PHYSICAL REVIEW E **96**, 032133 (2017)

Quantum statistical effects in the mass transport of interstitial solutes in a crystalline solid

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(Received 31 May 2017; published 20 September 2017)

The impact of quantum statistics on the many-body dynamics of a crystalline solid at finite temperatures containing an interstitial solute atom (ISA) is investigated. The Mori-Zwanzig theory allows the many-body dynamics of the crystal to be formulated and solved analytically within a pseudo-one-particle approach using the Langevin equation with a quantum fluctuation-dissipation relation (FDR) based on the Debye model. At the same time, the many-body dynamics is also directly solved numerically via the molecular dynamics approach with a Langevin heat bath based on the quantum FDR. Both the analytical and numerical results consistently show that below the Debye temperature of the host lattice, quantum statistics significantly impacts the ISA transport properties, resulting in major departures from both the Arrhenius law of diffusion and the Einstein-Smoluchowski relation between the mobility and diffusivity. Indeed, we found that below one-third of the Debye temperature, effects of vibrations on the quantum mobility and diffusivity are both orders-of-magnitude larger and practically temperature independent. We have shown that both effects have their physical origin in the athermal lattice vibrations derived from the phonon ground state. The foregoing theory is tested in quantum molecular dynamics calculation of mobility and diffusivity of interstitial helium in bcc W. In this case, the Arrhenius law is only valid in a narrow range between ∼300 and ∼700 K. The diffusivity becomes temperature independent on the low-temperature side while increasing linearly with temperature on the high-temperature side.

DOI: 10.1103/PhysRevE.96.032133

I. INTRODUCTION

The mobility and diffusivity of an interstitial solute atom (ISA) are commonly modeled within the one-body approximation as a random walker jumping among trapping centers at periodic lattice sites, with well-defined equilibrium and saddle-point configurations and energies [1–3]. Based on the transition-state theory (TST), the mean ISA jump frequency ν_J can be expressed within classical Boltzmann-Gibbs statistics as the product of the attempt frequency ν_0 and the escape probability $\exp(-\Delta G_m/k_B T)$. Here ΔG_m is the free-energy barrier that must be overcome for the detrapping of the ISA, k_B is the Boltzmann constant, and T the absolute temperature. Assuming detailed balance, the ISA diffusivity D can then be written in the Arrhenius form [1–3]:

$$D = D_0 e^{S_m/k_B} \exp(-E_m/k_B T). \qquad (1)$$

In Eq. (1), D_0 is the prefactor that depends on the jump geometry and vibration frequency of the ISA; S_m and E_m are, respectively, the migration entropy and enthalpy. If a reversible path can be assumed, ΔG_m can be evaluated via a thermodynamic integration approach.

Although Eq. (1) provides a convenient conduit that allows diffusion measurements to be physically interpreted, the dynamics involved in the mobility and diffusivity of interstitial solute atoms (ISAs) in a crystalline solid at finite temperatures is not one-body, but many body, in nature. The motion of the ISA and the "migration barrier" it encounters are coupled to the vibrating lattice. In principle, the many-body dynamics of a specific system can be readily treated numerically by directly solving the coupled equations of motion among all particles of the system, such as is achieved in a molecular dynamics approach. At the same time, the equation of motion of a state variable in a many-body system can also be formally expressed through a projection operator formalism in the form of a one-body generalized Langevin equation, with the dissipation and fluctuation terms expressed via the Liouvillian operator [4,5]. This representation of the many-body problem provides us with a route to an analytic solution via a pseudo-one-body scheme in which many-body effects may be subsumed into parametrized random forces and the associated dissipative friction. Indeed, in the earlier works of Einstein [6] and Smoluchowski [7], the many-body environment of a diffusing Brownian particle was already modeled using random forces and associated dissipative friction related through the classical fluctuation-dissipation theorem [4,8]. The mobility and diffusivity derived this way had a form not bearing any obvious resemblance to the Arrhenius law. Kramers [9], who studied the transition-state theory within the same framework, also showed that such stochastic effects derived from many-body dynamics are important unless the activation barrier is much higher than the thermal energy of the atoms; i.e., $E_m \gg k_B T$. Chandrasekhar [10] obtained similar results alternatively based on the linear response theory.

Based on the Mori-Zwanzig formalism [4,5], Munakata and Tsurui [11] and Combs and Kunz [12] showed that the dynamics of a highly mobile defect in a crystal can be modeled as a particle under stochastic forces in a periodic force field. Recent works using similar stochastic methodology on many other related areas also reported similar conclusions, such as adatom diffusion on the surface [13], kink diffusion along dislocation lines [14], solute diffusion [15], and migration of dislocation loops [16].

Nevertheless, key to the foregoing analyses is the use of the classical fluctuation-dissipation theorem [4,8], in which the quantum nature of lattice vibrations in a phonon theory is unaccounted for. The statistical distribution of the vibration

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modes of the crystal used in deriving these results is thus inaccurate [17]. Epic glitches that ensued, such as the ultraviolet catastrophe, are well known.

As a consequence of the noncommunicative relation, the importance of quantization in the thermal excitations of the crystal lattice is well known [18] in the explanation of the failure of the classical theory of low-temperature specific heat and the associated divergence of the classical entropy. Due to energy quantization, the excitation of phonons with frequency ω becomes increasingly improbable with decreasing temperature T. This limits the applicability of Boltzmann statistics only to the regime above the Debye temperature. The situation is similar regarding spin vibrations in ferromagnetic metals, but the constraint is even more serious [19].

Quantum uncertainty, similar to energy quantization, is another consequence of the noncommutative relation. Through the zero-point vibrations associated with the phonon ground state, quantum uncertainty in the free energy of the many-body system is expected to affect the dynamics of the ISA. Indeed, zero-point fluctuations have been envisaged as responsible for many physical effects, such as the Lamb shift, the Casimir force, the natural linewidths of energy levels, and the broadening of neutron scattering resonance lines in solids [20].

Despite their fundamental importance, quantum statistical effects of the lattice vibrations on the transport properties of the solid state, such as mobility and diffusivity, are not clearly understood. Indeed, even the scale of the errors involved is not well known. The aim of the present paper is to analyze and demonstrate such quantum statistical effects on the transport of solute atoms in a crystalline solid. In this regard, our present scope does not include consideration of effects due to coherent quantum tunneling caused by the spread of the one-particle wave function of the ISA over different sites across the migration barrier. Nevertheless, as we will further discuss, it is normally appreciable only for the diffusion of very light particles.

The present paper is organized as follows. In Sec. II, the thermodynamics of a system of particles in a noisy medium is shown to be completely governed by its fluctuation-dissipation ratio which can be formally related to the kinetic energy of the system. In a harmonic quantum crystal, this relation depends on the phonon density of state (DOS) and the thermodynamic temperature which we call the quantum fluctuation-dissipation relation (QFDR). In Sec. III, using the derived QFDR the many-body dynamics of the mobility and diffusivity of a model particle in a sawtooth potential is solved within a pseudo-one-body approach using the Langevin equation by following the Mori-Zwanzig theory [4,5]. In Sec. IV, with a Langevin heat bath based on QFDR, the many-body dynamics is directly solved for the mobility and diffusivity of He in bcc W by following the MD approach. Results of Secs. III and IV are compared and discussed. The paper is concluded with Sec. V.

II. FORMULATION

A. Statistical thermodynamics of a system of interacting particles in a noisy medium

We consider the dynamics of a general interactive system of atoms with Hamiltonian $\mathscr{H}$ expressed in the form

$$\mathscr{H}=\sum_n \frac{\mathbf{p}_n^2}{2m_n}+U(\{\mathbf{r}_n\}), \tag{2}$$

where m_n, $\mathbf{p}_n$, and $\mathbf{r}_n$, respectively, are the mass, momentum, and position of the nth atom. $U(\{\mathbf{r}_n\})$ is the total potential energy due to interatomic interactions corresponding to the configuration $\{\mathbf{r}_n\}$. For simplicity, we assume that the atoms are nonmagnetic.

Within the framework of the Ehrenfest theorem, the equations of motion for each atom can be written as [21]

$$\frac{d\langle\mathbf{r}_n\rangle_E}{dt}=\frac{\langle\mathbf{p}_n\rangle_E}{m_n}, \tag{3a}$$

$$\frac{d\langle\mathbf{p}_n\rangle_E}{dt}=-\left\langle\frac{\partial U}{\partial\mathbf{r}_n}\right\rangle_E, \tag{3b}$$

where $\langle\cdots\rangle_E$ denotes the expectation value of an observable.

If one may subsume the difference between the quantum and classical forces $\langle\frac{\partial U}{\partial\mathbf{r}_n}\rangle_E-\frac{\partial U(\mathbf{r}_n)}{\partial\mathbf{r}_n}$ that account for the quantum uncertainty due to the noncommutative relation between $\mathbf{r}$ and $\mathbf{p}$ into the Mori-Zwanzig random forces that account for the fluctuations due to many-body and quantum effects, one may formally put the equations of motion in Eqs. (3a) and (3b) in the Langevin form. We note that within this approximation, coherency of the one-particle wave function of the atoms over different sites is neglected, which is justifiable noting that the de Broglie wavelength of an atom in crystals is $\lambda\approx\frac{\hbar}{mv_G}\approx10^{-12}$ m which is much smaller than the interatomic distances under consideration. In an alternate but equivalent route, the direct application of the Mori-Zwanzig formalism [4,5] to the expectation values of the Heisenberg equation of motion also yields the same result.

Within this approximation, the dynamics of the nth atom in the many-body environment of the rest of the crystal can be treated with an equivalent set of pseudo-one-particle equations of motion in the Langevin form, assuming a local memory function,

$$\frac{d\mathbf{r}_n}{dt}=\frac{\partial\mathscr{H}}{\partial\mathbf{p}_n}=\frac{\mathbf{p}_n}{m_n}, \tag{4}$$

$$\frac{d\mathbf{p}_n}{dt}=-\frac{\partial U}{\partial\mathbf{r}_n}-\frac{g}{m_n}\mathbf{p}_n+\mathbf{f}_n(t), \tag{5}$$

where we have dropped the notation $\langle\cdots\rangle_E$ to simplify. In Eq. (5), the random forces on the atom n due to its environment (the bath or the rest of the crystal) arecharacterized by the dissipative friction with drag coefficient g and delta-correlated remnant fluctuations with strength characterized by s:

$$\langle\mathbf{f}_n(t)\rangle=0\quad\text{and}\quad\langle f_{in}(t)f_{jl}(t')\rangle=s\delta_{ij}\delta_{nl}\delta(t-t'). \tag{6}$$

Subscripts i and j denote Cartesian components and $\langle\cdots\rangle$ denotes the statistical mean taken over all the possible realizations of the stochastic forces.

The corresponding phase-space probability density $W(\{r_{ni}\},\{p_{ni}\},t)$ of the crystal is determined by the

Fokker-Planck equation:

$$\frac{\partial W}{\partial t}+\sum_{n,i}\left\{\frac{p_{ni}}{m_n}\frac{\partial}{\partial r_{ni}}-\left(\frac{\partial U}{\partial r_{ni}}\right)\frac{\partial}{\partial p_{ni}}\right\}W = \sum_{n,i}\frac{\partial}{\partial p_{ni}}\left[g\frac{p_{ni}}{m_n}+\frac{s}{2}\frac{\partial}{\partial p_{ni}}\right]W. \tag{7}$$

Statistically averaging $\langle\mathscr{H}\rangle$ over $W(\{r_{ni}\},\{p_{ni}\},t)$, one may write down the rate of change of the ensemble averaged energy $\bar{E}$,

$$\frac{d\bar{E}}{dt}=\sum_{n,i}\left\langle\left\{\frac{p_{ni}}{m_n}\frac{dp_{ni}}{dt}+\frac{\partial U}{\partial r_{ni}}\frac{p_{ni}}{m_n}\right\}\right\rangle = \sum_{n,i}\left\{-g\frac{\langle p_{ni}^2\rangle}{m_n^2}+\frac{\langle f_{ni}(t)p_{ni}\rangle}{m_n}\right\}. \tag{8}$$

The last term in Eq. (8) can be further simplified via the formal solution of Eq. (5), using Eq. (6). Thus,

$$\langle\mathbf{p}_n(t)\cdot\mathbf{f}_n(t)\rangle=\frac{g}{m_n}\int_0^t\langle\mathbf{p}_n(t')\cdot\mathbf{f}_n(t)\rangle dt' + \int_0^t\langle\mathbf{f}_n(t')\cdot\mathbf{f}_n(t)\rangle dt'=\frac{3s}{2}. \tag{9}$$

The first integral on the right-hand side vanishes because the argument of the integral $\langle\mathbf{p}_n(t')\cdot\mathbf{f}_n(t)\rangle$ is equal to zero everywhere in the interval $t'\in[0,t)$, except for the point $t'=t$ where it has a finite magnitude. The second term, on the other hand, integrates to give $3s/2$ according to Eq. (6). Equation (8) is a simple statement that the change of the internal energy of the system is equal to the work done by the fluctuation reduced by the energy dissipated (heat generated) by the friction, i.e., the first law.

In thermal equilibrium, $W(\{r_{ni}\},\{p_{ni}\})$ is the stationary solution of Eq. (7) with $\partial W/\partial t=0$. W can then be solved with a trial function of the form $W=C\exp(-\kappa\mathscr{H})$, where κ is an unknown parameter to be determined and C is a normalization constant. Substituting the trial solution into Eq. (7), we obtain

$$\sum_{n,i}\frac{p_{ni}}{m_n}\left(g-\frac{\kappa s}{2}\right)W=0, \tag{10}$$

yielding the solution (necessary and sufficient) $\kappa^{-1}=s/2g\equiv\eta$, the fluctuation-dissipation ratio which defines the Langevin heat bath for the canonical ensemble. The corresponding phase-space probability density is then given by

$$W(\{r_{ni}\},\{p_{ni}\})=Z\exp[-\kappa E(\{r_{ni}\},\{p_{ni}\})]. \tag{11}$$

The probability of the jth state of the $3N$ degrees of freedom is given by $P_j=Z\exp(-\kappa\varepsilon_j)$, where ε_j is the corresponding energy and $Z=\sum_{j=1}^{3N}e^{-\kappa\varepsilon_j}$ is the partition function of the many-body system. The thermodynamics of this system can be parametrized in terms of $\eta\equiv s/2g\equiv\kappa^{-1}$. Thus, by definition, Z yields the mean crystal energy $E=-\frac{\partial\ln Z}{\partial\kappa}$ and entropy $S=\kappa E+\ln Z$ (in units of k_B). In this regard, $F\equiv-\eta\ln Z=E-\eta S$ is the corresponding Helmholtz free energy of the stochastic system. Since both E and S are functions of κ that dictate the phase-space probability density we may write $dS=\kappa dE+Ed\kappa+\frac{d\ln Z}{d\kappa}d\kappa$, in which the last two terms cancel, yielding $\frac{dE}{dS}=\eta$. Thus, the thermodynamics (equilibrium) of the system is completely defined, if the functional relation between η and the temperature T is known, which is our next task. Noting that the effects of fluctuation and dissipation are balanced at equilibrium, Eq. (10) yields explicitly

$$\sum_{n,i}\frac{g}{m_n}\left\{-\frac{\langle p_{ni}^2\rangle}{m_n}+\eta\right\}=0$$

$$\Rightarrow\eta=\frac{\sum_n\frac{2}{3m_n}\left(\frac{\langle p_{ni}^2\rangle}{2m_n}\right)}{\sum_n\frac{1}{m_n}}=\frac{2}{3}E_K, \tag{12}$$

where E_K is the mean kinetic energy of the ensemble. In Eq. (12), we have used the fact that the mean kinetic energy of all atoms is equal at equilibrium. Equation (6) then becomes

$$\langle f_{in}(t)f_{jl}(t')\rangle=s\delta_{ij}\delta_{nl}\delta(t-t')=\frac{4}{3N}g\delta_{ij}\delta_{nl}\delta(t-t')E_K. \tag{13}$$

It is important to note that Eq. (12) holds formally independent of whether quantum or classical statistics is employed. If quantum effects are neglected, the equipartition theorem gives $E_K=3Nk_{\mathrm{B}}T/2$, yielding $\eta=k_{\mathrm{B}}T$, the classical fluctuation-dissipation relation (CFDR) [4,8]. In this case, the temperatures of the system (and the Langevin heat bath) are directly defined by $\frac{dE}{dS}=k_{\mathrm{B}}T$, and the Helmholtz free energy is given by $F=E-k_{\mathrm{B}}TS$, a standard result of classical thermodynamics.

B. Quantum fluctuation-dissipation relation in a crystalline solid

If we take into account the noncommutative relation in the dynamics of lattice vibrations in accord with the Bose-Einstein statistics, Eq. (12) yields [17]

$$\eta(T)=\frac{2}{3N}E_K=\frac{1}{3N}\sum_k\sum_{\alpha=1}^{3}\hbar\omega_\alpha(\mathbf{k})\left[\frac{1}{e^{\hbar\omega_\alpha(k)/k_BT}-1}+\frac{1}{2}\right]. \tag{14a}$$

In this case, η is a *nonlinear* function of temperature, defined by the phonon (vibration) spectrum.

We shall call $\eta(T)$ defined by Eq. (14a) the quantum fluctuation-dissipation ratio (QFDR). From the foregoing it is clear that all thermodynamic properties of the crystal are functions of temperature via the QFDR $\eta(T)$ in Eq. (14a).

Within the Debye model, Eq. (14a) yields convenient analytic expressions for all thermodynamic functions of the vibrating lattice via $\eta(T)$ [17], where

$$\eta(T)=\frac{3}{8}k_{\mathrm{B}}\Theta_D+3k_{\mathrm{B}}\Theta_D\left(\frac{T}{\Theta_D}\right)^4\int_0^{\frac{\Theta_D}{T}}\frac{x^3}{e^x-1}dx \tag{14b}$$

satisfies quantum statistics. Here Θ_D is the Debye temperature. In the high- and low-temperature limits, $\eta(T)$ in Eq. (14b) has the following values:

$$\eta(T)\to\begin{cases}k_{\mathrm{B}}T & \text{for } T\gg\Theta_D\\ \left[\frac{3}{8}+\frac{\pi^4}{5}\left(\frac{T}{\Theta_D}\right)^4\right]k_{\mathrm{B}}\Theta_D & \text{for } T\ll\Theta_D\end{cases}. \tag{14c}$$

The relation between η and T provides a direct bridge to the thermodynamic properties of the crystal. The heat capacity, for example, is given by $C_V(T) = \frac{\partial E}{\partial \eta}\frac{d\eta}{dT} = 3Nk_{\mathrm{B}} f_D(\frac{\Theta_D}{T})$, which is precisely the well-known expression for the heat capacity that can be derived within the Debye model directly from quantum statistics. The vibrational entropy $S = \int_{\eta(0)}^{\eta(T)} \frac{1}{\eta'}\frac{dE}{d\eta'} d\eta' = 3N \ln[\frac{\eta(T)}{\eta(0)}]$ can be derived from the thermodynamic relation $\frac{dE}{dS} = \eta$ obtained earlier. As $T \to 0$, $S \to 3N[\frac{8\pi^4}{15}(\frac{T}{\Theta_D})^4]$, which vanishes with T and obeys the third law, contrasting the diverging behavior of the entropy derived from the CFDR. At high temperatures, $S \to 3N\ln(\frac{8T}{3\Theta_D})$, which is consistent with the classical result.

It is clear from Eq. (14c) that at low temperatures $\eta(T)$ has an athermal component $\eta_Q = 3k_{\mathrm{B}}\Theta_D/8$ attributable to the phonon ground state, which has a pure quantum origin from the noncommutative relation between $\mathbf{r}$ and $\mathbf{p}$. In this regard, Van Kampen interpreted that the ensuing quantum uncertainty is effectively an internal noise [22]. Within this interpretation, the athermal term in the fluctuation-dissipation ratio η is simply a reflection of the contribution of quantum noise on the stochastic dynamics of the ensemble. This term corresponds to the difference between the quantum and classical forces $\langle \frac{\partial U}{\partial \mathbf{r}_n} \rangle_E - \frac{\partial U(\mathbf{r}_n)}{\partial \mathbf{r}_n}$ we mentioned earlier in the discussion of Eq. (3b).

In Eq. (14c), when $T > \Theta_D$, the thermal component is dominant. However, as temperature decreases this situation begins to reverse near $T \approx \Theta_D/3$. Indeed, at $\Theta_D/3$ the athermal component is already ~50% bigger than the thermal one and becomes 20 times bigger at $\Theta_D/5$. Thus, in this temperature range (i.e., below $\Theta_D/3$), the main activation force is a nonclassical one provided by ground-state phonons that (a) lowers the activation barrier by screening and (b) provides the momentum required for the jumps. This is effectively activation by phonon-assisted tunneling [23]. The foregoing will be further discussed in the specific case of diffusion and drag in the following section.

III. LANGEVIN DYNAMICS OF A PARTICLE IN A CRYSTAL AND THE RELATED DIFFUSIVITY AND MOBILITY

According to the foregoing, the many-body dynamics, classical or quantum, of an ISA in the environment made up of the rest of the crystal may be modeled by the pseudo-one-body Langevin dynamics of the ISA subjected to an applied force and the periodic potential that represents its interactions with the *static* periodic host lattice in its equilibrium configuration. Within this framework, the equations of motion of the ISA can be written in the form

$$\frac{d\mathbf{r}}{dt} = \mathbf{v}$$

$$m\frac{d\mathbf{v}}{dt} = \mathbf{F} - m\gamma_L \mathbf{v} + \sigma_L \zeta(t). \tag{15}$$

Here m, $\mathbf{r}$, and $\mathbf{v}$ are respectively the mass, position, and velocity of the ISA; $\mathbf{F} = -\nabla U(\mathbf{r}) + \mathbf{F}_{\mathrm{ext}}$ is the applied conserved force, including the periodic crystal potential $U(\mathbf{r})$ and an external applied force $\mathbf{F}_{\mathrm{ext}}$; $-m\gamma_L\mathbf{v}$ is the viscous drag, γ_L being the friction due to the lattice vibration; $\sigma_L\zeta(t)$ is the corresponding random force on the ISA, where $\zeta(t)$ is a Gaussian noise, i.e., $\langle\zeta(t)\rangle = 0$ and $\langle\zeta_i(t)\zeta_j(t')\rangle = \delta_{ij}\delta(t-t')$, with i, j denoting the Cartesian components. In this regard, the ISA described by Eq. (1) is like a Brownian particle embedded in the phonon gas under the action of an external force field.

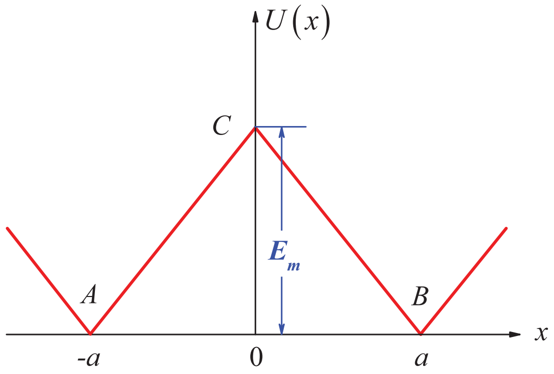

FIG. 1. Sawtooth model potential $U(x)$ for a Brownian particle in Eq. (1).

Let us model the migration barrier $U(\mathbf{r})$ by a sawtooth potential with barrier height E_m (Fig. 1) in each of the three Cartesian directions. Analytic expressions of the diffusivity D and mobility μ can be derived by solving the Fokker-Planck equation associated with the Langevin equation (15). The lengthy derivation is detailed in the Appendix, with the results summarized in the following simple equations:

$$D = \frac{\eta_L(T)}{m(\gamma_L + \gamma_m)}, \quad \mu = D/\eta_L(T), \tag{16}$$

where γ_L is the friction due to the phonon scattering and γ_m, that due to the migrating barrier effectively corrected for phonon screening. γ_L and γ_m are related via a function of temperature according to

$$\frac{\gamma_m}{\gamma_L} = \frac{e^{\xi} - 1 - \xi - \frac{1}{2}\xi^2}{\frac{1}{2}\xi^2}, \quad \xi = \frac{E_m}{\eta_L(T)}. \tag{17}$$

Here $\eta_L(T)$ is the fluctuation-dissipation ratio expressed in terms of the temperature-dependent energy of the phonons. γ_m/γ_L generally increases as temperature decreases.

According to Eq. (16), the mobility and diffusivity are governed by the same effective dissipative friction, which has two components. The first one, $-m\gamma_L$, is friction due to energy dissipation of the ISA motion resulting from phonon scattering (phonon wind). The second one, $-m\gamma_m$, is friction due to heat dissipation required to climb the vibrating migration barrier. In general, these components dominate the mobility and diffusivity of the ISA at high and low temperatures, respectively. In this regard, we note that the effectiveness of the sawtooth potential as a barrier to the migration of the ISA is reduced by the vibrating lattice (phonons) as the phonon density (amplitude of the vibrations) increases. This effective reduction of the migration barrier may also be interpreted as due to phonon screening of the interaction between the ISA and the host atoms and described as phonon-assisted tunneling [22]. These will be discussed in more detail in the following.

At high temperatures, i.e., $\xi \ll 1$, $\frac{\gamma_m}{\gamma_L} \approx \frac{\xi}{3} \ll 1$ according to Eq. (17). In this case, due to the relatively high vibrational energy $\eta_L(T)$, phonon density is high and phonon scattering dominates. The friction on the ISA is controlled by γ_L. γ_m is ineffective due to heavy screening of phonons at these temperatures. The high-temperature (i.e., well above the Debye temperature) mobility $\mu_{HT} = (m\gamma_L)^{-1}$ and diffusivity $D_{HT} = \mu_{HT} k_{\mathrm{B}} T$ then follow from Eq. (16). Accordingly, γ_L can be measured directly from the high-temperature mobility using the relation $\gamma_L = (m\mu_{HT})^{-1}$. Comparing with the Einstein-Smoluchowski relation $D_E = \mu k_{\mathrm{B}} T = \frac{k_B T}{m\gamma_L}$ [6,7], D_{HT} is thus the same as Einstein's Brownian diffusivity D_E.

For low temperatures, η_L is small. In this case, phonon density is low and the friction due to the migration barrier dominates. Indeed, putting $\xi \gg 1$ in Eq. (17) yields $\frac{\gamma_m}{\gamma_L} \approx 2\xi^{-2}\exp(\xi) - 1 \gg 1$. According to Eq. (16), the mobility of the ISA faces a friction dominated by γ_m. The low- and high-temperature mobilities are related by

$$\mu_{LT} \approx \frac{\mu_{HT}}{2}\left(\frac{E_m}{\eta_L}\right)^2 \exp\left(-\frac{E_m}{\eta_L}\right). \tag{18}$$

We note that the foregoing results are independent of whether classical or quantum statistics is used in the derivation. Since classical results can be recovered from the quantum version by taking the limit $\hbar \to 0$, we only need to continue along the quantum route. In this regard, the quantum fluctuation-dissipation relation (QFDR) evaluated from Eq. (14) using the phonon density of state (DOS) can be written as

$$\eta_L(T) = \int_0^\infty \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/k_{\mathrm{B}}T} - 1}\right) g(\omega)d\omega, \tag{19}$$

where $g(\omega)$ is the phonon DOS of the crystal environment with $g(\omega) = \frac{4\pi k^2 \Omega}{(2\pi)^3}\frac{1}{\nabla_{\mathbf{k}}\omega}$ where Ω is the atomic volume and $\mathbf{k}$ the phonon wave vector. The DOS can be obtained from experiments, or from first-principle calculations, or by simply using the Debye model if one pursues an analytic route, as done in Refs. [17,19]. From Eq. (19), it is clear that the friction due to phonon scattering involves both thermal vibrations $\langle n\rangle\hbar\omega$ and the ground-state athermal ones $\hbar\omega/2$.

For high temperatures, $\hbar\omega/k_{\mathrm{B}}T \ll 1$ and $\eta_L \approx k_{\mathrm{B}}T$. The QFDR is reduced to the classical fluctuation-dissipation relation (CFDR), and the traditional Einstein-Smoluchowski relation between the mobility and diffusivity, namely, $D = \mu k_{\mathrm{B}} T$, is recovered.

For very low temperatures, the density of the phonon gas is low; i.e., $\langle n\rangle \to 0$. However, the energy $\hbar\omega/2$ due to the phonon ground state allows the probable appearance of the ISA on the other side of the migration barrier without thermal excitation, a phenomenon we may identified as ground-state-phonon-assisted tunneling. Within the Debye model, $\eta_L(T) = [\frac{3}{8} + \frac{\pi^4}{5}(\frac{T}{\Theta_D})^4] k_{\mathrm{B}}\Theta_D$ [17], where Θ_D is the Debye temperature. It is then clear that as temperatures decreases below $\sim\Theta_D/3$, the second term in the square brackets decreases rapidly as T^4, as η_L tends to a constant value of $\eta_L \approx \frac{3}{8}k_{\mathrm{B}}\Theta_D$. Following Eq. (18), the near-zero mobility μ_Z and diffusivity D_Z are related to the high-temperature mobility μ_{HT} and can be written as

$$\mu_Z \approx \frac{\mu_{HT}}{2}\left(\frac{8E_m}{3k_{\mathrm{B}}\Theta_D}\right)^2 \exp\left(-\frac{8E_m}{3k_{\mathrm{B}}\Theta_D}\right), \quad \text{and}$$

$$D_Z \approx \frac{3\mu_{HT}k_{\mathrm{B}}\Theta_D}{16}\left(\frac{8E_m}{3k_{\mathrm{B}}\Theta_D}\right)^2 \exp\left(-\frac{8E_m}{3k_{\mathrm{B}}\Theta_D}\right), \quad \text{for}$$

$$T < \frac{\Theta_D}{3} \quad \text{and} \quad \Theta_D \ll 8E_m/k_{\mathrm{B}}. \tag{20}$$

Both are nonzero and both are independent of temperature. The complete departure of the diffusivity and mobility in Eq. (20) from the Arrhenius behavior and the Einstein-Smoluchowski relation is obvious. Thus, for a tungsten crystal with $\Theta_D \approx 360$ K and an ISA migration barrier of 0.1 eV, $\mu_Z \approx 0.01\mu_{HT}$ which is nonzero even at 0 K. The nonzero quantum transport at 0 K in Eq. (20) is a consequence of quantum uncertainty discussed earlier in this paper. In addition, we note that from a third of the Debye temperature down to absolute zero, the quantum statistical version of the Einstein relation between the diffusivity and mobility is changed to $D_Z^{\text{Einstein}} = \frac{3}{8}\mu k_{\mathrm{B}}\Theta_D$ in which both the mobility (or viscosity) and diffusivity are temperature independent. Indeed, below the Debye temperature the conventional Einstein relation $D = \mu k_{\mathrm{B}} T$ no longer holds due to quantum effects. This relation may have important consequences in the interpretation of solid-state transport in low-temperature experiments.

Figure 2(b) plots the variable $\xi(T) = \frac{E_m}{\eta_L(T)}$ as a function of temperature T in an example where for simplicity E_m is hypothetically put equal to the Debye energy of bcc W; i.e., $E_m = k_{\mathrm{B}}\Theta_D = 0.032$ eV [24]. It can be easily seen that above the Debye temperature, i.e., $T > \Theta_D$, quantum effects disappear and $\xi_Q \approx \xi_C$. Below the Debye temperature, i.e., $T < \Theta_D$, CFDR neglects the freezing out of phonons and overestimates the phonon density. This is reflected in Fig. 2(b) in the large difference between $\xi_C \to \infty$ calculated using CFDR and $\xi_Q = 8/3$ calculated using QFDR as $T \to 0$. The use of ξ_C instead of ξ_Q in Eq. (17) results in a large overestimation of the friction due to γ_m, causing a serious underestimation of both the diffusivity and mobility. Thus, quantum diffusivity and mobility are much larger than their classical counterparts. Indeed, referring to Fig. 2(b), at $T = 10$ K, QFDR gives a value of $\xi_Q \approx 8/3$ yielding a $D \approx 0.1D_E$, while CFDR gives a value of $\xi_C \approx 40$ yielding a $D \approx 10^{-14}D_E$ which is 13 orders of magnitude smaller. Alternatively, the enhanced transport may also be understood in terms of quantum tunneling.

In the following section, results of the foregoing Langevin-equation approach for the diffusion and mobility of interstitial helium in bcc tungsten will be compared with those obtained by directly solving the many-body problem via an MD approach. The diffusivity and mobility according to Eqs. (16) and (17) are evaluated as functions of temperature with migration energy E_m obtained using conjugate-gradient techniques.

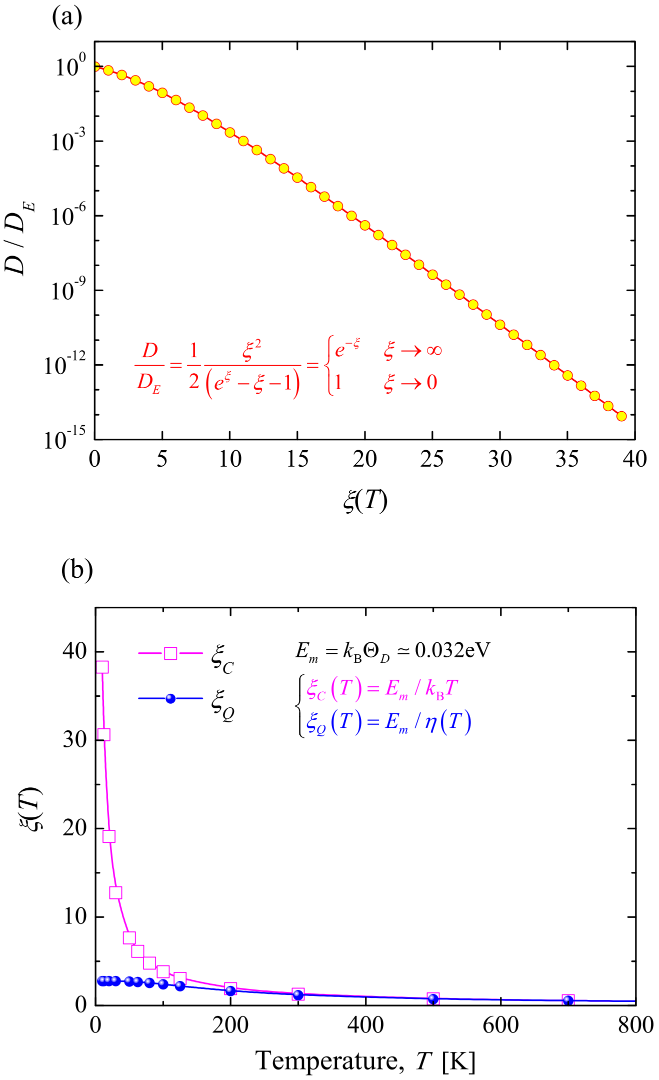

FIG. 2. (a) The ratio of diffusivity of the impurity in a periodic potential and the diffusivity of free Brownian motion, D/D_E, against the ratio ξ of the height of migratory energy barrier E_m and the fluctuation-dissipation ratio $\eta = \sigma^2/2m\gamma$; i.e., $\xi = E_m/\eta$. (b) ξ as function of temperature based on classical fluctuation-dissipation relation (CFDR), $\xi_C = E_m/k_B T$, and quantum fluctuation-dissipation relation (QFDR) $\xi_Q = E_m/\eta(T)$, where $\eta(T)$ is given in Eq. (4) and $E_m = k_B\Theta_D = 0.032$ eV.

IV. QUANTUM STATISTICAL MD SIMULATION OF MOBILITY AND DIFFUSIVITY OF He IN bcc W

Helium (He) is chosen in this study because it is one of the common insoluble impurities in metals, the accumulation and complex formation of which is a fundamental cause of many adverse effects affecting the usefulness of metals and alloys as structural components [25]. A well-known example is the high-temperature embrittlement of deflector materials in fusion reactors of the international thermonuclear experimental reactor (ITER) type caused by He bubble formation in bcc W. In such cases, the diffusion of He inside the metallic crystals is often the first step of kinetic processes in the clustering dynamics.

The diffusion behavior of helium in W is complex. Theoretical and experimental studies reveal that diffusion of He in metals may occur via the interstitial mechanism [26]. Interpreted in terms of the Arrhenius law, He diffusion in W measured between 90 and 110 K with atom-probe field-ion microscopy (FIM) was characterized by an enthalpy of 0.24–0.32 eV [27,28]. However, first-principle static calculations yield a much smaller energy barrier of 0.06 eV [29,30], which is more consistent with the activation enthalpy of ~0.1 eV obtained from recent molecular dynamics (MD) simulations [31–33]. Higher-temperature measurements between 1120 and 1400 K, on the other hand, yield diffusivities consistent with a much larger migration enthalpy of 0.71 eV [34,35]. MD simulations found that He diffusion in bcc tungsten in this temperature range did not obey the Arrhenius law. The lack of coherency in the Arrhenius interpretation in the foregoing seems to bear out the problems in the understanding of interstitial solute diffusion in crystalline solids based on a one-particle classical picture which has been discussed at some length in the foregoing sections.

In this section, direct solution of the many-body dynamics of a bcc tungsten crystal with an interstitial helium atom is performed using canonical molecular dynamics (MD) simulation. The heat bath is constructed based on the quantum statistical frameworks described in Sec. II [see Eq. (14)]. The mobility and diffusivity obtained from the MD simulation is compared with those from Eqs. (16) derived within the Langevin equation approach. A migration energy $E_m = 0.12$ eV determined from constrained energy optimization using the conjugate-gradient method is employed [36]. The accuracy and the range of applicability of the classical treatment is also evaluated by comparing with the quantum results.

The MD simulation is based on a Hamiltonian of the many-body system in a thermal bath which can be written in the general form

$$\mathscr{H} = \sum_n \frac{\mathbf{p}_n^2}{2m_n} + U(\{\mathbf{R}_n\}) + \mathscr{H}_{\mathrm{B}}, \tag{21}$$

where m_n, $\mathbf{p}_n$, and $\mathbf{R}_n$, respectively, are the mass, momentum, and position of the nth atom, and $U(\{\mathbf{R}_n\})$ is a many-body interatomic potential corresponding to the lattice configuration $\{\mathbf{R}_n\}$. Here, the dynamics of He is modeled by the ensemble of interacting atoms embedded in a noisy environment $\mathscr{H}_{\mathrm{B}}$ that represents a thermal heat bath at temperature T. The equation of motions of each atom in Eq. (19) can be written in the Langevin form:

$$\begin{aligned}\frac{d\mathbf{R}_n}{dt} &= \frac{\mathbf{p}_n}{m_n}\\ \frac{d\mathbf{p}_n}{dt} &= -\frac{\partial U}{\partial \mathbf{R}_n} - \gamma_{\mathrm{B}}\mathbf{p}_n + \sigma_{\mathrm{B}}\zeta_n(t),\end{aligned} \tag{22}$$

where $\gamma_{\mathrm{B}} = m_n\gamma_n$ characterize the corresponding dissipative drags $-\gamma_{\mathrm{B}}\mathbf{p}_n$ on the atom. The random forces $\sigma_{\mathrm{B}}\zeta_n(t)$ of the Langevin thermostat are defined in a Gaussian and frequency-independent delta-correlated form according to $\langle\zeta_k(t)\rangle = 0$ and $\langle\zeta_{n\alpha}(t)\zeta_{l\beta}(t')\rangle = \delta_{nl}\delta_{\alpha\beta}\delta(t-t')$. Noting that the bath is in equilibrium with the phonon system, the fluctuation-dissipation ratio of the bath is given by $\sigma_{\mathrm{B}}^2 = 2\gamma_{\mathrm{B}}\eta_L(T)$, where

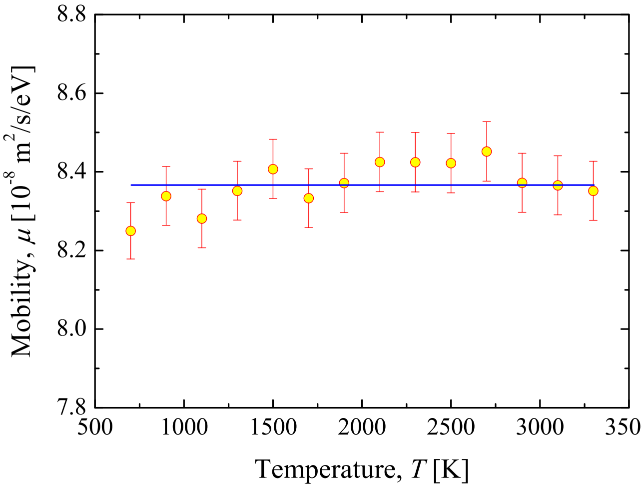

FIG. 3. The mobility of helium in bcc W (700 K $< T <$ 3300 K) calculated using drag dynamics simulations. The average $\mu = (m\gamma)^{-1} = 8.4 \times 10^{-8}$ m^2/s/eV. The solid line is to guide the eye.

$\eta_L(T)$ is given by Eq. (19) with the DOS given by the Debye model [17].

We performed *NVT* MD simulations for helium diffusion in tungsten according to Eq. (22) using embedded-atom potentials, with W-W interactions from Ackland and Thetford [37] as modified by Juslin and Wirth [38], and He-W interactions from Juslin and Wirth [38]. The simulation cell contains 30 bcc W unit cells along each dimension in a Cartesian coordinate system, for a total of 54 000 W atoms. The helium atom is introduced into a tetrahedral interstitial site (TIS) of the bcc W host lattice, near the center of the simulation cell. Periodic boundary conditions are applied and simulation-cell dimension dependence checked. The Langevin heat bath and zero-external-pressure equilibrium atomic volume at the corresponding temperature are used to define the lattice constants. The computation is performed using the velocity Verlet method, with a time step of 1 fs. Trajectories of the helium atom (with 4-ns durations) are generated and recorded for various temperatures.

From the phase-space trajectory $\mathbf{r}(t)$ of He obtained, the diffusivity can be calculated using the Einstein formula derived independent of the transport mechanism; i.e., $D = \lim_{t\to\infty}\langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle/6t$ [6]. At sufficiently high temperatures, the diffusivity of He can also be evaluated from the mobility μ, i.e., $D(T) = \mu\eta_L(T)$, which can be obtained by performing drag dynamics simulations, where

$$\mu = \lim_{\mathbf{F}_d\to 0} \frac{\mathbf{v}_d}{\mathbf{F}_d}. \tag{23}$$

Here $\mathbf{v}_d$ is the terminal velocity of the He atom under the action of applied external drag force $\mathbf{F}_d$. For temperatures above 700–3300 K, the mobility obtained this way is shown in Fig. 3, which is practically temperature independent, with a mean value of $\mu_{HT} = 8.4 \times 10^{-8}$ m^2/s/eV.

Figure 4(a) is an Arrhenius plot of the MD simulated He diffusivity we obtained. The most prominent feature is the constant value of the diffusivity below a third of the Debye temperature, i.e., ∼120 K down to 0 K, as predicted by Eq. (20). Plotted in comparison are the diffusivities D_Q and D_C, analytically calculated from Eqs. (16)–(18), using QFDR-derived ξ_Q and CFDR-derived ξ_C, respectively. Figure 4(a) shows that above the Debye temperature there is little difference among the diffusivities D_Q and D_C from MD simulation and those from Eq. (16). On the other hand, below the Debye temperature, D_Q becomes much larger than D_C as temperature decreases. Similar results are also reported in a recent calculation on the low-temperature diffusivity of self-interstitial defects in tungsten [40].

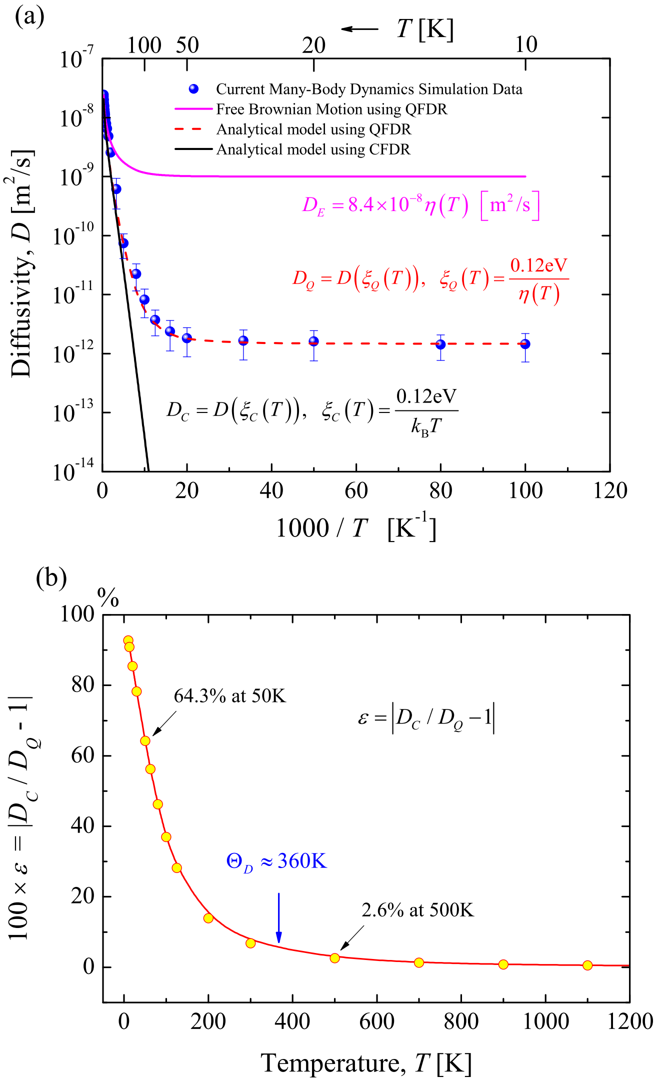

FIG. 4. (a) The diffusivity of He in bcc W at temperatures from 10 to 3300 K, calculated using the Einstein formula $D = \lim_{t\to\infty}\langle[\mathbf{r}(t) - \mathbf{r}(0)]^2\rangle/6t$, where the He trajectory $\mathbf{r}(t)$ is collected from the many-body dynamical simulation [Eq. (6)] with the QFDR used to control the temperatures of bcc W, as well as the comparisons with the estimation of diffusivity D_Q and D_C, derived from the analytical model [Eq. (2)] based on QFDR and CFDR, respectively. Here, in the analytical expression [Eq. (2)], $E_m = 0.12$ eV is obtained using the modified conjugated-gradient method (MCG) [36,39]; the mobility $\mu = 8.4 \times 10^{-8}$ m^2 s^{-1} eV^{-1} is calculated from the drag simulation following Eq. (7). The simulation details were documented in Ref. [39]. (b) The relative error of D_C with respect to D_Q, i.e., $\varepsilon = |D_C/D_Q - 1|$ at temperatures ranging from 10 to 1200 K.

The foregoing behavior is predicted in the Langevin formulation in Sec. III. The difference at low temperatures can be traced to the difference between quantum and classical statistics used in the two cases. Indeed, within the Debye model [17], using a value of $8E_m/3k_{\rm B}\Theta_D = 10$, Eq. (20) gives $\frac{D_Z}{D_E} = 2.27 \times 10^{-3}$ for temperatures below $\Theta_D/3$ which verifies the MD results in Fig. 4(a). In this regard, the corresponding classical value is $D_C \to 0$, demonstrating the remarkable difference between results from quantum and classical statistics. This difference vanishes when quantum effects in the many-body dynamics are neglected, i.e., when $\Theta_D \to 0$.

Based on a Debye frequency of 8×10^{13} the de Broglie wavelength of the W atoms is $\lambda^{\rm W} = \sqrt{\frac{\pi h}{m^{\rm W}\omega^{\rm W}}} \approx 0.1$ Å. At equilibrium the kinetic energies of all atoms are equal, from which the de Broglie wavelength of the He can be estimated at ~0.43 Å, indicating a negligible multisite spread of the one-particle wave function and coherent tunneling probability. Indeed, using the Wentzel, Kramers, and Brillouin (WKB) approximation, the tunneling probability of a He atom through a barrier of height 0.12 eV and width 0.1 nm at 0 K is on the order of 10^{-12}. It dominates over the thermal jump rates and thus the diffusivity only below ~40 K, at which the corresponding Arrhenius diffusivity is at least six orders of magnitude smaller than that due to the momentum transfer from the phonon ground state which is already apparent below 120 K [see Fig. 4(a)]. This confirms that the effect on the He diffusivity due to coherent tunneling is negligible compared with that due to the ground-state-phonon-assisted tunneling presently considered.

Figure 4(a) shows that the quantum statistical effects are important when considering He diffusion below the Debye temperature of the host crystal. We calculate the relative error $\varepsilon = |D_C/D_Q - 1|$ and plot it in Fig. 4(b). It can be seen that ε is small for $T > \Theta_D$, e.g., $\varepsilon = 2.6\%$ at 500 K, but increases rapidly as the temperature dips below the Debye temperature, i.e., $T < \Theta_D$, where quantum statistical effects become significant. For example, $\varepsilon = 64.3\%$ at 50 K, which means quantum diffusion is three times faster than the corresponding classical results.

V. SUMMARY AND CONCLUSION

The dynamics involved in the mobility and diffusivity of interstitial solute atoms (ISAs) in a crystalline solid at finite temperatures is many body in nature. As such, the motion of the ISA and the "migration barrier" it encounters are coupled to the lattice vibrations via the interaction between the ISA and the ground-state phonons. The aim of the present paper is to investigate the impact of such quantum effects.

Modeling the difference between Ehrenfest and Newtonian forces in the equations of motion of the atoms as a perturbative stochastic noise, the characteristic fluctuation-dissipation ratio (FDR) is formally related to the thermodynamic temperature via the phonon DOS of the crystal. The many-body dynamics can be directly solved by following the MD approach with a Langevin heat bath based on the quantum FDR. At the same time, the Mori-Zwanzig theory allows one to also describe the many-body dynamics of the crystal via the pseudo-one-particle Langevin equation approach, using a phonon DOS based on the Debye model. Both approaches are used in the present paper, yielding results which are in excellent agreement with each other. Below the Debye temperature of the host lattice, ground-state phonons are found to produce a major effect on the transport properties of the ISA, causing them to seriously depart from the Arrhenius law of diffusion as well as the Einstein-Smoluchowski relation between the mobility and diffusivity. Thus, below a third of the Debye temperature all the way down to 0 K, both the quantum mobility and diffusivity are essentially constant and are orders-of-magnitude larger than the classical results and those due to coherent tunneling. The diffusivity of He in bcc W obtained from the molecular dynamics simulation is found to only follow the Arrhenius law in a narrow temperature range between ~300 and ~700 K, and tends to a constant on the low-temperature side while obeying Einstein's theory and becoming a linear function of temperature on the high-temperature side. The mobility, on the other hand, is basically temperature independent, except in the temperature range between ~100 and 700 K, in which its value drops 100-fold with the phonon density as temperature decreases.

ACKNOWLEDGMENT

This project is initiated and funded by Grant No. 11214114 from the Hong Kong Research Grant Council, to which the authors are thankful.

APPENDIX

We consider in this Appendix the finite-temperature dynamics of a particle in a noisy medium under the action of an external force field, governed by Langevin equation (15). We assume that the friction is such that $|\gamma_L v| \gg |\dot{v}|$. When $\Delta\mathbf{F} \to \mathbf{0}$, the corresponding probability density $P(\mathbf{r},t)$ of the ISA at location $\mathbf{r}$ and time t is governed by the Fokker-Planck equation [18],

$$\frac{\partial}{\partial t}P(\mathbf{r},t) = \boldsymbol{\nabla}\cdot\left[\frac{\boldsymbol{\nabla}U}{m\gamma_L}P(\mathbf{r},t)\right] + D_{\rm E}\nabla^2 P(\mathbf{r},t) = -\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r},t), \tag{A1}$$

where $D_{\rm E} \equiv \sigma_L^2/2(m\gamma_L)^2$ is the *Einstein diffusivity* for a free Brownian particle. The fluctuation-dissipation ratio $\eta_L = \frac{\sigma_L^2}{2m\gamma_L}$ is a function of temperature from which the temperature dependence of $D_{\rm E}$ is derived, through $D_{\rm E} = \eta_L/m\gamma_L$. Classically, $\eta_L = k_{\rm B}T$, and quantum mechanically, η_L is a nonlinear function of T given by Eq. (14). We may also define the Einstein mobility accordingly as $\mu_{\rm E} \equiv (m\gamma_L)^{-1}$. When $\boldsymbol{\nabla}U \neq 0$, Eq. (A1) is called the *Smoluchowski diffusion equation* [16]. The corresponding flux of Brownian particles can be written in the mesoscopic scale as

$$\mathbf{j}(\mathbf{r},t) = -D_{\rm E}e^{-U(\mathbf{r})/\eta_L}\boldsymbol{\nabla}[e^{U(\mathbf{r})/\eta_L}P(\mathbf{r},t)]. \tag{A2}$$

Within the pseudo-one-particle model in our case, the ISA moves in a one-dimensional sawtooth potential field $U(x)$, jumping from troughs $A(x_A = -a)$ to $B(x_B = a)$, across the saddle point $C(x_C = 0)$, as shown as in Fig. 1, i.e.,

$$U(x) = \begin{cases} E_m(1 + x/a) & -a < x < 0 \\ E_m(1 - x/a) & 0 < x < a \end{cases}, \tag{A3}$$

where $E_m = U(x_C) - U(x_A)$ is the migration-energy barrier. According to Eq. (A2), the one-dimensional flux is given by

$$j(x,t) = -D_{\mathrm{E}} e^{-U/\eta_L} \frac{\partial}{\partial x}(e^{U/\eta_L} P). \tag{A4}$$

Performing the integration on both sides of Eq. (A4), we obtain

$$\int_A^B j e^{U(x)/\eta_L} dx = -D_{\mathrm{E}}(e^{U/\eta_L} P)|_A^B. \tag{A5}$$

Instead of an explicit consideration of the ISA motion from A to B, we will solve a closely related steady-state problem, assuming that $P(x_A) = P_A$, and $P(x_B) = 0$. This assumes the near-equilibrium condition that particles at the point $x = x_A$ are replaced as quickly as they leak away, and taken out at the point $x = x_B$ as quickly as they arrive there. In this case, the populations of the wells A and B remain time independent $[\partial P(x,t)/\partial t = 0]$, and the flux j between the wells can be calculated as

$$j = e^{U_A/\eta_L} P_A D_{\mathrm{E}} \left\{ \int_A^B e^{U(x)/\eta_L} dx \right\}^{-1}. \tag{A6}$$

From Eq. (A3), we have

$$\int_A^B e^{U(x)/k_{\mathrm{B}}T} dx$$
$$= 2\int_0^a e^{E_m(1-x/a)/\eta_L} dx = 2a\frac{\eta_L}{E_m}(e^{E_m/\eta_L} - 1). \tag{A7}$$

Thus

$$j = \frac{D_{\mathrm{E}} P_A}{2a} \frac{E_m}{\eta_L} \frac{1}{e^{E_m/\eta_L} - 1}. \tag{A8}$$

One may check that the probability density satisfying Eq. (A4) with $j = \mathrm{const}$ is

$$P(x) = j/D_{\mathrm{E}} \exp\left[-\frac{U(x)}{\eta_L}\right] \left\{ \int_{-a}^{a} e^{U(x)/\eta_L} dx - \int_{-a}^{x} e^{U(x')/\eta_L} dx' \right\}. \tag{A9}$$

For the specific case of $U(x)$ given in the sawtooth form by Eq. (A3), we obtain

$$P(x) = j/D_{\mathrm{E}} \frac{a\eta_L}{E_m} \left\{ 2e^{-\frac{E_m x}{a\eta_L}} - 1 - \exp\left[-\frac{E_m(1 + x/a)}{\eta_L}\right] \right\}, \quad x \leqslant 0, \tag{A10}$$

$$P(x) = j/D_{\mathrm{E}} \frac{a\eta_L}{E_m} \left\{ 1 - \exp\left[-\frac{E_m(1 - x/a)}{\eta_L}\right] \right\}, \quad x \geqslant 0, \tag{A11}$$

and

$$\frac{dP}{dx} = -j/D_{\mathrm{E}} - \frac{\nabla U}{\eta_L} P = -j/D_{\mathrm{E}} \mp \frac{E_m}{a\eta_L} P(x). \tag{A12}$$

Integrating Eq. (A12) over the intervals $[-a,0]$ and $[0,a]$, we obtain

$$P(0) - P(-a) = -ja/D_{\mathrm{E}} - \frac{E_m}{a\eta_L} \int_{-a}^{0} P(x) dx$$
$$\equiv -ja/D_{\mathrm{E}} - \frac{E_m}{a\eta_L} P_{[-a,0]}, \tag{A13}$$

$$P(a) - P(0) = -ja/D_{\mathrm{E}} + \frac{E_m}{a\eta_L} \int_{0}^{a} P(x) dx$$
$$\equiv -ja/D_{\mathrm{E}} + \frac{E_m}{a\eta_L} P_{[0,a]}. \tag{A14}$$

Taking the sum of the last two equations, we obtain

$$P_A = \frac{2ja}{D_{\mathrm{E}}} + \frac{E_m}{a\eta_L} \Delta P_{AB}, \tag{A15}$$

where $\Delta P_{AB} = P_{[-a,0]} - P_{[0,a]}$ is the difference of the probabilities to find a particle in the corresponding intervals.

The number of particles moving from one well to another during the time dt is given by $j_C(t)dt$, where $j_C(t)$ is the flux across the saddle point C. This results in ΔP_{AB} changing by $[-2j_C(t)dt]$; i.e., $d\Delta P_{AB}(t)/dt = -2j_C(t)$. One may then calculate the effective particle transfer rate τ^{-1} defined by the decay equation $d\Delta P_{AB}(t)/dt = -\Delta P_{AB}/\tau$ according to

$$\frac{1}{\tau} = \frac{2j}{\Delta P_{AB}} = \frac{D_{\mathrm{E}} E_m}{a^2 \eta_L} \frac{2ja/P_A D_{\mathrm{E}}}{(1 - 2ja/P_A D_{\mathrm{E}})}$$
$$= \frac{E_m D_{\mathrm{E}}}{a^2 \eta_L} \frac{1}{(P_A D_{\mathrm{E}}/2ja - 1)}$$
$$= \frac{\eta_L}{m\gamma_L a^2} \frac{(E_m/\eta_L)^2}{(e^{E_m/\eta_L} - E_m/\eta_L - 1)}. \tag{A16}$$

To cross the saddle point C a particle that originated at the point A has to move over a distance equal to a. Thus the average square distance $\langle l^2 \rangle$ traveled by the particle during the time τ can be approximated by a^2, and the long-range diffusion coefficient of particles D can be found from the conventional relation $2D\tau = \langle l^2 \rangle \cong a^2$; i.e.,

$$D = \frac{a^2}{2\tau} = \frac{\eta_L}{m\gamma_L} \frac{\frac{1}{2}(E_m/\eta_L)^2}{(e^{E_m/\eta_L} - E_m/\eta_L - 1)}. \tag{A17a}$$

Modeling the ISA in the foregoing as a Brownian particle in a noisy medium with an effective friction coefficient γ^*, D may be written as $D = \frac{\eta_L}{m\gamma^*}$. Physically, γ^* emulates the increased friction on the ISA due to the presence of migration barriers in a dissipative medium. For this reason we may write $\gamma^* = \gamma_L + \gamma_m$, where γ_m represents the contribution to the friction from the migration barrier. From Eq. (A17a), defining $\xi = E_m/\eta_L$ we may write

$$1 + \frac{\gamma_m}{\gamma_L} = \frac{2(e^{\xi} - 1 - \xi)}{\xi^2}, \tag{A17b}$$

from which it can be seen that $\gamma_m \gg \gamma_L$ at low temperatures and $\gamma_m \ll \gamma_L$ at high temperatures. In the former case, we may say that the diffusion is *migration-barrier controlled*, while in the latter case, it is *phonon-drag controlled*.

The mobility of the Brownian particle can be obtained from the change in current density due to the application of a small constant external force ΔF on the particle. In this case, Eq. (A9) still holds as a stationary solution of Eq. (A1) with the total potential given by $U(x) - \Delta F x$. Equations (A13) and (A14) then become

$$P'(0) - P'(-a) \cong -ja/D_{\mathrm{E}} - \frac{E_m}{a\eta_L} P'_{[-a,0]} + \frac{\Delta F}{\eta_L} P_{[-a,0]}, \tag{A18}$$

$$P'(a) - P'(0) \cong -ja/D_{\mathrm{E}} + \frac{E_m}{a\eta_L} P'_{[0,a]} + \frac{\Delta F}{\eta_L} P_{[0,a]}, \tag{A19}$$

where $P'(x)$ replaces $P(x)$ as the probability density to account for ΔF. Since ΔF is small in the atomic scale, only terms linear in ΔF need to be kept on the right-hand sides of Eqs. (A18) and (A19).

Similarly, one may also replace Eq. (A15) by

$$P'_A = \frac{2ja}{D_{\mathrm{E}}} + \frac{E_m}{a\eta_L}\Delta P'_{AB} - \frac{\Delta F}{\eta_L}\int_{-a}^{a} P(x)dx. \tag{A20}$$

Since the periodic potential is symmetrical at $x = 0$, Eq. (A9) gives

$$\begin{aligned} P'_A &= j/D_{\mathrm{E}} \exp\left(-\frac{\Delta F a}{\eta_L}\right)\left\{\int_{-a}^{a} e^{U(x)/\eta_L} dx\right\} \\ &\cong P_A - \frac{j}{D_{\mathrm{E}}}\frac{2a^2\Delta F}{E_m}(e^{E_m/\eta_L} - 1). \end{aligned} \tag{A21}$$

Using Eq. (A15), Eq. (A21) can be rewritten as

$$\begin{aligned} &-\frac{2ja^2}{D_{\mathrm{E}}}\frac{\Delta F}{E_m}(e^{E_m/\eta_L} - 1) \\ &= \frac{E_m}{a\eta_L}(\Delta P'_{AB} - \Delta P_{AB}) - \frac{\Delta F}{\eta_L}\int_{-a}^{a} P(x)dx. \end{aligned} \tag{A22}$$

Integration of Eqs. (A10) and (A11) gives

$$\int_{-a}^{a} P(x)dx = \frac{2ja^2}{D_{\mathrm{E}}}\left(\frac{\eta_L}{E_m}\right)^2 [e^{E_m/\eta_L} - 2 + e^{-E_m/\eta_L}]. \tag{A23}$$

As a result,

$$\begin{aligned} \Delta P'_{AB} - \Delta P_{AB} = &-\frac{\Delta F a}{\eta_L}\frac{2ja^2}{D_{\mathrm{E}}}\left(\frac{\eta_L}{E_m}\right)^2\bigg[e^{E_m/\eta_L} - 1 \\ &- \frac{\eta_L}{E_m}(e^{E_m/\eta_L} - 2 + e^{-E_m/\eta_L})\bigg]. \end{aligned} \tag{A24}$$

Thus the effective particle transfer rate $(\tau')^{-1}$ in the presence of F is given by

$$\begin{aligned} \frac{1}{\tau'} &= \frac{2j}{\Delta P'_{AB}} \cong \frac{2j}{\Delta P_{AB}}\left(1 - \frac{\Delta P'_{AB} - \Delta P_{AB}}{\Delta P_{AB}}\right) \\ &= \frac{1}{\tau}\left(1 - \frac{\Delta P'_{AB} - \Delta P_{AB}}{\Delta P_{AB}}\right) \\ &= \frac{1}{\tau}\left(1 - \frac{\Delta P'_{AB} - \Delta P_{AB}}{2j\tau}\right). \end{aligned} \tag{A25}$$

If l (a stochastic variable) is the actual jump distance between the two spatial intervals, then it is related to the particle diffusivity D in the presence of a drift velocity v_d by

$$\langle (l - v_d\tau')^2 \rangle = 2D\tau', \tag{A26}$$

Using Eq. (A25) and $\langle l^2 \rangle = 2D\tau$, for small velocities, Eq. (A26) gives

$$\begin{aligned} v_d &= -\frac{D(\tau' - \tau)}{\langle l \rangle \tau'} = -\frac{D}{\langle l \rangle}(1 - \tau/\tau') \\ &= -\frac{D}{\langle l \rangle}\frac{\Delta P'_{AB} - \Delta P_{AB}}{2j\tau}. \end{aligned} \tag{A27}$$

Defining

$$\langle l \rangle \equiv a\frac{e^{E_m/\eta_L} - 1 - \frac{\eta_L}{E_m}(e^{E_m/\eta_L} - 2 + e^{-E_m/\eta_L})}{e^{E_m/\eta_L} - E_m/\eta_L - 1}, \tag{A28}$$

and substituting Eq. (A16) for τ using Eq. (A24), Eq. (A27) gives the well-known expression relating the mobility to the diffusivity through the Einstein particle mobility,

$$\mu(T) = \frac{D(T)}{\eta_L} = \frac{1}{m(\gamma_L + \gamma_m)}, \tag{A29}$$

if we define the mobility $\mu(T)$ through the drift velocity v_d according to $v_d = \mu(T)\Delta F$. We note that the Einstein relation here is expressed via the fluctuation-dissipation ratio η_L which is a natural variable in the present stochastic formulation. The traditional formula $\mu = D/k_{\mathrm{B}}T$ can be obtained by using the classical equipartition theorem which does not apply to quantum vibrations (phonons).

We note that according to Eq. (A28), $\langle l \rangle = a$ in both limits $E_m \gg \eta_L$ and $E_m \ll \eta_L$. This is particularly important in the case of Arrhenius diffusion where the diffusing particle does move over a distance equal to a during the transfer between the wells.

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