Thermal mobility of interstitial defects in irradiated materials

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Thermally activated mobility of clusters of interstitial atoms is an important factor driving microstructural evolution of materials under irradiation. Molecular dynamics simulations show that the statistics of one-dimensional Brownian motion of clusters is characterized by unusual correlated jumps spanning many interatomic distances. We use the Frenkel-Kontorova model to investigate the dynamics of one-dimensional Brownian motion of a spatially delocalized interstitial defect interacting with acoustic phonon excitations. Using a quantum-mechanical approach, we evaluate the coefficient of dissipative friction characterizing the stochastic motion of the defect. We show that the origin of unusual features observed in atomistic simulations is associated with low friction experienced by an interstitial defect propagating through the crystal lattice in the presence of thermal fluctuations. We also find that the coefficient of dissipative friction is highly sensitive to the character of interatomic bonding in the material.

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I. INTRODUCTION

The evolution of the microstructure of a material under irradiation is characterized by the presence of dynamic quasiequilibrium between the generation of lattice defects by incident energetic particles and recombination and absorption of defects at dislocations, grain boundaries, and free surfaces. The rates characterizing the temporal evolution of microstructure depend on the type of mobility of defects formed in collision cascades. Trinkaus *et al.*[1] showed that one-dimensional glide of small interstitial clusters, as opposed to the more conventional three-dimensional diffusion of point defects, may have a significant effect on the accumulation of radiation defects in the material. The recognition of this fact has stimulated several recent studies, where relationships between the structure of defects and the type of thermally activated motion performed by those defects, and the microstructure of irradiated materials were investigated numerically using molecular dynamics [2–7] and kinetic Monte Carlo[8,9] approaches. For example, Caturla *et al.*[10] performed a comprehensive comparative study of accumulation of radiation damage in Cu and Fe using a combined molecular dynamics and kinetic Monte Carlo approach.

One of the striking observations that emerged from computer simulations was the discovery of high thermally activated mobility of small clusters of interstitial atoms formed during the solidification of collision cascades. Clustering of interstitial atoms in collision cascades predicted by molecular dynamics simulations[4] is responsible for a number of experimentally observed phenomena that involve both mobile and immobile defects.[11,12] These phenomena include the segregated growth of voids and dislocations observed in some materials, the spatially inhomogeneous swelling that often occurs in the vicinity of grain boundaries, and high rates of growth of voids observed in the limit of low irradiation doses. The very small size of interstitial clusters makes direct observation of their motion a difficult experimental problem,[13] and the development of theoretical models relating properties of microscopic and mesoscopic defects to the observed macroscopic behavior of materials under irradiation is presently considered to be an important element of the fusion materials research.[14]

Glissile clusters of interstitial atoms interacting with thermal fluctuations perform stochastic one-dimensional Brownian motion in one of the close-packed crystallographic directions. By treating an interstitial cluster as a defect that retains its shape in the process of Brownian motion, we obtain that the coordinate $X(t)$ of the center of the cluster, projected on the direction of motion, satisfies the Langevin equation

$$m^*\ddot{X} = -m^*\gamma\dot{X} + \eta(t), \tag{1}$$

where m^* is the effective mass of the defect, γ is the coefficient of thermal friction, and the random thermal force $\eta(t)$ satisfies conditions[15]

$$\langle \eta(t) \rangle_T = 0, \quad \langle \eta(t)\,\eta(t') \rangle_T = 2m^*\gamma T\,\delta(t-t'), \tag{2}$$

where T is the absolute temperature. Equations (1) and (2) are equivalent[15,16] to the Fokker-Planck equation

$$\frac{\partial F}{\partial t} + \frac{p}{m}\frac{\partial F}{\partial x} - \frac{\partial}{\partial p}\left[\gamma\left(pF + m^*T\frac{\partial F}{\partial p}\right)\right] = 0 \tag{3}$$

for the distribution function $F(p,x,t)$. The term in round brackets in Eq. (3) vanishes in the limit $F(p,x,t) \sim \exp(-p^2/2m^*T)$ corresponding to thermal equilibrium. This asymptotic condition does not depend of the magnitude of the friction coefficient γ, which is a function of the absolute temperature and the effective mass of the moving defect.[17]

The statistics of real-space Brownian motion of an interstitial cluster does depend strongly on the magnitude of the friction coefficient γ. At a given temperature the mean square displacement of the defect $\langle X^2 \rangle$ scales with γ as $\langle X^2 \rangle \sim \gamma^{-2}$. This gives rise to the occurence of long-distance jumps in the low-friction limit.[18] Similar jumps were observed experimentally for clusters of adsorbed atoms moving on crystal surfaces.[19,20]

In this paper we evaluate the coefficient of thermal friction characterizing one-dimensional Brownian motion of a spatially delocalized interstitial defect moving in a crystal

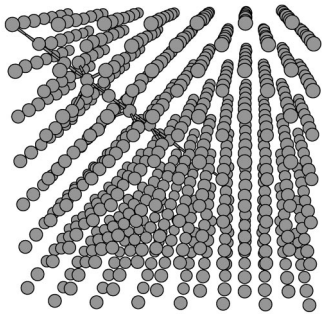

FIG. 1. Atomic structure of a mobile interstitial defect (a $\langle 111 \rangle$ crowdion) in a body-centered cubic lattice. The equilibrium atomic structure shown in this figure was computed using the Finnis-Sinclair-type many-body interatomic potential developed by Ackland *et al.* (Ref. 24) for the bcc iron. Although the energy of formation of this configuration is slightly higher than the energy of formation of the $\langle 110 \rangle$ dumbbell, this configuration is important for determining the pathway of diffusion of a single interstitial atom in the bcc lattice.

lattice in the presence of thermal fluctuations. To obtain an analytical solution, we consider a single-atom defect (a crowdion) described by the Frenkel-Kontorova model and assume that it performs thermally activated motion in one of the close-packed crystallographic directions. Although molecular-dynamics simulations show that a real single atom crowdion may frequently change its direction of motion by switching between equivalent crystallographic directions, the motion of clusters containing two or more interstitial atoms is known to be almost perfectly one dimensional.[3–5] Therefore the model considered below is likely to be applicable to the description of Brownian motion of a relatively broad class of interstitial defects interacting with phonon excitations in the crystal lattice.

In this paper we derive the quantum-mechanical Hamiltonian of interaction between a mobile defect, considered as a soliton quasiparticle solution of the Frenkel-Kontorova model, and acoustic phonons. We then use this Hamiltonian to derive the kinetic equation for the one-particle density matrix of the soliton describing creation and annihilation of phonons by the moving defect. Considering the Fokker-Planck limit of this equation, we obtain an explicit expression for the thermal friction coefficient. We show that in the case where the degree of spatial delocalization of the defect is substantial, its motion is well described by the low-friction approximation.

II. THE INTERACTION HAMILTONIAN

We begin by deriving a Hamiltonian that describes the interaction between a mobile interstitial defect and acoustic phonon excitations of the surrounding crystal lattice. To investigate the dynamics of the defect we use the Frenkel-Kontorova model. In this model we take into account the interaction between atoms constituting a closed-packed string and the interaction of the string with the lattice. Figure 1 gives an example of an interstitial defect, which can be described by the Frenkel-Kontorova model. Although the energy of formation of this defect (a $\langle 111 \rangle$ crowdion) in bcc iron is known to be higher than the energy of formation of a more localized dumbbell configuration,[24] the defect structure shown in Fig. 1 is representative of a broader class of mobile interstitial clusters of similar type containing several interstitial atoms that, according to molecular dynamics simulations,[3–5] are thermally stable. The defect shown in Fig. 1 was created by embedding a *single* extra atom in the body-centered cubic lattice and by the subsequent constrained minimization of energy of the entire ensemble of atoms shown in the figure. The perturbation of the crystal structure caused by embedding an atom spreads in one of the close-packed $\langle 111 \rangle$ directions. The resulting field of displacements of atoms along this direction can be described by the analytical model considered below.

The Lagrangian function of the Frenkel-Kontorova model describing a string of atoms embedded in a crystal lattice has the form[21,22]

$$\mathcal{L}=\sum_{n=-\infty}^{\infty}\frac{m\dot{x}_n^2}{2}-\frac{\alpha}{2}\sum_{n=-\infty}^{\infty}(x_{n+1}-x_n-a)^2 - V(x_1,\ldots,x_n,\ldots), \tag{4}$$

where α is a constant characterizing (in the harmonic approximation) the strength of repulsion between neighboring atoms in the string, n is the index of an atom in the string, and x is the coordinate in the direction parallel to the axis of the string (see Fig. 1). In the absence of thermal fluctuations the potential of interaction of the string with the surrounding lattice $V(x_1,\ldots,x_n,\ldots)$ is a periodic function of atomic coordinates $x_1,\ldots,x_n,\ldots$. To simplify the subsequent analytical treatment of the problem, we choose this potential in the form

$$V(x_1,\ldots,x_n,\ldots)=\frac{m\omega_0^2a^2}{2\pi^2}\sum_{n=-\infty}^{\infty}\sin^2\left(\frac{\pi x_n}{a}\right). \tag{5}$$

Several other realizations of potential $V(x_1,\ldots,x_n,\ldots)$ were studied in the literature[22] leading to results qualitatively similar to those obtained using Eq. (5). In Eq. (5) parameter a denotes the period of translations of the potential of the lattice, and frequency ω_0 characterizes the amplitude of variation of this potential. Figure 2 illustrates how the magnitude of ω_0 reflects the character of interatomic bonding in the material. In the case where the interaction between atoms is directionless (case A of Fig. 2), the motion of the string with respect to the surrounding lattice gives rise to a relatively small variation of the total energy of the system. The effective value of parameter ω_0 corresponding to case A shown in Fig. 2 is therefore relatively small. However, in the limit where the interaction between atoms is highly directional (case C shown in Fig. 2), the motion of the defect is characterized by a large value of ω_0.

Introducing the displacement $u_n(t)=x_n(t)-an$ of the nth atom from its equilibrium position in the string, from Eq. (4) we find equations of motion of atoms in the string

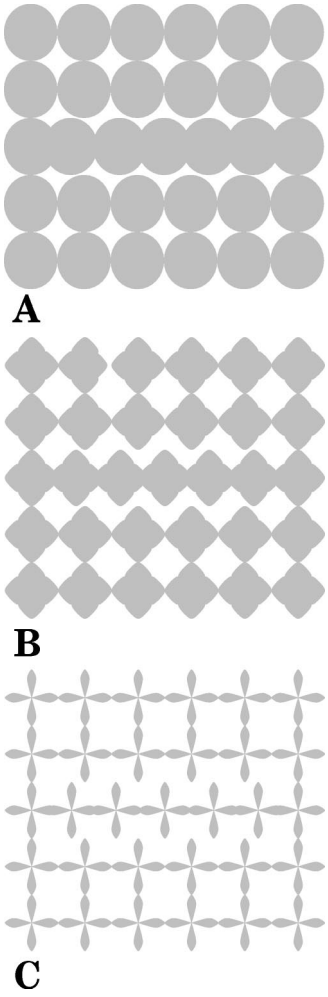

FIG. 2. Sketches illustrating how the directionality of interatomic bonding affects the behavior of the energy of an atomic system considered as a function of the displacement of atoms of the mobile string (shown in the center of each sketch) with respect to the surrounding lattice. The effective potential $V(x_1, \ldots, x_n, \ldots)$ given by Eq. (5) varies stronger as a function of x_n in the case C than it does in the case A. Note that although the structure of interstitial defects depends on parameters characterizing the shape of the potential function (5) only in the form of dimensional combination $\mathcal{N}=c/\omega_0 a$ (see Fig. 3 below), the coefficient of thermal friction γ cannot be expressed as a function of $\mathcal{N}$ alone, see formula (24).

$$m\frac{d^2u_n}{dt^2}=\alpha(u_{n+1}+u_{n-1}-2u_n)-\frac{m\omega_0^2 a}{2\pi}\sin\left(\frac{2\pi u_n}{a}\right).$$

In the limit of slowly varying displacement field $u(x,t) \approx u(x_n,t)\equiv u_n(t)$ these equations can be tranformed into the sine-Gordon equation[23]

$$m\frac{\partial^2 u}{\partial t^2}=\alpha a^2\frac{\partial^2 u}{\partial x^2}-\frac{m\omega_0^2 a}{2\pi}\sin\left(\frac{2\pi u}{a}\right). \tag{6}$$

A soliton solution of this non-linear equation, describing a glissile interstitial defect moving uniformly in the positive direction of x, is given by[21,22]

$$u(x,t)=\frac{2a}{\pi}\arctan\left(\exp\left\{-\frac{\omega_0[x-X(t)]}{\sqrt{c^2-V^2}}\right\}\right), \tag{7}$$

where $X(t)=Vt$ is the coordinate of the center of the defect, V is its velocity, and $c=(\alpha a^2/m)^{1/2}$ is the speed of sound. The field of displacements $u(x,t)$ given by Eq. (7), satisfies boundary conditions $u(-\infty,t)=a$ and $u(\infty,t)=0$, and describes the case where the string contains one extra atom.

To assess how well solutions of the Frenkel-Kontorova model describe the structure of interstitial defects in real materials, in Fig. 3 we plotted the field of atomic displacements evaluated for two types of interstitial defects (a crowdion and a double crowdion) using molecular dynamics simulations carried out for a system containing approximately 30 000 atoms. For comparison, in the same figure we also plotted the field of displacements calculated analytically using expression (7). Ratio $c/a\omega_0$ represented the only adjustible parameter of the model and the comparison involved no rescaling of analytical solution (7). The good correspondence between values obtained by using numerical molecular dynamics simulations and by solving the Frenkel-Kontorova model confirms the validity of the analytical solution (7). Note the substantial degree of spatial delocalization of interstitial defects shown in Fig. 3. Results plotted in Fig. 3 also illustrates an important point that it is not the value of ω_0 itself but a dimensionless combination $\mathcal{N}=c/\omega_0 a$ of parameters of the Frenkel-Kontorova model (4) that characterizes the structure of an interstitial defect in a given material. Parameter $\mathcal{N}$ has a simple meaning, namely, it equals the effective number of atoms participating in the formation of the crowdion.

In the presence of thermal phonon excitations in the lattice surrounding the defect, positions of minima of the potential of the lattice (5) undergo random displacements and the equation of motion of the string acquires the form

$$m\frac{\partial^2 u}{\partial t^2}=\alpha a^2\frac{\partial^2 u}{\partial x^2}-\frac{m\omega_0^2 a}{2\pi}\sin\left\{\frac{2\pi[u(x,t)-\xi(x,t)]}{a}\right\}, \tag{8}$$

where $\xi(x,t)$ describes the field of acoustic phonon displacements of the lattice. The field of phonon displacements $\xi(x,t)$ vanishes after averaging over the thermodynamic equilibrium $\langle\xi(x,t)\rangle_T=0$. Note that at low temperatures only the long wavelength acoustic phonons are excited with appreciable probability[25] and it is in this temperature limit where the motion of an interstitial cluster can be treated as one dimensional.

Looking for a solution of this equation in the form $u(x,t)=u_0[x-X(t)]+\Phi(x,t)$, where $u_0[x-X(t)]$ is given by Eq. (7) and where $X(t)$ is now assumed to be an arbitrary function of time t, and retaining terms linear and quadratic in $\Phi(x,t)$ and $\xi(x,t)$, we obtain

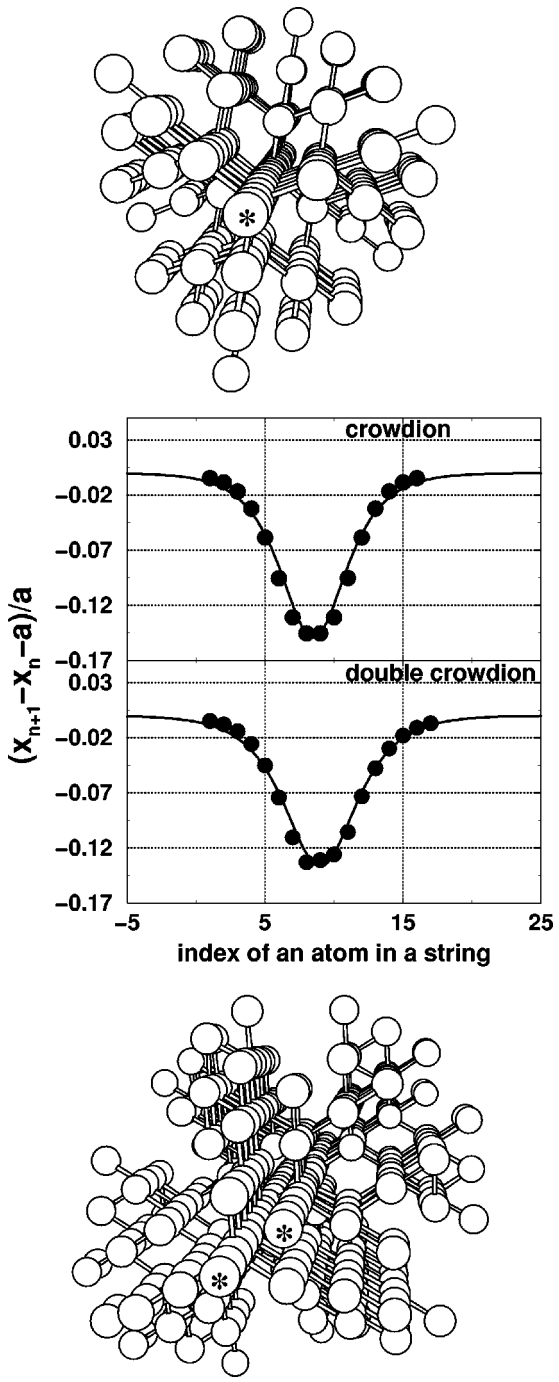

FIG. 3. The structure and the displacement field of two interstitial defects in bcc iron. The structure shown at the top results from embedding a single extra atom in the string marked by the star and the subsequent relaxation of the entire crystal. The structure shown in the bottom figure results from embedding two extra atoms in the two adjacent atomic strings. Only atoms with potential energy exceeding by 0.01 eV the average potential energy of an ideal lattice are shown. In the graph shown in the middle circles indicate positions of atoms in the corresponding crystal structure. Solid curves were calculated using Eq. (7) assuming $c/\omega_0 a = 2.11$ in the case of a single and $c/\omega_0 a = 2.34$ in the case of a double crowdion.

$$u_0''[x-X(t)]\left(\frac{dX}{dt}\right)^2 - u_0'[x-X(t)]\left(\frac{d^2X}{dt^2}\right) + \frac{\partial^2\Phi}{\partial t^2}$$
$$= c^2\frac{\partial^2\Phi}{\partial x^2} - \omega_0^2[\Phi(x,t)-\xi(x,t)]\left\{1-2\,\mathrm{sech}^2\left[\frac{x-X(t)}{l_0}\right]\right\}$$
$$+ \frac{4\pi\omega_0^2}{a}[\Phi(x,t)-\xi(x,t)]^2\tanh\left[\frac{x-X(t)}{l_0}\right]$$
$$\times\,\mathrm{sech}\left[\frac{x-X(t)}{l_0}\right], \qquad (9)$$

where $l_0 = c/\omega_0$. Bearing in mind the treatment of Brownian motion of the defect, we assume that the velocity of the defect dX/dt is small in comparison with the speed of sound c in the material.

In Eq. (9) the term proportional to $\xi(x,t)$ plays the part of a random force disturbing the motion of atoms in the string and giving rise to stochastic time-dependent fluctuations of the position of the center of the interstitial defect. Function $\Phi(x,t)$ describes phonon excitations in the string itself.

To obtain a closed equation describing the motion of the center of the defect $X(t)$, we use an approach analogous to the conventional quantum-mechanical perturbation theory.[26,22] Consider a linearised equation describing phonon excitations of the string for a given position X of the center of the defect

$$\frac{\partial^2\Phi}{\partial t^2} = c^2\frac{\partial^2\Phi}{\partial x^2} - \omega_0^2\Phi(x,t)\left\{1-2\,\mathrm{sech}^2\left[\frac{x-X}{l_0}\right]\right\}. \qquad (10)$$

A general solution of this equation has the form

$$\Phi(x,t) = A_0\Phi_0(x) + \int_{-\infty}^{\infty}\frac{dk}{2\pi}A_k\Phi_k(x,t), \qquad (11)$$

where

$$\Phi_0(x) = \mathrm{sech}\left(\frac{x-X}{l_0}\right),$$

and

$$\Phi_k(x,t) = \left[kl_0 + i\tanh\left(\frac{x-X}{l_0}\right)\right]\exp(ikx - i\omega_k t).$$

Here $\Phi_k(x,t)$ are the internal phonon modes of the string characterized by the dispersion relation $\omega_k = \omega_0\sqrt{1+(kl_0)^2}$, and $\Phi_0(x)$ is the Goldstone mode describing translations of the center of the defect along the string.[21] Note that $\lim_{k\to 0}\omega_k = \omega_0 > 0$, and therefore there are no acoustic modes in the spectrum of vibrational excitations of the string itself.

By multiplying Eq. (9) by $\Phi_0(x)$, integrating it over x and taking into account the orthogonality[27] of functions $\Phi_0(x)$ and $\Phi_k(x,t)$, we obtain a closed equation describing the motion of the center of the defect in the presence of an external phonon displacement field[28,29,22]

$$m^*\frac{d^2X}{dt^2}=\frac{m\omega_0^2}{\pi l_0}\int_{-\infty}^{\infty}dx\,\mathrm{sech}\left(\frac{x-X(t)}{l_0}\right)\times\left[1-2\,\mathrm{sech}^2\left(\frac{x-X(t)}{l_0}\right)\right]\xi(x,t)+\frac{4m\omega_0^2}{al_0}\int_{-\infty}^{\infty}dx\times\tanh\left(\frac{x-X(t)}{l_0}\right)\mathrm{sech}^2\left(\frac{x-X(t)}{l_0}\right)\xi^2(x,t),\qquad(12)$$

where $m^*=m(2a/\pi^2 l_0)$ is the effective mass of the defect. In the case where the degree of spatial delocalization of the defect is substantial $l_0\gg a$, the effective mass of the defect m^* is many times smaller than the mass m of an individual atom. Note also that in the case where the fluctuating force is associated with phonon excitations in the lattice surrounding the defect, we only retain terms that are linear and quadratic in the displacement field $\xi(x,t)$. For comparison, in the case where the defect interacts with the field of internal phonon excitations $\Phi(x,t)$ of the string itself and where the external potential of the lattice (5) is assumed to remain unaffected by thermal fluctuations, the first nonvanishing contribution to the force acting on the defect is proportional to the third power of the amplitude of phonon displacements.[30,29]

Consider the process of creation or annihilation of an acoustic phonon by an interstitial defect. Energy conservation requires that $\epsilon_{p+\hbar f}-\epsilon_p-\hbar c|f|=0$, where f is the projection of the wave vector of the phonon on the direction of motion of the defect and $\epsilon_p=p^2/2m^*$. In the limit of small f this is equivalent to the condition $p/m^*=c$, which is impossible to satisfy in the case where the defect performs slow thermal Brownian motion. It is therefore only the second-order two-phonon term in Eq. (12) that gives a nonvanishing contribution to the friction force.

The field of displacements $\xi(x,t)$ associated with an acoustic phonon mode propagating in the lattice surrounding the soliton has the form

$$\xi_k(x,t)=c_k\exp(ikx-ic|k|t).\qquad(13)$$

Since in the Frenkel-Kontorova model (4) we only consider displacements of atoms in the direction of the string and neglect displacements in the plane normal to the axis of the crowdion, only the projection of the phonon displacement field on the x axis needs to be retained in Eq. (13). Substituting Eq. (13) into Eq. (12) we find

$$m^*\frac{d^2X}{dt^2}=i\frac{\pi m\omega_0^2}{a}\left[c_kc_{k'}\frac{(k+k')^2l_0^2}{\sinh\left(\frac{\pi}{2}(k+k')l_0\right)}\times\exp[i(k+k')X(t)-ic(|k|+|k'|)t]+c_kc_{k'}^*\frac{(k-k')^2l_0^2}{\sinh\left(\frac{\pi}{2}(k-k')l_0\right)}\exp[i(k-k')X(t)-ic(|k|-|k'|)t]+\mathrm{c.c.}\right].\qquad(14)$$

We now introduce a fully three-dimensional field of phonon excitations and note that the right-hand side of Eq. (14) can be represented in a conventional form as a gradient $-\partial U(X,t)/\partial X$ of an effective interaction potential, the second quantized matrix element of which is equal to

$$\hat U(x,t)=\Omega\frac{\pi m\omega_0^2l_0^2}{2\varrho ca}\sum_{\alpha,\alpha'}\int\frac{d^3fd^3f'}{(2\pi)^6}\exp[i(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})x]\times\frac{(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})}{\sinh\left[\frac{\pi}{2}l_0(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})\right]}\frac{\hbar}{\sqrt{|\mathbf{f}||\mathbf{f}'|}}(\mathbf{e}_{\mathbf{f},\alpha}\cdot\mathbf{n})(\mathbf{e}_{\mathbf{f}',\alpha'}\cdot\mathbf{n})\times[\hat a^\dagger_{-\mathbf{f}\alpha}\hat a_{\mathbf{f}'\alpha'}\exp[-ic(|\mathbf{f}'|-|\mathbf{f}|)t]+\hat a^\dagger_{\mathbf{f}\alpha}\hat a_{-\mathbf{f}'\alpha'}\exp[ic(|\mathbf{f}'|-|\mathbf{f}|)t]].\qquad(15)$$

To obtain Eq. (15) we used the second quantized representation of the projection of the phonon displacement field on the direction $\mathbf{n}$ of the axis of the string (see Ref. 31)

$$\hat\xi(x,t)=\Omega\sum_\alpha\int_{\mathrm{BZ}}\frac{d^3f}{(2\pi)^3}\sqrt{\frac{\hbar}{2\varrho c|\mathbf{f}|\Omega}}\times[(\mathbf{e}_{\mathbf{f},\alpha}\cdot\mathbf{n})\hat a_{\mathbf{f},\alpha}e^{i\mathbf{f}\cdot\mathbf{n}x-ic|\mathbf{f}|t}-(\mathbf{e}^*_{\mathbf{f},\alpha}\cdot\mathbf{n})\hat a^\dagger_{\mathbf{f},\alpha}e^{-i\mathbf{f}\cdot\mathbf{n}+ic|\mathbf{f}|t}],\qquad(16)$$

where the summation is over branches of the acoustic phonon spectrum α, Ω is the volume of the crystal, ϱ is the mass density of the material, and BZ denotes integration over the Brillouin zone. In Eq. (16) $\mathbf{e}_{\mathbf{f},\alpha}$ is the vector of polarization of the αth branch of the phonon spectrum, and $\hat a_{\mathbf{f},\alpha}$ and $\hat a^\dagger_{\mathbf{f},\alpha}$ are the annihilation and creation operators for phonons in the normal mode $(\mathbf{f},\alpha)$. The minus sign before the second term in the right-hand side of Eq. (16) takes into account the change in the sign of the projection of the displacement field on the direction of propagation of the defect in the crystal.

In Eq. (16) we approximate the field of phonon displacements by a superposition of acoustic excitations propagating in all directions with the same velocity c that is assumed to be independent of the direction of polarization of a phonon mode. This approximation neglects the difference between longitudinal and transverse phonons. It is important to take this difference into account, for example, in the treatment of surface Rayleigh waves.[32] However, in the case where only scattering by bulk phonons is involved, contributions from longitudinal and transverse phonons to the correlation function of atomic displacements are qualitatively similar (see, e.g., formula (23) of Ref. 32) and this justifies the use of approximate representation (16).

Having obtained the explicit form of the Hamiltonian of interaction between an interstitial defect and phonon excitations in the lattice surrounding the defect, we can now derive the quantum kinetic equation for the density matrix of the

defect. Considering the Fokker-Planck limit of this kinetic equation, we shall find the coefficient of thermal friction γ entering the Langevin equation (1).

Before proceeding further, we note that although a mobile interstitial defect is a classical object, a consistent treatment of the interaction between the defect and phonon excitations requires using a quantum-mechanical approach. This stems from the fact that in many materials even at room temperature it is necessary to take into account the Bose statistics obeyed by phonons. We also note that the process of thermal equilibration of the defect is accompanied by the emission and absorption of phonons, and here effects of non-Boltzmann statistics play an important part, too.

III. KINETIC EQUATION FOR THE DENSITY MATRIX

We now derive the quantum kinetic equation for the density matrix of the mobile interstitial defect. Since in the absence of an external random force the motion of the defect is uniform, it is convenient to use the momentum representation of the density matrix and write the Liouville equation in the form

$$i\hbar\frac{\partial}{\partial t}\rho(q,q',n,l,t)=(\epsilon_q-\epsilon_{q'}+E_n-E_l)\rho(q,q',n,l,t)\times\int\frac{dk}{2\pi}\sum_f[\langle n|\hat{U}_k|f\rangle\times\rho(q-k,q',f,l,t)-\rho(q,q'+k,n,f,t)\langle f|\hat{U}_k|l\rangle], \quad (17)$$

where the energy of the defect ϵ_q is related to its wave vector $q=p/\hbar$ via $\epsilon_q=\hbar^2q^2/2m^*$. E_n is the energy of the nth excited state of the phonon subsystem of the crystal. In Eq. (17) $\hat{U}_k$ is a matrix element of the Hamiltonian corresponding to the exchange of momentum $\Delta p=k/\hbar$ between the defect and the phonon sybsystem of the crystal.

To obtain a self-consistent equation for the diagonal elements of the one-particle density matrix of the defect

$$\rho(q,q',t)=\mathrm{Tr}_{\mathrm{ph}}\hat{\rho}(t)=\sum_n\rho(q,q',n,n,t) \quad (18)$$

we follow a conventional procedure (see, e.g., Refs. 33,34) and assume that the density matrix entering the right-hand side of the kinetic equation is representable in the form of a direct product of the one-particle density matrix of the defect and the equilibrium density matrix of the phonon subsystem of the crystal. After some relatively lengthy algebra we arrive at

$$\frac{\partial}{\partial t}\rho(q,t)=\int dk\int d\omega S(k,\omega)\delta(\epsilon_{q+k}-\epsilon_q-\hbar\omega)\rho(q+k,t)-\int dk\int d\omega S(k,\omega)\delta(\epsilon_{q+k}-\epsilon_q+\hbar\omega)\rho(q,t), \quad (19)$$

where the structure factor $S(k,\omega)$ is given by

$$S(k,\omega)=\hbar\left(\frac{\pi ml_0\omega_0^2}{\varrho ca}\right)^2\frac{(kl_0)^2}{\sinh^2\left(\frac{\pi kl_0}{2}\right)}\int_{\mathrm{BZ}}\frac{d^3fd^3f'}{(2\pi)^5}\times\delta[k-(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})]\frac{1}{|\mathbf{f}||\mathbf{f}'|}\overline{n}_{\mathbf{f}}(\overline{n}_{\mathbf{f}'}+1)\times\delta[\omega-c(|\mathbf{f}'|-|\mathbf{f}|)]. \quad (20)$$

In this equation the equilibrium number $\overline{n}_{\mathbf{f}}$ of phonons occupying a given mode α is independent of α and is equal to

$$\overline{n}_{\mathbf{f}}=\langle\hat{a}^\dagger_{\mathbf{f}\alpha}\hat{a}_{\mathbf{f}\alpha}\rangle_T=\frac{1}{\exp(\hbar c|\mathbf{f}|/T)-1}.$$

Taking the Fokker-Planck limit of Eq. (19)

$$\frac{\partial}{\partial t}\rho(q,t)=\frac{\partial}{\partial q}\left[B\left(\frac{\hbar^2q}{m^*T}\rho(q,t)+\frac{\partial}{\partial q}\rho(q,t)\right)\right], \quad (21)$$

where

$$B=\left(\frac{ml_0^2\omega_0^2}{\varrho ca}\right)^2\int_{\mathrm{BZ}}\frac{d^3fd^3f'}{(2\pi)^5}\frac{(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})^4}{\sinh^2\left[\frac{\pi}{2}(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})l_0\right]}\times\frac{1}{|\mathbf{f}||\mathbf{f}'|}\overline{n}_{\mathbf{f}}(\overline{n}_{\mathbf{f}'}+1)\,\delta[\epsilon_{q+(\mathbf{f}\cdot\mathbf{n}+\mathbf{f}'\cdot\mathbf{n})}-\epsilon_q-\hbar c(|\mathbf{f}'|-|\mathbf{f}|)] \quad (22)$$

and comparing it with Eq. (3), we obtain the coefficient of thermal friction γ,

$$\gamma=\frac{\hbar^2B}{m^*T}. \quad (23)$$

In the high-temperature limit $\overline{n}_{\mathbf{f}}\approx T/\hbar c|\mathbf{f}|\gg1$ by carrying out integration in Eq. (22) we find

$$\gamma=1.06\omega_0\left(\frac{a\omega_0}{c}\right)^3\left(\frac{T}{mc^2}\right)\ln\left(\frac{2\pi c}{\omega_0 a}\right). \quad (24)$$

In the low-temperature limit $Ta/\hbar c\ll1$ (this limit corresponds to the case where effects associated with the Bose statistics of phonons are significant) we obtain that

$$\gamma=5.53\frac{\hbar\omega_0}{amc}\left(\frac{Ta}{\hbar c}\right)^4. \quad (25)$$

In the high-temperature limit (24) the friction coefficient depends on parameter ω_0 characterizing the strength of interaction between atoms of the string and the potential of the lattice (5) as $\gamma\sim\omega_0^4$. This functional dependence is similar to that known from the treatment of the Rayleigh scattering of light by density fluctuations in the atmosphere,[35] where the ω_0^4 dependence is responsible for the blue color of the sky.

IV. DISCUSSION

Consider the classical high-temperature limit (24). The average length L_T of random thermal displacements of the defect is given by $L_T \sim v_T \tau$, where $v_T \sim (T/m)^{1/2}$ is the average thermal velocity of atoms in the crystal [note that according to Eq. (7) the defect propagates through the crystal lattice as a free quasiparticle] and $\tau \sim \gamma^{-1}$ is the average time over which the defect retains memory about its direction of motion. Substituting expression (24) in this formula, we obtain an estimate for the average length of a thermal jump

$$L_T \sim a\left(\frac{c}{v_T}\right)\left(\frac{c}{\omega_0 a}\right)^4. \tag{26}$$

Considering thermal motion of an interstitial defect at room temperature, where $v_T \sim 10^4$ cm/s and $c/v_T \sim 10$, and using data shown in Fig. 3, we obtain that Brownian motion of a single crowdion may involve correlated jumps that are as large as 10^2 interatomic distances. Long-range jumps of defects have indeed been observed in molecular-dynamics simulations (see, e.g., the analysis performed by Wirth *et al.*[3] and Fig. 10 of Ref. 5), but the typical scale of these jumps is approximately one order of magnitude smaller than that predicted by formula (26). This shows that formula (24) may underestimate the value of the thermal friction coefficient γ by approximately one order of magnitude. This inaccuracy may partly be associated with the very strong functional dependence of the friction coefficient on parameters characterizing interatomic interactions in the material. For example, L_T given by Eq. (26) depends on the speed of sound in the material as $L_T \sim c^5$ and on frequency ω_0 characterizing the degree of directional bonding in the material as $L_T \sim \omega_0^{-4}$. This strong functional dependence makes it difficult to obtain accurate numerical values of L_T directly from Eq. (26).

There is an additional important point that needs to be taken into account when applying results obtained using the continuous displacement field approximation (6) to the interpretation of molecular dynamics simulations. It is the effect of discreteness of the lattice on the dynamical behavior of solutions of the Frenkel-Kotorova model (4). On one hand, discreteness leads to trapping of interstitial defects in the lattice at sufficiently low temperatures. Indeed, the treatment of the discrete Frenkel-Kontorova model (4) gives rise to the Peierls-Nabarro potential barriers.[36,37] By substituting solution (7) into Eq. (4), we obtain that the energy of the moving defect is equal to

$$E = m^* c^2 + \frac{m^* \dot{X}^2(t)}{2} + 8mc^2 \exp\left(-\frac{\pi^2 c}{\omega_0 a}\right)\cos\left(\frac{2\pi X(t)}{a}\right). \tag{27}$$

The third (periodic) term in the right-hand side of this equation is the Peierls-Nabarro potential energy of the defect. At low temperatures mobile interstitial defects are trapped in the minima of the Peierls-Nabarro potential. The height of Peierls-Nabarro barriers is given by

$$E_{\mathrm{PN}} = 16mc^2 \exp\left(-\frac{\pi^2 c}{\omega_0 a}\right). \tag{28}$$

This equation shows that the smaller the effective value of ω_0 the lower are the Peierls-Nabarro potential barriers (28) and the larger is the average length of random thermal jumps of the defect (26). The limit $c/a\omega_0 \gg 1$ corresponds both to low Peierls-Nabarro barriers and also to low thermal friction experienced by defects performing random Brownian motion in the lattice. This observation correlates well with results of recent molecular dynamics simulations[5] performed using directionless embedded atom many-body potentials and showing relatively low (~ 0.025 eV) activation energies corresponding to the translational motion of interstitial clusters.

The discreteness of the original Frenkel-Kontorova model (4),(5) gives rise to an additional channel of scattering through which a moving defect may dissipate energy to phonon excitations.[22,38] Although this type of scattering has not been included in the treatment described above, it may contribute to the rate of dissipation of energy of a moving defect giving rise to a larger value of the friction coefficient γ than that estimated on the basis of equations (24) and (25). The dependence of the friction coefficient on parameter ω_0 associated with this additional channel of scattering is likely to be qualitatively similar to that characterizing scattering by thermal fluctuations, but the temperature dependence of the contribution to the friction coefficient arising from the discreteness of the model may be different from that given by Eq. (24).

The fact that the coefficient of thermal friction γ shows strong dependence on parameters characterizing the interaction between atoms in the material and in particular to the value of frequency ω_0, may offer some insight into the origin of the long-range effect observed in experiments on ion implantation.[39–41] Experimentally it is observed that the depth characterizing radiation damage induced by the incident high-energy ions in fcc metals may exceed many times the range of ions in the material. The long-range effect is also observed, though in a somewhat weaker form, in bcc metals but it is almost absent in silicon. Assuming that interstitial defects formed in collision cascades occurring near the surface diffuse into the bulk of the material, we may reasonably expect that the depth characterizing the long-range effect should be inversely proportional to the coefficient of thermal friction γ. It is known that the degree of directional bonding increases from fcc through bcc to diamond-structure materials.[42] Given the strong functional dependence of the thermal friction coefficient on the type of interatomic bonding, the conclusion that thermal friction is greater in materials characterized by a substantial degree of directional bonding agrees with what is found in experimental investigations of the long-range effect in ion implantation. Furthermore, the same experimental data suggest that there may be a connection between the presence of directional bonding in bcc metals[42] and their higher swelling and creep resistance under irradiation.[43]

V. SUMMARY

By using the analytically solvable Frenkel-Kontorova model we investigated how a mobile interstitial defect interacts with phonon excitations in the lattice, and how this in-

teraction gives rise to the random one-dimensional Brownian motion of the defect. We found that in the case where the degree of spatial delocalization of the defect is significant, its motion is characterized by low thermal friction. This correlates well with recent observations of unusual statistics of displacements observed in molecular dynamics simulations of Brownian motion of interstitial defects.[3–5] Our model also shows that parameters characterizing the dynamical properties of interstitial defects are sensitive to the degree of directionality of interatomic bonding in the material, pointing to the significance of using accurate models of interatomic forces in predictive modelling of microstructural evolution of irradiated materials.

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