^* is the reduced volume per atom for $p^* = 0$. The results are shown in Table I in reduced units.

To produce results that are suitable for comparison with real materials, we chose values for r_0 and ϵ . We define in each simulation $r_0 = 3.035 \text{ \AA}$, and $\epsilon = 0.5838 \text{ eV}$. With these

FIG. 1. Computed values of the reduced pressure p^* as a function of the reduced volume per atom V^* at a reduced temperature $T^* = 0.15$. The results were determined for potential parameters $\alpha r_0 = 4.55$ (black circles), $\alpha r_0 = 6.0$ (red squares), and $\alpha r_0 = 8.0$ (green diamonds).

TABLE I. Computed materials parameters in reduced units for Morse potentials with different values for αr_0 .

Property	$\alpha r_0 = 4.55$	$\alpha r_0 = 6.0$	$\alpha r_0 = 8.0$
B_0^*	53.8	68.7	106.1
V_0^*	0.607	0.685	0.711
B_0'	5.45	7.48	9.31

choices, we obtain $a_0 = 4.08 \text{ \AA}$ and $B_0 = 180 \text{ GPa}$ at a reduced temperature $T^* = 0.15$ and pressure $p^* = 0$ for the potential with $\alpha r_0 = 4.55$. These values correspond to the experimentally measured properties of Au at room temperature. The resulting materials properties for each potential, including the value of α that characterizes the three potentials, are reported in Table II. We also compute the cohesive energy predicted by each potential using the volume predicted for $p^* = 0$ and $T^* = 0.15$. In comparison to the experimental value $E_{coh} = 3.81 \text{ eV}$ for Au, we see that the potential with $\alpha r_0 = 4.55$ predicts a significantly larger value. Therefore, the potential with $\alpha r_0 = 4.55$, while representative of Au, is not rigorously fit. The potentials with parameterization $\alpha r_0 = 6.0$ and $\alpha r_0 = 8.0$ do not fit any particular materials system but are included here to determine how $Q_v^* - h_{fv}$ might systematically depend or be correlated with other materials properties. From the value ϵ and the reduced temperature $T^* = 0.15$, we obtain the actual simulation temperature $T = 1016 \text{ K}$. Defining the atomic mass to be equal to that of Au, we find that the reduced MD time step of $\Delta t^* = 0.001$ corresponds to an actual value of $\Delta t = 0.568 \text{ fs}$, which is sufficient to ensure good energy conservation.

The EAM potential for Ni used here is described in Refs. 13 and 14. The potential was optimized for the Ni-Al system, but the empirical potential used here was specifically developed in Ref. 13 for pure Ni. Included in the fitting database were the lattice parameter, cohesive energy, and elastic constants. Reasonable phonon dispersion curves were reported in Ref. 13, although zone-edge phonon modes appear to be over predicted by $\sim 10\%$ – 20% in comparison to experiment. In addition, vacancy formation and migration energies, which are quite relevant for the heat of transport, were found to be within a few percent of experimental values. For example, the vacancy formation energy was computed to be 1.19 eV , which is quite close to the experimental value 1.30 eV .¹³ These points will be revisited in Sec. IV.

The simulation supercell was a rectangular prism. We define a Cartesian coordinate system coincident with the vectors that define the supercell. The x-, y-, and z- directions

TABLE II. Potential parameters and resulting material properties computed at $T^* = 0.15$.

Parameter	$\alpha r_0 = 4.55$	$\alpha r_0 = 6.0$	$\alpha r_0 = 8.0$
$\alpha (\text{\AA}^{-1})$	1.4992	1.9769	2.6359
$\epsilon (\text{eV})$	0.5838	0.5838	0.5838
$r_0 (\text{\AA})$	3.0350	3.0350	3.0350
$B_0 (\text{GPa})$	180.0	229.9	355.0
$V_0 (\text{\AA}^3)$	16.98	19.19	20.02
$a_0 (\text{\AA})$	4.08	4.25	4.31
$E_{coh} (\text{eV})$	4.85	4.01	3.66

were coincident with the $[1\bar{1}0]$, $[001]$, and $[110]$ crystal directions, respectively. With this supercell, it is convenient to define a two-atom unit cell. For the Morse potentials, the supercell used consisted of $10 \times 7 \times 28$ unit cells with a total of $N = 3920$ fcc lattice sites. For simulations using the EAM Ni potential, a slightly smaller supercell was used due to the fact that the EAM potentials were more computationally intense. Specifically, for EAM Ni simulations, a supercell with $8 \times 6 \times 28$ unit cells and a total of $N = 2688$ fcc lattice sites was used. We introduced a single vacancy near the center of the simulation cell and constrained one of the atoms at various points corresponding to a vacancy hop along the $[110]$ direction. Specifically, at the beginning of each MD simulation, the hopping atom was displaced by the desired amount from the equilibrium position z_1 . In addition, its initial velocity component along $[110]$ was set to zero. During the MD simulation, the forces were computed on all the atoms, including the force $\vec{F}$ felt by the hopping atom due to the interactions with the neighboring atoms in the simulation cell. Next, the component of $\vec{F}$ along the $[110]$ direction, which is coincident with the z -axis in the Cartesian system defined above, was computed from $\vec{F} \cdot \hat{k}$. The constraint force $\vec{F}_c$ is then given by

$$\vec{F}_c = -(\vec{F} \cdot \hat{k})\hat{k}. \quad (14)$$

This constraint force was then added to the force acting on the hopping atom, so that the resulting force $\vec{F}'$ was

$$\vec{F}' = \vec{F} + \vec{F}_c. \quad (15)$$

The hopping atom followed the appropriate dynamics corresponding to $\vec{F}'$. Because $\vec{F}'$ has no component along the $[110]$ direction, there was no motion in that direction. However, the hopping atom was not constrained in the directions perpendicular to $[110]$, so that effectively all possible trajectories from z_1 to z_2 are explored. Finally, so that the center of mass of the system does not move when $\vec{F}_c$ was applied to the constrained atom, and equal but opposite force was applied to the other atoms in the system. In particular, in a system with N lattice sites and $N - 1$ atoms, the force on the hopping atom is given by Eq. (15), and the forces on the $N - 2$ other atoms were given by

$$\vec{F}'_k = \vec{F}_k - \frac{\vec{F}_c}{N - 2}, \quad (16)$$

where $\vec{F}'_k$ is the resulting force on atom k , and $\vec{F}_k$ is the force on atom k determined from the empirical potential. Thus, the additional force due to the constraint is added uniformly to the $N - 2$ atoms, and apart from the hopping atom, the other $N - 2$ atoms followed the dynamics suggested by Eq. (16). It might also be added that dynamics that result from Eq. (15) for the hopping atom and Eq. (16) for the other $N - 2$ atoms allow the system to relax fully when the atom is placed in between z_1 and z_2 . In general, placing the hopping atom near the transition state results in large forces which cause a local distortion in the lattice.

The simulation details for the Morse potentials and the Ni EAM potentials were somewhat different. In the case of

the Morse potentials, for each constrained position along the transition path, we first simulated for 10^6 MD steps at constant reduced temperature $T^* = 0.15$. After 10^5 MD steps to reach equilibrium, statistics for the average energy and constraint force are accumulated. Next, we use the final positions and velocities of the atoms as a starting point for simulation in the presence of a temperature gradient. The basic approach is what was previously reported in Ref. 1. In particular, we designate two regions of thickness $\delta = 0.05L_z$, where L_z is the length of the simulation cell along the z -direction. The midpoints of the two regions are separated by a distance $L_z/2$, and the vacancy is approximately equidistant from the regions. In these two regions, velocity rescaling following the algorithm developed in Ref. 15 is used to create hot and cold reservoirs. At each MD step, an energy $\Delta E = 0.05\epsilon$ is added to the hot region, and the same amount of energy ΔE is removed from the cold region. After turning on the velocity rescaling, the simulation is run for 2×10^6 MD steps for each location of the constrained atom. The first 10^5 MD steps are used to achieve steady-state with the imposed thermal current. After achieving steady state, the constraint force is time averaged over the remaining 1.9×10^6 MD steps.

For simulations using the EAM potential, the MD time step was taken to be $\Delta t = 0.358$ fs. The system was first equilibrated at constant temperature $T = 450$ K for 2×10^5 MD steps. After equilibration, the temperature gradient is added using the same approach as described above, including the thickness $\delta = 0.05L_z$ of the hot and cold reservoirs. At each MD step, an energy 0.01 eV is added/removed from the hot/cold reservoirs. The simulation with the applied heat current included 2×10^6 MD steps. After 10^5 MD steps to reach a steady-state temperature gradient, the statistics for the average constraint force were accumulated over the remaining 1.9×10^6 MD steps.

The integrated work $W(z)$ performed by the constraint force was computed as a function of z using Eq. (2). In equilibrium, the integrated work $W(z)$ is related to the free-energy profile. When a temperature gradient is applied, using the approach described above, the integrated work from the starting position z_1 to the final local minimum z_2 is determined, with $W_{1 \rightarrow 2} = W(z_2)$. This quantity is used in Eq. (1) to compute $Q_v^* - h_{fv}$.

It should be remarked that a similar procedure has been applied in Ref. 11 to compute the thermodiffusion of nanoparticles in a solvent. Specifically, in Ref. 11, the nanoparticle was connected to a spring which provides, on average, a force that opposes the thermodiffusion driving force due to an applied heat current. By computing the average spring force required to hold the nanoparticle in place, the thermodiffusion coefficient was determined. We believe that this approach is similar to the constrained-dynamics approach in that the external force required to balance the driving force for thermodiffusion is computed. However, the approach in Ref. 11 cannot be applied to the problem of vacancy thermodiffusion due to the very long time scales associated with vacancy hopping. However, we do think that the constrained-dynamics approach could be applied to the problems studied in Ref. 11.

FIG. 2. The internal energy $\Delta U(z)$ (dashed line) and free-energy $\Delta A(z)$ (solid line) in units of ϵ as a function of the coordinate z of the constrained atom for $\alpha r_0 = 4.55$. The results were computed in isothermal conditions $\nabla T^* = 0$ with $T^* = 0.15$.

IV. RESULTS

We begin by presenting the results obtained using the Morse potentials. In isothermal conditions $\nabla T^* = 0$, integration of the average constraint force is related to the potential of mean force, or, alternately, the free-energy profile. The free energy difference $\Delta A(z) = A(z) - A(z_1)$ is found from integrating the time-averaged constraint force $\langle F_c(z) \rangle$. Hence, $\Delta A(z) = W(z)$ with $W(z)$ computed using Eq. (2). We define the energy difference $\Delta U(z) = U(z) - U(z_1)$. In Fig. 2, we show the computed profiles $\Delta A(z)$ and $\Delta U(z)$ for $\alpha r_0 = 4.55$. The transition state occurs exactly in the middle of the path at $z/r_0 \approx 0.475$. We find the activation free energy $\Delta A_a = (3.017 \pm 0.002) \epsilon$. For the activation energy, we find $\Delta U_a = (3.15 \pm 0.02) \epsilon$. The magnitude of the numerical error in the calculation of ΔA_a and ΔU_a for $\alpha r_0 = 6.0$ and $\alpha r_0 = 8.0$ is similar. In Table III, we show the results for ΔA_a and ΔU_a computed for each value of αr_0 simulated in isothermal conditions with $T^* = 0.15$. As the value αr_0 increases, both ΔA_a and ΔU_a increase. This is easily understood. In particular, as αr_0 increases, the interatomic potential becomes increasingly short-ranged, and as a result both $\Delta A(z)$ and $\Delta U(z)$ exhibit larger increases as the transition state is approached. We also note from Table III that for $\alpha r_0 = 4.55$ and $\alpha r_0 = 6.0$, $\Delta U_a > \Delta A_a$, whereas for $\alpha r_0 = 8.0$, $\Delta U_a < \Delta A_a$. This indicates a change in sign of the activation entropy ΔS_a as αr_0 increases.

In Fig. 3, we plot the entropy difference $\Delta S(z)$ defined by

$$\Delta S(z) = \frac{\Delta U(z) - \Delta A(z)}{T}, \quad (17)$$

for the case $\alpha r_0 = 4.55$. We find generally that $\Delta S(z) > 0$, although noise in the data makes it impossible to conclude that $\Delta S(z)$ is positive for all values of z . This is opposite the behavior found in Ref. 1, where $\Delta S(z)$ was found to be negative. The noise in the plot of $\Delta S(z)$ is the result primarily of numerical fluctuations in the value of $\Delta U(z)$, since fluctuations throughout the entire system are involved in the computed value of $\Delta U(z)$. The entropy at the transition state, known as the activation entropy ΔS_a , is positive and equal to $\Delta S_a = (0.85 \pm 0.15)k_B$. Measurement of ΔS_a is not straightforward, and different methods of calculation can yield different results.¹⁶ However, we are unaware of any argument that suggests that either $\Delta S_a < 0$ or $\Delta S_a > 0$ is not possible.

We find that the activation entropy ΔS_a depends sensitively on the choice of the parameter αr_0 . In Fig. 4, we show the computed profile $\Delta S(z)$ for $\alpha r_0 = 6.0$, and in Fig. 5, we show the same quantity for $\alpha r_0 = 8.0$. Comparison of Figs. 3–5 shows that ΔS_a gradually decreases (i.e., trends towards negative values) as αr_0 increases. For example, in Fig. 4 for $\alpha r_0 = 6.0$, ΔS_a is positive, but significantly smaller than ΔS_a for $\alpha r_0 = 4.55$. Likewise, in Fig. 5, $\Delta S(z)$ appears to be negative across the entire region between z_1 and z_2 . In Table III, the computed values of ΔS_a are given for each value of αr_0 along with the associated numerical error. We will show below that the observed trend of decreasing ΔS_a with increasing αr_0 appears to be closely linked with the computed value of $Q_v^* - h_{fv}$.

To determine the reduced heat of transport $Q_v^* - h_{fv}$, we followed the general approach developed in Ref. 1 and discussed thoroughly above. Specifically, the work $W_{1 \rightarrow 2}$ is the work done by the constraint force to drive the constrained atom from z_1 to z_2 , where z_1 and z_2 represent the positions of the constrained atom that correspond to a local minima of the integrated work. The integrated work $W(z)$ is given by Eq. (2), with $W_{1 \rightarrow 2} = W(z_2)$. We take z_1 to be the position of the local minimum nearest to the hot region, and z_2 be the position of the local minimum nearest to the cold region. To accurately determine z_1 , z_2 , and $W_{1 \rightarrow 2}$, we fit the integrated work $W(z)$ to a cubic polynomial in the vicinity of z_1 and z_2 .

In Fig. 6, we show the integrated work $W(z)$ near $z = z_2$ along with the fits to a cubic polynomial for each value of

TABLE III. Computed quantities related to diffusion of a vacancy given in reduced units. The values in parentheses are the corresponding energies determined using $\epsilon = 0.5838 \text{ eV}$. The values for the activation free energy ΔA_a , energy ΔU_a , and entropy ΔS_a are computed in thermal equilibrium at reduced temperature $T^* = 0.15$. When a temperature gradient is present, there is a difference ΔT^* in the reduced temperature between the initial and final location of the diffusing atom. The values for the activation entropy ΔS_a are given in units of k_B . The temperature difference ΔT^* is also given in reduced units.

Parameter	$\alpha r_0 = 4.55$	$\alpha r_0 = 6.0$	$\alpha r_0 = 8.0$
ΔA_a	3.017 ± 0.002 (1.762)	4.829 ± 0.002 (2.819)	7.397 ± 0.002 (4.319)
ΔU_a	3.15 ± 0.02 (1.84)	4.86 ± 0.02 (2.84)	7.24 ± 0.02 (4.23)
$\Delta S_a (k_B)$	0.85 ± 0.15	0.20 ± 0.15	-1.05 ± 0.10
ΔT^*	0.0101 ± 0.0020	0.0072 ± 0.0015	0.0063 ± 0.0014
$W_{1 \rightarrow 2}$	-0.025 ± 0.002 (-0.013)	-0.011 ± 0.002 (-0.006)	0.004 ± 0.002 (0.002)
$Q_v^* - h_{fv}$	-0.39 ± 0.08 (-0.22)	-0.23 ± 0.05 (-0.13)	0.09 ± 0.01 (0.06)

FIG. 3. Entropy change $\Delta S(z)$ (in units of k_B) as a function of the coordinate z/r_0 of the constrained atom for $\alpha r_0 = 4.55$. The simulation is performed in isothermal conditions $\nabla T^* = 0$ with reduced temperature $T^* = 0.15$.

αr_0 . The minimum of the fit curve is used to determine z_2 and $W_{1 \rightarrow 2}$. The position $z = z_2$ corresponds to the constrained atom in a region with slightly lower local temperature in comparison to the local temperature at $z = z_1$. The most important result of this paper is the systematic dependence of $W_{1 \rightarrow 2}$ on the potential parameter αr_0 . In particular, Fig. 6 shows that for $\alpha r_0 = 4.55$, $W_{1 \rightarrow 2}$ is strongly negative. For $\alpha r_0 = 6.0$, $W_{1 \rightarrow 2}$ is still negative but is much closer to zero. In Ref. 1, $W_{1 \rightarrow 2}$ was also found to be negative and of very similar magnitude. In sharp contrast to these results, we found that for $\alpha r_0 = 8.0$, the value of $W_{1 \rightarrow 2}$ becomes positive.

To determine the value of $Q_v^* - h_{fv}$, we use Eq. (11). Hence, we need the computed temperature difference ΔT^* , which is given by

$$\Delta T^* = T^*(z_1) - T^*(z_2) = T_1 - T_2, \quad (18)$$

which is found by fitting the computed temperature profile in the region near the vacancy as was previously done in Ref. 1. In Table III, we show the computed values of $W_{1 \rightarrow 2}$, ΔT^* , and $Q_v^* - h_{fv}$. The numerical error for $W_{1 \rightarrow 2}$, ΔT^* , and $Q_v^* - h_{fv}$ are also given in Table III. The primary source of error in $Q_v^* - h_{fv}$ is due to uncertainty about the value of ΔT^* . We find that $Q_v^* - h_{fv}$ is large and negative for $\alpha r_0 = 4.55$ and trends towards positive values as αr_0 increases. For $\alpha r_0 = 8.0$, $Q_v^* - h_{fv}$ is rather small but

FIG. 4. Entropy change $\Delta S(z)$ (in units of k_B) as a function of the coordinate z/r_0 of the constrained atom for $\alpha r_0 = 6.0$. The simulation is performed in isothermal conditions $\nabla T^* = 0$ with reduced temperature $T^* = 0.15$.

FIG. 5. Entropy change $\Delta S(z)$ (in units of k_B) as a function of the coordinate z/r_0 of the constrained atom for $\alpha r_0 = 8.0$. The simulation is performed in isothermal conditions $\nabla T^* = 0$ with reduced temperature $T^* = 0.15$.

nevertheless clearly positive. This indicates that the details of the empirical potential can result in a qualitative change in the nature of the driving force for thermodiffusion. In particular, when $Q_v^* - h_{fv} < 0$, the tendency is for a vacancy to be driven towards the high-temperature region. By contrast, the fact that $Q_v^* - h_{fv} > 0$ for $\alpha r_0 = 8.0$ indicates that in that case, vacancies will tend to be driven towards the low-temperature region.

We next consider the possibility of temperature dependent values of $Q_v^* - h_{fv}$. In Ref. 8, the reported calculations suggest that $Q_v^* - h_{fv}$ exhibits strong temperature dependence. To explore the question of temperature dependence, we also simulated the case where $\alpha r_0 = 4.55$ for an average temperature $T^* = 0.20$. The system volume was chosen to be the same as that of the system with $T^* = 0.15$, which resulted in larger pressure due to the tendency of the system to expand at higher temperatures. In Fig. 7, we show the integrated work for $\alpha r_0 = 4.55$ for the two temperatures $T^* = 0.15$ and $T^* = 0.20$. We indeed observe a significant dependence on T^* . For $T^* = 0.20$, we find $W_{1 \rightarrow 2} = (-0.031 \pm 0.002) \epsilon$, which results in a reduced heat of transport $Q_v^* - h_{fv} = (-0.59 \pm 0.12) \epsilon$.

FIG. 6. Work $W(z)$ performed by the constraint force in the presence of a temperature gradient. The data are shown for the final state of the constrained atom near z_2 for $\alpha r_0 = 4.55$ (black circles), $\alpha r_0 = 6.0$ (red squares), and $\alpha r_0 = 8.0$ (green diamonds). The direction of the temperature gradient ∇T^* is indicated, with the arrow direction from low T^* towards high T^* . The lines are fits to the simulation data using a third-order polynomial.

FIG. 7. Work $W(z)$ performed by the constraint force in the presence of a temperature gradient. The data are shown for the final state of the constrained atom near z_2 for $\alpha r_0 = 4.55$. The results correspond to two different average temperatures, $T^* = 0.15$ (black circles) and $T^* = 0.20$ (red squares).

Using the value $\epsilon = 0.5838$ eV, we obtain $Q_v^* - h_{fv} = -0.34$ eV. This is significantly more negative than the value $Q_v^* - h_{fv} = -0.22$ eV computed at $T^* = 0.15$ for $\alpha r_0 = 4.55$ reported in Table III.

To determine the value of Q_v^* , an independent calculation of h_{fv} is required. To determine h_{fv} and u_{fv} , we simulate at constant volume and constant temperature for a total of 10^6 integration time steps. The system size used to find u_{fv} and h_{fv} was the same as in the constrained MD simulations reported above. However, in this case no atom was constrained. For each value of αr_0 , the system volume was held at the volume previously determined to be near the $p^* = 0$ at $T^* = 0.15$. To obtain u_{fv} and h_{fv} , the time-averaged pressure and internal energy are computed for a perfect crystal with $N = 3920$ atoms, and a crystal with a single vacancy and $N - 1 = 3919$ atoms. The initial 10^4 steps we used as equilibration time and not included in the time averages. We compute the vacancy formation energy from

$$u_{fv} = (u_{N-1} - u_N)(N - 1), \quad (19)$$

where u_{N-1} is the energy per atom of the system with the vacancy, u_N is the energy per atom of the perfect crystal, and $N = 3920$ is the total number of lattice sites. Likewise, the vacancy formation enthalpy is computed using

$$h_{fv} = (h_{N-1} - h_N)(N - 1), \quad (20)$$

where the enthalpy per atom h_{N-1} of the system with a vacancy and h_N of the perfect crystal are given by

$$h_{N-1} = u_{N-1} + \left(\frac{p_{N-1} V}{N - 1} \right), \quad (21)$$

where p_{N-1} is the internal pressure of the system with a single vacancy, and

$$h_N = u_N + \left(\frac{p_N V}{N} \right), \quad (22)$$

where p_N is the pressure of the perfect crystal. While the pressure may be fairly small in each case, because the volume is the same for both the system with a vacancy and the

TABLE IV. Computed values in reduced units for the energy u_{fv} and enthalpy h_{fv} of vacancy formation. The reduced temperature $T^* = \frac{k_B T}{\epsilon}$ is also given. In the last column, the computed values for Q_v^* are presented, using the reduced heat of transport values from Table III. The values in parentheses for u_{fv} , h_{fv} , and Q_v^* are the values in eV determined for $\epsilon = 0.5838$ eV.

αr_0	T^*	u_{fv}	h_{fv}	Q_v^*
4.55	0.15	8.05 (4.70)	5.72 (3.34)	5.33 (3.11)
4.55	0.20	8.11 (4.74)	5.19 (3.03)	4.60 (2.69)
6.0	0.15	6.87 (4.01)	6.78 (3.96)	6.55 (3.82)
8.0	0.15	6.29 (3.68)	7.11 (4.16)	7.20 (4.20)

perfect crystal systems, the value of p_N and p_{N-1} differ. As a result, h_{fv} can differ significantly from u_{fv} .

We include in Table IV results for each value of αr_0 at $T^* = 0.15$, and also $\alpha r_0 = 4.55$ at reduced temperature $T^* = 0.20$. In this latter case, the volume is held at the $p = 0$ volume for $\alpha r_0 = 4.55$ and $T^* = 0.15$, and as a result the system has a significant internal pressure. The numerical error for u_{fv} and h_{fv} is about $\pm 0.01\epsilon$, which is significantly smaller than the numerical error for the computed values $Q_v^* - h_{fv}$, and hence does not contribute significantly to the numerical error for Q_v^* . We find that Q_v^* and h_{fv} both tend to increase as αr_0 is increased. The increase in h_{fv} with αr_0 is largely due to pressure effects, since we also find that u_{fv} actually tends to decrease as αr_0 increases. The increase of Q_v^* with increasing αr_0 is due in part to the computed increase in the reduced heat of transport $Q_v^* - h_{fv}$ but is in fact dominated by the strong dependence of h_{fv} on αr_0 .

Next, we present results for the reduced heat of transport for the EAM Ni potential. In Fig. 8, the integrated work $W_{1 \rightarrow 2}$ in the presence of a temperature gradient at an average temperature $T = 450$ K for the Ni EAM potentials is shown. The integrated work to displace the atom from z_1 to z_2 is -0.004 ± 0.002 eV. For the imposed heat current, the temperature difference $\Delta T = T_1 - T_2 = 20.8 \pm 2$ K. Using these values in Eq. (1), the value $Q_v^* - h_{fv} = -0.08 \pm 0.04$ eV is obtained. This value is clearly negative, but of a rather small magnitude in comparison to the values obtained with the

FIG. 8. Work $W(z)$ performed by the constraint force in the presence of a temperature gradient for the Ni EAM potential with $T = 450$ K. The data are shown for the final state of the constrained atom near z_2 .

Morse potentials. The activation entropy was also computed during the first 2×10^5 MD steps and found to be $\Delta S_a = (2.2 \pm 0.2)k_B$. This value is positive, as are the values for the Morse potentials with $\alpha r_0 = 4.55$ and $\alpha r_0 = 6.0$, but is of an even larger magnitude. The vacancy heat of formation was computed to be $h_{fv} = 1.19$ eV, resulting in a value $Q_v^* = 1.11$ eV. As expected, the more realistic value of h_{fv} obtained when using an EAM potential leads to a more reasonable value for Q_v^* in comparison to pair potentials, which are known to greatly overestimate h_{fv} .

V. ANALYSIS

In this paper, we report extensive simulation results relevant to thermodiffusion of vacancies in a single-component system. In contrast to previous studies, the objective was to gain some understanding of what controls the relevant transport parameters $Q_v^* - h_{fv}$ and Q_v^* by systematically varying the potential parameters in a simple model. We find, as previously reported in Ref. 1, that the value of Q_v^* is close to the vacancy formation enthalpy h_{fv} . This prediction is in agreement with simulations reported in Refs. 2 and 24 for the heat of transport of hydrogen in a Pd lattice. We think that this is an important insight that likely is characteristic of most thermodiffusion problems. This point remains to be verified by exploring other materials systems.

The reduced heat of transport $Q_v^* - h_{fv}$ was found to depend systematically on the value of αr_0 used in the Morse potential. More insight was obtained from the observation that the activation entropy ΔS_a also depended systematically on αr_0 . The results here suggest an important correlation between $Q_v^* - h_{fv}$ and ΔS_a that can enable improved physical understanding.

It can be readily understood why $Q_v^* - h_{fv}$ might be correlated to ΔS_a . In particular, the activation entropy is related to differences between the work required to drive an atom to the transition state and the change in internal energy when the system is maintained at constant and uniform temperature T . If the vacancy is driven through the transition state from one free-energy minimum to another, the net change in energy, entropy, and free energy is zero. When there is a temperature gradient present, T is not uniform, and as a result the work $W_{1 \rightarrow 2}$ required to drive the diffusing atom is non-zero primarily due to entropic effects along the diffusion path. The general trend we predict here is that $Q_v^* - h_{fv}$ tends to be negative when ΔS_a is large and positive. When ΔS_a trends towards zero, the magnitude of $Q_v^* - h_{fv}$ becomes smaller. As ΔS_a becomes large and negative, $Q_v^* - h_{fv}$ can become positive.

Agreement between theoretical predictions and experimental results is still not completely realized for the case of single-component materials. In Table V, we compare to previous experimental and computational results. For temperatures near $T = 1100$ K, the simulations reported here and in Refs. 8 and 9 agree qualitatively with experiment for Au.^{21–23} In particular, for the case of Au, the value of $Q_v^* - h_{fv}$ is found to be negative in both experiment and simulation. However, the magnitude of the values predicted by simulation is significantly different from what is found in

TABLE V. Comparison between simulation and experimental results for $Q_v^* - h_{fv}$ and Q_v^* . Experimental results are from Refs. 17, 18, and 23–25 for Au and Cu. Simulation results from Ref. 8 most closely correspond to Au, as do the simulation results reported in this paper for $\alpha r_0 = 4.55$. The values for the temperatures used in the experiment are comparable to the average values reported.

System	Exp./Sim.	T (K)	$Q_v^* - h_{fv}$ (eV)	h_{fv}	Q_v^* (eV)
Au (Ref. 8)	Sim.	730	−3.9	3.31	−0.59
Au (Ref. 8)	Sim.	1100	−2.0	3.31	1.31
Au (Ref. 8)	Sim.	1440	−1.2	3.31	2.11
Au (Refs. 17, 18, and 22)	Exp.	~1100	−0.59	0.98	0.39
Au (Refs. 17, 18, and 21)	Exp.	~1100	−0.68	0.98	0.30
Au (Refs. 17, 18, and 23)	Exp.	~1100	−0.80	0.98	0.18
Cu (Refs. 18 and 23)	Exp.	~1100	−1.37	1.17	−0.20
Au $\alpha r_0 = 4.55$ (This work)	Sim.	1016	−0.22	3.34	3.11
Au $\alpha r_0 = 4.55$ (This work)	Sim.	1354	−0.34	3.03	2.69
Ni EAM (This work)	Sim.	450	−0.08	1.19	1.11

experiment. The calculations reported in Refs. 8 and 9 predict the magnitude of $Q_v^* - h_{fv}$ at least twice that found in experiment for Au. In the present calculations, we find that $Q_v^* - h_{fv}$ is smaller than the experimental results for Au by at least a factor of two.

By computing h_{fv} , we determined values for Q_v^* that also can be compared with experiment. In the case of the results reported in Refs. 8 and 9, we use the computed value for h_{fv} at $T = 0$ using the Cherns potential.¹² For the experimental results, we use the reported values for $Q_v^* - h_{fv}$ ^{21–23} and h_{fv} .^{17,18} We find that for the case of Au at $T \sim 1100$ K, the results in Table V all predict a positive value for Q_v^* , and hence experiment and simulation are at least in qualitative agreement. However, the simulations here and in Refs. 8 and 9 predict values substantially larger than what is seen in experiment. The results in Table V suggest perhaps the most significant source of error in predicting Q_v^* is due to the inability of both the Cherns and Morse potentials to accurately reproduce the value of h_{fv} . In fact, the results in Table V show that the Morse and Cherns potentials all systematically overestimate the value of h_{fv} .

It seems very likely, therefore, that the most important source of error in the present calculations of Q_v^* lies in the fact that no simple pair potential can accurately predict h_{fv} . However, we also note that the simulations reported here for $\alpha r_0 = 4.55$ and those in Refs. 8 and 9 do not accurately predict the enthalpy of vacancy migration h_{mv} . As we have seen here, the details of the energetics through the transition state are closely related to the predicted value of $Q_v^* - h_{fv}$, and so it seems likely that the predictions reported here and in Refs. 8 and 9 might be significantly in error when compared to experimental results for Au. For example, the results in Table III for $\alpha r_0 = 4.55$ show that the energy of activation for vacancy migration is $\Delta U_a = 1.84$ eV. The value of ΔU_a should be quite close to h_{mv} . In Ref. 8 and 9, the value of h_{mv} is significantly larger, in particular $h_{mv} = 2.64$ eV. In contrast to these calculated values, the experimental value of $h_{mv} = 0.83$ eV (Ref. 23) is significantly smaller. Thus, the details of the energy profiles along the diffusion path, and

most likely the entropy profile as well, are not accurately predicted by the Morse or Cherns potentials.

Results obtained using the EAM potential for Ni demonstrate a value for Q_v^* that is significantly smaller in magnitude than those reported for the Morse potentials primarily due to the smaller value of h_{fv} . It is well known that EAM potentials are able to reproduce accurately the formation enthalpy of vacancies due to the many-body effects incorporated in the formalism.

Finally, we comment on the negative value of Q_v^* reported in experiment for Cu.^{18,21} We note that the measured value of $Q_v^* - h_{fv}$ is negative, but of the same general magnitude as those predicted using simulation here and in Refs. 8 and 9. Therefore, it is entirely reasonable that a pair-type potential could predict the observed value for $Q_v^* - h_{fv}$ in Cu. However, given the inability of simple pair potentials to predict h_{fv} , we expect that pair potentials will always predict a positive value for Q_v^* . While a positive value for Q_v^* was found using the EAM model for Ni, it may be possible for an EAM potential to result in a negative value for Q_v^* . We also note that, based on the insight obtained in this paper, the rather large negative value for $Q_v^* - h_{fv}$ measured for Cu suggests that ΔS_a should be fairly large and positive. We do not know of any existing calculations that predict values for ΔS_a in bulk Cu and Au using either EAM or density-functional theory calculations. However, it would be interesting to establish whether this correlation between ΔS_a and $Q_v^* - h_{fv}$ can be verified for the two cases of Cu and Au.

The value of $Q_v^* - h_{fv}$ and Q_v^* were found to depend on system temperature. Temperature dependence was also predicted in Refs. 8 and 9. In experiments, there have been few systematic studies of temperature dependence, and so the situation from experiment is not totally clear. There are exceptions, however. For example, systematic dependence in ionic crystals has been known for some time (see Ref. 19, for a review). In the case of metals, a systematic study in the case of Pt has been reported in Ref. 20, where the heat of transport for vacancies was found to be negative with a magnitude that increases with temperature. In the calculations reported here, we find that as T^* increases, $Q_v^* - h_{fv}$ becomes more negative for the case studied with $\alpha r_0 = 4.55$. Consequently, Q_v^* , while still positive in the simulations reported here, tends to decrease in magnitude as T^* increases. In the simulations reported here, internal stress may also play a role, but this aspect was not investigated. In particular, the system volume was kept the same for $T^* = 0.15$ and $T^* = 0.20$ with $\alpha r_0 = 4.55$, resulting in very different internal stress. It is therefore not possible to isolate dependence on temperature and stress. Nevertheless, temperature dependence has clearly been demonstrated, which is consistent with the observation that $Q_v^* - h_{fv}$ is strongly correlated with the sign and magnitude of the activation entropy ΔS_a .

VI. SUMMARY AND CONCLUSIONS

In summary, using pair potentials and EAM potentials, the constrained-dynamics method was used to compute the heat of transport in single-component fcc crystals. Simulations included three different Morse potentials and an

EAM potential for Ni. The results were consistent with recently published Green-Kubo simulations for hydrogen thermodiffusion in a Pd lattice. Specifically, the heat of transport is comparable to the partial enthalpy of the diffusing species. In the results here, this leads to relatively small values for $Q_v^* - h_{fv}$. In addition, the results here were qualitatively similar to the previous study of thermodiffusion in Lennard-Jones crystals.¹

The results suggest a possibly important trend; namely, that $Q_v^* - h_{fv}$ is strongly correlated with ΔS_a , indicating that entropic effects along the diffusion path control thermodiffusion. Dependence on system temperature was also observed, which could also be attributed to entropic effects. However, while the correlation is clearly established, it is not clear if there is any physical significance underlying the correlation, nor whether or not this is a general result.

The lack of agreement between theory and experiment is still an important shortcoming of this work and those published by other authors. One clear problem is that there is generally very little data for single-component systems, and published experimental results, for example, for Au and Cu, have rather large error bars. For predictions of Q_v^* , we have shown that pair potentials are generally unsuitable because they fail to accurately predict h_{fv} . The study of binary alloys is another important direction due to the greater relevance to applications and the existence of experimental data still not explained theoretically. For example, the methodology developed in Ref. 1 and used here should be applied to dilute solid solutions, with the results compared to experiment.

In Ref. 24, it was demonstrated that the thermodiffusion of hydrogen atoms in a Pd lattice could be understood by computing individual contributions to the integrated correlation functions. In particular, it was found that the hopping hydrogen atoms have slightly higher kinetic and potential energies than average. In addition, in Ref. 24, we showed that the contribution due to the virial terms in the heat current was slightly less than what might be expected based on the average partial pressure of hydrogen. These results suggest that essentially the reduced heat of transport is the difference between the partial enthalpy of a hydrogen atom during a hop and the average enthalpy of a hydrogen atom. Specifically, hydrogen atoms that undergo a hopping event have a different kinetic energy, potential energy, and different contribution to the stress tensor than an average hydrogen atom. Assuming this is a general result, it should be possible to apply this picture to the thermodiffusion of vacancies. In particular, the results here indicate that $Q_v^* - h_{fv}$ is relatively small. We propose that differences between Q_v^* and h_{fv} are due to the difference between the partial enthalpy of a vacancy undergoing a hopping event and a vacancy at a potential minimum in the lattice.

Finally, we comment on the relationship between the constrained-dynamics method and previous approaches, including Green-Kubo and the method derived from the original work due to Gillan.³⁻⁵ We think that the constrained-dynamics method as presented can be compared directly to experiment and Green-Kubo simulations. As already noted, essentially exact agreement has been found between constrained-dynamics and Green-Kubo for thermodiffusion

in the Pd:H system.² As for comparison with the method originally due to Gillan, the significant disagreement reported here requires some additional comment. In the Gillan approach, the dynamics of atomic hops is explicitly computed, in contrast with the constrained-dynamics approach. In simulating the dynamics of atom hops, a large heat flux was observed that makes a dominant contribution to the computed value of the heat of transport.^{6–9} This effect is not present in the constrained-dynamics method. Some of us discuss this further elsewhere.²⁵

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APPENDIX: CONSTRAINED DYNAMICS AND THE SECOND LAW OF THERMODYNAMICS

Here, we describe the origin of Eq. (1) in terms of a series of thermodynamic processes, as we did in Ref. 1, with an emphasis on the role of entropy production. We also note that no violation of the second law of thermodynamics is implied.

We first envision that a vacancy has hopped from z_2 to z_1 irreversibly with entropy generation $\Delta_i S_{hop} > 0$ given by

$$\Delta_i S_{hop} = (Q_v^* - h_{fv}) \frac{T_2 - T_1}{T^2}. \quad (\text{A1})$$

Rather than viewing this process in terms of the displacement of the vacancy, it can equivalently be viewed as the hopping of an atom from z_1 to z_2 . After the irreversible hop occurs, we next envision the process of returning the system to its original state by applying an external force to displace the vacancy from z_1 to z_2 , or equivalently displacing an atom from z_2 to z_1 . Hence, we view the process of returning the system to its original state as using work $W_{2 \rightarrow 1}$ done on the system by the external force to move an atom from z_2 to z_1 . In this process, the atom is displaced infinitely slowly and the heat flux J_q is held constant. If this process is done infinitely slowly, then it can be done reversibly (i.e., without generating any entropy in the system). However, this process increases the internal energy of the system by an amount $W_{2 \rightarrow 1}$, and in order to return the system to its original state this energy must be removed from the system to the external environment. This changes the entropy of the system by an amount $-W_{2 \rightarrow 1}/T$. After returning the vacancy to its original position and releasing heat $W_{2 \rightarrow 1}$ to the environment, the entropy of the system should be the same as it was before the irreversible vacancy hop from z_2 to z_1 . Hence, we have for the overall change in entropy of the system

$$-W_{2 \rightarrow 1}/T + Q_v^{*f} \left(\frac{T_2 - T_1}{T^2} \right) = 0. \quad (\text{A2})$$

From this expression, Eq. (1) can be derived.

The process outlined above does not violate the laws of thermodynamics. Specifically, after an irreversible process, in this case a vacancy hop in the presence of a temperature gradient, the system can be returned to its original state only by increasing the entropy of the environment. In the process outlined above, the reversible work due to the external constraint force returns the system to its original state, but only with the release of heat $W_{2 \rightarrow 1}$ to the environment. For example, if the environment is also at temperature T , then the increase in the entropy of the environment is $W_{2 \rightarrow 1}/T$. Therefore, after the process outlined above, the entropy of the system is unchanged, but the entropy of the environment has increased.

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