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Thermal friction and Brownian motion of interstitial defects in irradiated materials

S.L. Dudarev *

Culham Science Centre, EURATOM/UKAEA Fusion Association, Oxfordshire, OX14 3DB Oxford, UK

Abstract

We investigate the origin of long-range correlated jumps observed in molecular-dynamics simulations of Brownian motion of interstitial clusters in irradiated crystalline materials. We show that the presence of long jumps is associated with low thermal friction experienced by a cluster propagating through the crystal lattice in the presence of thermal fluctuations. Using the equation for the friction coefficient, we estimate the length of ballistic trajectories of clusters ejected from high-energy cascades and analyse implications of our findings for understanding the nature of the long-range effect observed in experiments on ion implantation in fcc and bcc metals, and the connection between this effect and the stability of metals under irradiation.

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1. Introduction

Thermally activated mobility of interstitial clusters in irradiated materials is believed to represent one of the main factors driving the evolution of microstructure of irradiated materials. A number of molecular-dynamics computer simulations performed in recent years addressed this issue [1,2]. It was found that the statistics of motion of clusters is somewhat unusual and involves the presence of long-range correlated jumps spanning many interatomic distances. Similar long-range jumps were observed in the case of motion of clusters of adsorbed atoms on a crystal surface [3]. These observations were interpreted in terms of the low-friction limit of surface diffusion [4]. In this paper we show that the motion of interstitial clusters in a crystal in the presence of thermal fluctuations is also characterised by low thermal friction.

The value of the thermal friction coefficient can be found by calculating the rate of dissipation of energy by a moving interstitial defect. Our treatment is based on the representation of the defect by a soliton (crowdion) solution of the Frenkel–Kontorova model. Solutions of the Frenkel–Kontorova model, as we will show, give a highly accurate description of the structure of the core of small interstitial clusters. By considering the process of creation and annihilation of phonons by a moving defect we find an explicit expression for the coefficient of thermal friction. We show that, depending on the parameters of the model, Brownian motion of the defect can often be classified as corresponding to the low-friction limit. Values of the friction coefficient obtained from the study of Brownian motion of interstitial clusters may also be applied to the evaluation of the length of ballistic trajectories of interstitial clusters ejected from high-energy collision cascades. This may help in understanding the origin of the long-range effect observed in experiments on implantation of high-energy ions in crystalline materials and its connection with the observed differences in the stability of fcc and bcc metals under irradiation.

2. Atomic structure of defects and the Frenkel–Kontorova model

A large body of recent work on atomistic simulation of the structure and mobility of defects in irradiated

* Tel.: +44-1235 466 513; fax: +44-1235 466 435.
E-mail address: sergei.dudarev@ukaea.org.uk (S.L. Dudarev).

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crystalline materials [1,2] was focused on establishing a connection between the structure of a defect and its macroscopic elastic field necessary for the description of long-range interactions between the defect and other elements of the microstructure of the material. On the other hand, dynamical properties of the defect, for example its thermally activated mobility, are largely determined by the structure of its core, where the theory of elasticity is not applicable. In this section we examine how well the core of interstitial defects can be described by the Frenkel–Kontorova model [5], which provides a convenient way of matching the discrete and continuous descriptions of an atomistic system. In the one-dimensional Frenkel–Kontorova model we consider a linear string (or a set of equivalent linear strings in the case of an interstitial cluster) of atoms interacting via short-range forces and embedded into the periodic potential of the crystal lattice surrounding the string. The Lagrangian function of the string has the form

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

where α is a constant characterising the strength of elastic interaction between neighbouring atoms, 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. The parameter a denotes the equilibrium distance between atoms in the string. The potential of the surrounding lattice is normally chosen in the form

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

where ω_0 is a variable parameter characterising the amplitude of variation of this potential. The choice of (2) is not unique, and the main requirement that Eq. (2) has to satisfy is that the potential of the lattice must be periodic with the period of translations a. The number of atoms in the string (1) does not have to be equal to the number of minima of the potential (2). In the case where the string contains only one extra atom, the solution of the model (1) is given by [5]

$$u(x) = \frac{2a}{\pi} \arctan\left\{ \exp\left[-\frac{\omega_0(x - X)}{c} \right] \right\}, \quad (3)$$

where the field of displacements of atoms $u(x)$ is assumed to be varying slowly in comparison with the interatomic distance a, $a|\mathrm{d}u/\mathrm{d}x| \ll 1$. $c = (\alpha a^2/m)^{1/2}$ is the speed of sound in the material and X is the coordinate of the centre of the defect. Eq. (3) represents a soliton (crowdion) solution of equations (1) and (2). The shape of the soliton is characterised by a dimensionless combination of parameters of the model $\mathscr{N} = c/\omega_0 a$. This quantity has the meaning of the effective number of atoms participating in the formation of the crowdion.

To examine how well Eqs. (1)–(3) describe the field of atomic displacements near the core of a glissile interstitial defect we consider the structure of three interstitial clusters of the $\langle 1\,1\,1\rangle$ type in bcc iron containing, respectively, one, two and three extra atoms embedded in atomic strings running parallel to the [1 1 1] direction. Fig. 1 shows how well the analytical solution (3) matches the set of discrete atomic displacements obtained by minimizing the energy of a simulation cell containing approximately 10^5 atoms. Results shown in Fig. 1 indicate that the Frenkel–Kontorova model does indeed provide a good description of the equilibrium structure of small interstitial clusters. It is therefore reasonable to apply the model to the investigation of thermal mobility and Brownian motion of interstitial clusters in a crystalline material.

3. Brownian motion of defects and the coefficient of thermal friction

Assuming that the cluster retains its shape in the process of stochastic thermal motion, the evolution of the centre of the cluster follows the Langevin equation

$$m^*\ddot{X} = -m^*\gamma\dot{X} + \eta(t), \quad (4)$$

where X is the projection of the coordinate of the centre of the cluster on the direction of motion, m^* is the effective mass of the cluster and γ is the coefficient of dissipative thermal friction. $\eta(t)$ is a random force satisfying conditions

$$\langle \eta(t) \rangle_T = 0; \quad \langle \eta(t)\eta(t') \rangle_T = 2m^* k_B T \delta(t - t'), \quad (5)$$

where T is the absolute temperature. The thermal diffusion coefficient D is related to γ via $D = k_B T/m^*\gamma$ and the average length L_b of ballistic trajectories of interstitial clusters ejected from collision cascades is given by $L_b = c/\gamma$. To have an estimate of the latter quantity is important for evaluating how far the clusters can propagate during the initial ballistic phase of the cascade.

Since the Langevin equation provides no means for the evaluation of γ, our approach will be based on the mapping of (4) to the Fokker–Planck equation for the distribution function $F(p, x, t)$ of moving defects [6]

$$\frac{\partial F}{\partial t} + \frac{p}{m^*}\frac{\partial F}{\partial x} - \frac{\partial}{\partial p}\left[\gamma\left(pF + m^* k_B T \frac{\partial F}{\partial p}\right)\right] = 0. \quad (6)$$

The Fokker–Planck equation (6) can be derived from first principles starting from equations of motion of the

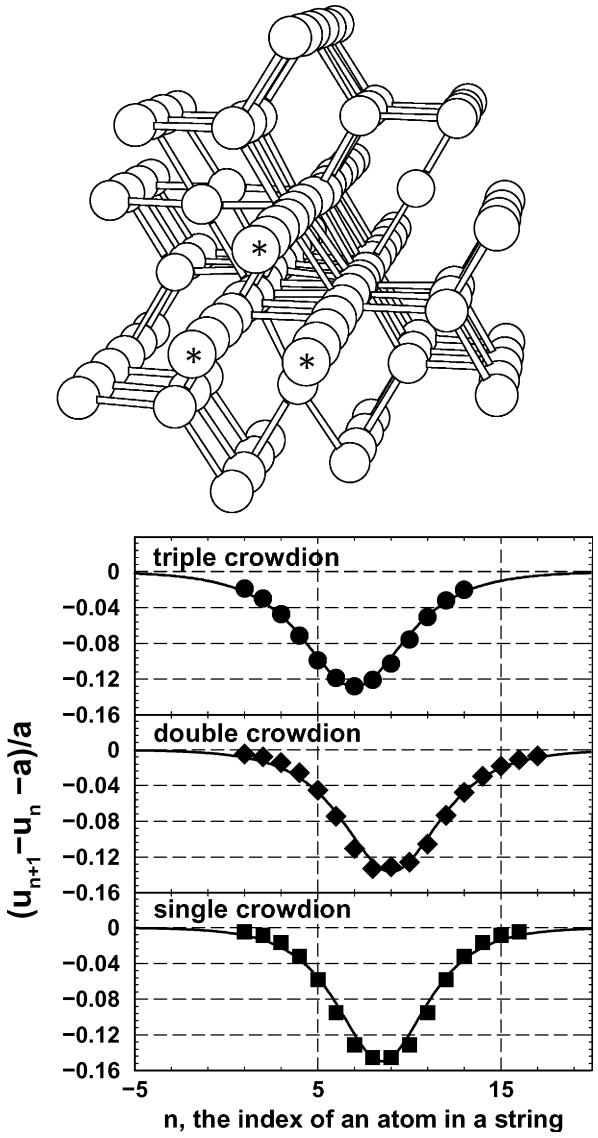

Fig. 1. Top: Atomic structure of an $\langle 1\,1\,1\rangle$ interstitial cluster in bcc iron containing three extra atoms. This structure was calculated using conjugate gradient energy minimisation and embedded-atom potentials. Strings of atoms marked by a star each contains an extra atom. Only those atoms are shown the potential energy of which exceeds by 0.01 eV the average potential energy of atoms in the lattice. Bottom: Comparison of displacement fields of atoms in single, double and triple crowdion interstitial clusters. Solid lines represent analytical solutions Eq. (3) of the Frenkel–Kontorova model. Values of $\mathcal{N}$ used in Eq. (3) to fit the atomic displacements are $\mathcal{N} = 2.11$ for the single, $\mathcal{N} = 2.31$ for the double and $\mathcal{N} = 2.46$ for the triple crowdion configuration, $a = 2.48$ Å.

interstitial defect. By following this approach we shall be able to calculate the thermal friction coefficient γ.

To derive the equation of motion of a cluster we use the method proposed by McLaughlin and Scott [7]. In the presence of thermal phonon excitations in the lattice surrounding the defect, positions of minima of the potential of the lattice (2) undergo random displacements and the equation of motion of the atomic string acquires the form

$$m\frac{\partial^2 u}{\partial t^2} = \alpha a^2 \frac{\partial^2 u}{\partial x^2} - \frac{m\omega_0^2 a}{2\pi} \sin\left\{\frac{2\pi[u(x,t) - \xi(x,t)]}{a}\right\}, \quad (7)$$

where $\xi(x,t)$ describes the field of acoustic phonon displacements of the lattice. 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 (3) and where $X(t)$ is now assumed to be an arbitrary function of time t, and using the projection technique described in [7], we obtain

$$m^*\frac{\mathrm{d}^2X}{\mathrm{d}t^2}=\frac{4m\omega_0^3}{ac}\int_{-\infty}^{\infty}\mathrm{d}x\tanh\left(\omega_0\frac{x-X(t)}{c}\right)\operatorname{sech}^2\left(\omega_0\frac{x-X(t)}{c}\right)\xi^2(x,t)+\cdots, \tag{8}$$

where $m^*=2m/\pi^2\mathscr{N}<m$ is the effective mass of the defect. In Eq. (8) we neglected the terms linear in $\xi(x,t)$. These terms do not contribute to phonon friction because of the incompatibility between dispersion relations of the defect and of acoustic phonons. Eq. (8) has the form of the Newton equation for a particle moving in one dimension under the influence of fluctuating force associated with displacements of atoms in the lattice. It is important to recognise that friction is a dissipative process and it is associated with the exchange of energy between the defect and phonon excitations in the crystal. Eq. (8) therefore describes not only the acceleration and deceleration of the mobile defect, but also recoil effects giving rise to the creation and annihilation of phonons.

The subsequent calculation of the friction coefficient is performed in three steps [8]. First, Eq. (8) needs to be second quantized. This makes it possible to introduce the phonon variables and to obtain an explicit expression for the effective Hamiltonian of interaction between the defect and phonons. By using this Hamiltonian, we derive the kinetic equation for the density matrix of the defect. Subsequently we consider the Fokker–Planck limit of this kinetic equation and, by comparing the coefficients of that equation of those of (6), we obtain an explicit expression for γ, namely,

$$\gamma=\begin{cases}1.06\omega_0^4\left(\dfrac{a}{c}\right)^3\left(\dfrac{k_{\mathrm{B}}T}{mc^2}\right)\ln\left(\dfrac{2\pi c}{\omega_0 a}\right), & k_{\mathrm{B}}Ta/\hbar c\gg 1,\\ 5.53\dfrac{\hbar\omega_0}{amc}\left(\dfrac{k_{\mathrm{B}}Ta}{\hbar c}\right)^4, & k_{\mathrm{B}}Ta/\hbar c\ll 1.\end{cases} \tag{9}$$

In the high temperature limit (in practice this limit corresponds to temperatures higher than room temperature) the friction coefficient depends on the parameter ω_0 characterising the amplitude of variation of the potential of the lattice (2) as $\gamma\sim\omega_0^4$. This functional dependence is the same as that known from the treatment of Rayleigh scattering of light by density fluctuations in the atmosphere [9], where the ω_0^4 dependence is responsible for the blue colour of the sky.

4. Correlated jumps, the long-range effect and ballistic propagation of clusters

An important piece of evidence illustrating the difference in the behaviour of fcc and bcc metals under irradiation is provided by the observation of the long-range effect in ion implantation [10–12]. In fcc metals the damage occurs at depths that are significantly larger than the range of ions in the material. The effect is also observed in bcc metals but is almost absent in silicon [13]. Evidently, the long-range damage effects must also occur in materials irradiated by high-energy neutrons. The difference between the two cases is associated with the difference in the *geometry of sources* of mobile defects generated by collision cascades. In the case of ion implantation defects are generated in the surface layer of the crystal. In the case of high-energy neutron irradiation defects are produced homogeneously in the bulk of the material. Understanding the origin of differences between observations of the long-range effect in bcc and fcc metals may help in understanding the origin of higher resistance of bcc metals to irradiation. Note that the depth characterising the long-range effect is primarily sensitive to the crystal structure rather than to the density of dislocations in the material. A possible mechanism responsible for the occurrence of the long-range effect is associated with collective events of formation of mobile interstitial clusters in high-energy collision cascades [14]. Data shown in Fig. 2 make it possible to obtain a numerical estimate of the effective mass m^* of the cluster and evaluate the length of the ballistic trajectory of a cluster ejected from a cascade.

Indeed, by noting that in thermal equilibrium the motion of the centre of mass of the cluster must satisfy the equipartition principle and by evaluating the average squared projection of the velocity of the centre of the cluster $\langle V_z^2\rangle_T$, we find that the effective mass m^* of the cluster is equal to $m^*=k_{\mathrm{B}}T(\langle V_z^2\rangle_T)^{-1}$. Using molecular-

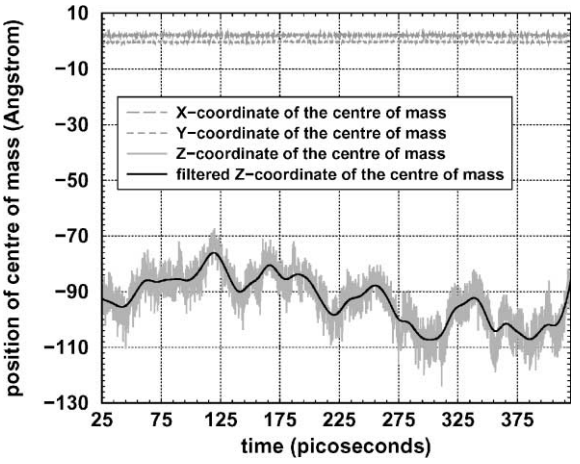

Fig. 2. Time evolution of the position of the centre of a three-interstitial cluster at $T=50$ K. The simulation involved 265 305 atoms and was performed using the system of coordinates with x, y, z axis parallel to the $[1\,1\,\bar{2}]$; $[\bar{1}\,1\,0]$ and $[1\,1\,1]$ directions. The fact that the X and Y coordinates of the centre of the cluster are nearly independent of time illustrates the one-dimensional nature of Brownian motion of the cluster.

dynamics simulations, we obtain that $\langle V_z^2\rangle_{T=50\ \mathrm{K}} = 7.87\times10^7$ (cm/s)^2 and $\langle V_z^2\rangle_{T=100\ \mathrm{K}} = 21.55\times10^7$ (cm/s)^2 for a three-interstitial cluster. From these values we find that $m^* = 8.77\times10^{-23}$ g for $T = 50$ K and $m^* = 6.41\times10^{-23}$ g for $T = 100$ K. In agreement with Eq. (8) the effective mass of the cluster is smaller than the total bare mass of interstitial atoms forming the cluster, and is a decreasing function of temperature (the latter effect is associated with the part played by the Peierls–Nabarro barriers [15]). Using the high-temperature value of the diffusion coefficient $D_0 = 1.7\times10^{-3}$ cm^2/s given in Ref. [2], we obtain $\gamma = k_{\mathrm{B}}T/m^*D \sim 1.27\times10^{11}$ s^{-1} for $T = 100$ K. This estimate compares well with $\gamma \sim 10^{11}$ s^{-1} following from Eq. (9) for $\omega_0 \sim 10^{13}$ s^{-1}, $c \sim 10^5$ cm/s, $m \sim 10^{-22}$ g and $a \sim 10^{-8}$ cm. We can now estimate the average length of random thermal displacements of a cluster performing thermal Brownian motion as $L_{T=100\ \mathrm{K}} \sim \sqrt{\langle V_z^2\rangle_{T=100\ \mathrm{K}}}/\gamma = 15$ Å. The fact that L_T is many times the lattice constant explains the origin of long-range jumps observed in molecular-dynamics simulations of Brownian motion of interstitial clusters [1,2]. Knowing the thermal friction coefficient we can also estimate the average length of the ballistic trajectory of a cluster formed in a collision cascade as $L_{\mathrm{b}} = c/\gamma \sim 10$ nm. This value is lower that the characteristic scale of the long-range effect observed in fcc metals, where the range of ballistic propagation of clusters approaches a few hundred nanometres. Larger values of L_{b} can be explained using Eq. (9) taking into account that L_{b} depends strongly both on the speed of sound in the material $L_{\mathrm{b}} \sim c^5$ and on the frequency ω_0 characterising the degree of directionality of interatomic bonding in the material $L_{\mathrm{b}} \sim \omega_0^{-4}$. The presence of this strong functional dependence makes it difficult to obtain accurate estimates directly from Eq. (9). However, the trend exhibited by (9) and in particular the rapid increase of the value of γ as a function of directionality of inter-atomic bonding (ω_0 increases from fcc through bcc to the diamond-structure materials) agrees with the trend found in experimental studies of the long-range effect in Refs. [10–12].

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