



Materials subjected to fast neutron irradiation/Matériaux soumis à irradiation par neutrons rapides

## The non-Arrhenius migration of interstitial defects in bcc transition metals

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### Abstract

Thermally activated migration of defects drives microstructural evolution of materials under irradiation. In the case of vacancies, the activation energy for migration is many times the absolute temperature, and the dependence of the diffusion coefficient on temperature is well approximated by the Arrhenius law. On the other hand the activation energy for the migration of self-interstitial defects, and particularly self-interstitial atom clusters, is very low. In this case a trajectory of a defect performing Brownian motion at or above room temperature *does not* follow the Arrhenius-like pattern of migration involving infrequent hops separated by the relatively long intervals of time during which a defect resides at a certain point in the crystal lattice. This article reviews recent atomistic simulations of migration of individual interstitial defects, as well as clusters of interstitial defects, and rationalizes the results of simulations on the basis of solutions of the multistring Frenkel–Kontorova model. The treatment developed in the paper shows that the origin of the non-Arrhenius migration of interstitial defects and interstitial defect clusters is associated with the interaction between a defect and the classical field of thermal phonons. **To cite this article:** *S.L. Dudarev, C. R. Physique 9 (2008)*. Crown Copyright © 2007 Published by Elsevier Masson SAS on behalf of Académie des sciences. All rights reserved.

### Résumé

**Migration de type non-Arrhenius des défauts interstitiels dans les métaux de transition de structure cubique centrée.** La migration thermiquement activée des défauts ponctuels contrôle l'évolution de la microstructure des matériaux sous irradiation. Pour la migration des lacunes la valeur de l'énergie d'activation équivaut généralement à plusieurs fois la température absolue, et, la dépendance thermique du coefficient de diffusion est bien décrite par une loi de type Arrhenius. Cependant l'énergie d'activation de la migration des auto-interstitiels isolés ou sous forme de boucle est très faible. Dans ce cas la trajectoire d'un défaut effectuant un mouvement brownien à la température ambiante ou au-dessus ne suit pas une diffusion de type Arrhenius, c'est-à-dire des sauts peu fréquents séparés par des durées relativement longues pendant lesquelles le défaut réside dans un site déterminé du cristal. Ce papier fait la revue des simulations atomiques récentes de la migration d'auto-interstitiels isolés ou sous forme de boucle, et, rationalise les résultats de ces simulations sur la base des solutions du modèle « multi-corde » de Frenkel–Kontorova. L'approche développée dans ce papier montre que l'origine de la migration de type non-Arrhenius d'auto-interstitiels ou de boucles d'interstitiels est à associer à l'interaction du défaut considéré avec le champ classique des phonons d'origine thermique. **Pour citer cet article :** *S.L. Dudarev, C. R. Physique 9 (2008)*.

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## 1. Introduction

The thermally activated migration of vacancy and self-interstitial atom defects is the main mechanism driving microstructural evolution of materials under irradiation. The migration of defects is responsible for the climb of dislocations, nucleation and growth of voids and vacancy clusters, for the decoration of dislocations by radiation defects, and for radiation hardening and embrittlement of materials. The ‘standard model’ for migration of radiation defects is given by the Arrhenius law, where the frequency  $\nu_{i \rightarrow f}$  of hops between the initial ( $i$ ) and the final ( $f$ ) equilibrium configurations of a defect in the crystal lattice is given by the equation [1–3]

$$\nu_{i \rightarrow f} = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

where  $\nu_0$  is the attempt frequency,  $E_a$  is the activation energy for migration, and  $T$  is the absolute temperature. In Eq. (1) the attempt frequency  $\nu_0$  is a constant quantity, and the magnitude of  $E_a$  depends only on the type of the defect and on the local environment of the defect in the initial ( $i$ ) and final ( $f$ ) configurations. The calculated activation energies for migration of single vacancies in body-centred cubic (bcc) transition metals vary between approximately 0.62 eV in vanadium [4], 0.65 eV in iron [5], and 1.78 eV in tungsten [4,6]. These values are many times  $k_B T$  even for the highest temperatures of operation of materials in a fusion or a fission power plant. Hence migration of vacancies in materials is well described by the Arrhenius equation (1), in which the exponential factor is very small  $\exp(-E_a/k_B T) \ll 1$ .

On the other hand, the migration of self-interstitial atom defects in non-magnetic bcc metals is characterized by comparatively low activation energies. In ferromagnetic iron the activation energy for migration of a single interstitial atom defect is approximately 0.34 eV [7], which is half the migration energy for a vacancy. In all the *non-magnetic* bcc metals a self-interstitial atom defect adopts the linear  $\langle 111 \rangle$  crowdion configuration, and the activation energy for migration of this configuration is exceedingly low, ranging between 0.02 and 0.05 eV for all the metals forming groups V and VI of the Periodic Table [4,8–10]. Furthermore, molecular dynamics simulations show that similar small activation energies characterize thermal migration of mesoscopic self-interstitial atom clusters in *all* the bcc metals, including iron [11,12]. In this case, at and above room temperature, we have  $E_a \leq k_B T$ , and the exponential factor in Eq. (1) is of the order of unity. The pattern of migration of a self-interstitial defect now no longer looks like an Arrhenius-like sequence of infrequent hops between equilibrium positions, separated by the relatively long intervals of time during which a defect resides at a certain point in the crystal lattice.

In the case where the hopping of defects in the lattice is well approximated by the Arrhenius law (1), the diffusion coefficient describing the evolution of an *ensemble* of defects is given by

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (2)$$

where  $D_0 \approx \nu_0 l^2$ ,  $l$  is the average length of a hop, and  $E_a$  is the activation energy defined by Eq. (1). According to Eq. (2), the diffusion coefficient approaches a constant value  $D = D_0$  in the limit where  $T \geq E_a/k_B$ . A plot illustrating how the diffusion coefficient given by Eq. (2) varies as a function of absolute temperature  $T$  is shown in Fig. 1. The Arrhenius parametrization (2) for the diffusion coefficients of defects has been implemented in a number of kinetic Monte-Carlo computer programmes [13–16].

In this article we address the question of the validity of the Arrhenius parametrization (2) for self-interstitial atom defects in non-magnetic bcc metals in the high temperature limit. By using molecular dynamics simulations and by investigating the solutions of the multistring Frenkel–Kontorova model [17], and also by rationalizing the results of simulations through a combined application of the Langevin equation and the fluctuation–dissipation theorem, we find that in the high temperature limit the diffusion coefficient of self-interstitial defects and defect clusters varies linearly as a function of absolute temperature  $T$ . This finding is at odds with the Arrhenius formula for the diffusion coefficient (2), pointing to the strongly non-Arrhenius nature of the diffusion of interstitial defects and clusters of interstitial defects in bcc metals at elevated temperatures.

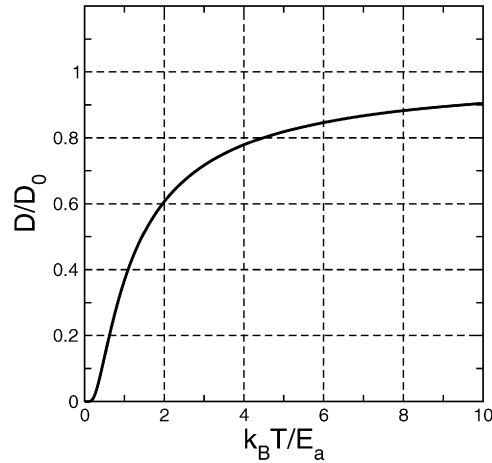


Fig. 1. Plot illustrating the temperature dependence of the diffusion coefficient of defects given by Eq. (2). Assuming that  $E_a = 0.025$  eV (see e.g. Ref. [12]), we find that for  $T = 300$  K the argument of the Arrhenius equation is  $k_B T / E_a = 1.034$ , for  $T = 800$  K it is  $k_B T / E_a = 2.74$ , and for  $T = 1100$  K it is  $k_B T / E_a = 3.78$ . In the last case the diffusion coefficient is already very close to its asymptotic value corresponding to the limit  $T \rightarrow \infty$ .

## 2. Brownian motion of single interstitial defects in non-magnetic bcc metals

A self-interstitial atom (SIA) defect is an object formed by embedding an extra atom in the crystal lattice followed by the subsequent minimization of the total energy of all the atoms in the simulation cell. Since the extra atom is indistinguishable from any other atom in the material, it is not possible to associate the notion of the defect with any particular atom in the defect structure. A self-interstitial atom defect hence represents a collective entity corresponding to an excited state of the crystal lattice or, in other words, a quasiparticle. In bcc metals a self-interstitial atom defect adopts one of the several possible geometrically distinct configurations, each having its own characteristic formation energy. The two most significant configurations are the so-called  $\langle 111 \rangle$  crowdion/dumbbell that has the lowest energy of formation in all the non-magnetic bcc metals [4], and the  $\langle 110 \rangle$  configuration that corresponds to the lowest formation energy of a self-interstitial atom defect in ferromagnetic bcc iron [5,7].

At a finite temperature all the atoms forming the structures shown in Fig. 2 vibrate around their equilibrium positions. The centre of the self-interstitial atom defect, corresponding to the region of the highest strain, does not remain stationary as a function of time. The defect performs a random walk in the lattice as illustrated by the projection of a simulated trajectory of migration of the defect shown in Fig. 3.

Once a representative trajectory of a defect is simulated, the diffusion coefficient for a migrating defect can be found using the Einstein formula [18]

$$D = \lim_{t \rightarrow \infty} \frac{\overline{[\mathbf{R}(t) - \mathbf{R}(0)]^2}}{6t} \quad (3)$$

which is subject to the condition that  $\mathbf{R}(t) - \mathbf{R}(0)$  is a random process with zero mean, i.e. that  $\overline{[\mathbf{R}(t) - \mathbf{R}(0)]} = 0$ . Here the bar above a function denotes averaging over statistical realizations of the trajectory of a migrating defect. Condition  $\overline{[\mathbf{R}(t) - \mathbf{R}(0)]} = 0$  means that *on average* a migrating defect remains at its initial position  $\mathbf{R}(0)$ . Since the diffusion coefficient (3) represents a measure of fluctuations of the position of the defect, the presence of any ‘drift’ terms giving rise to the non-zero values of  $\overline{[\mathbf{R}(t) - \mathbf{R}(0)]}$  has to be excluded from the statistical analysis involving Eq. (3).

It is instructive to establish a connection between Eq. (3) and the treatment of Brownian motion based on the classical Langevin equation

$$m^* \frac{d\mathbf{v}}{dt} = -\gamma \mathbf{v}(t) + \mathbf{f}(t) \quad (4)$$

Here  $m^*$  is the effective mass of the defect,  $\gamma$  is the coefficient of dissipative friction and  $\mathbf{v}(t)$  is the velocity of migrating defect. The term  $\mathbf{f}(t)$  in the right-hand side of the above equation represents a random thermal force acting

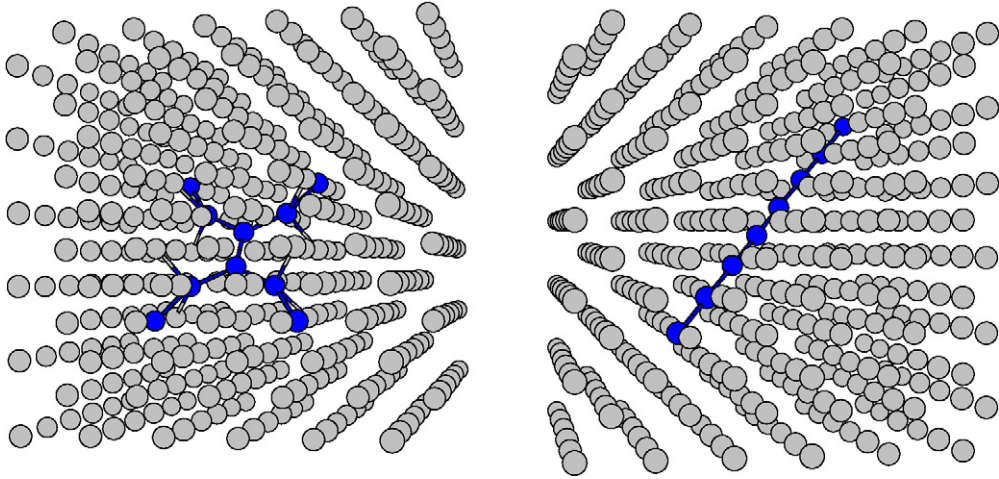


Fig. 2. Atomic structures of the  $\langle 110 \rangle$  (left panel) and of the  $\langle 111 \rangle$  (right panel) self-interstitial atom defects in tungsten. Both defect configurations are formed by inserting an extra atom in the crystal lattice followed by the relaxation of positions of all the atoms in the structure. The atoms forming these defect structures are all identical. Colour highlights (i.e. darker atoms) the symmetry of the defect configuration. In metallic tungsten the energy of formation of the  $\langle 111 \rangle$  self-interstitial atom configuration is lower than the energy of formation of the  $\langle 110 \rangle$  configuration by approximately 0.3 eV [4].

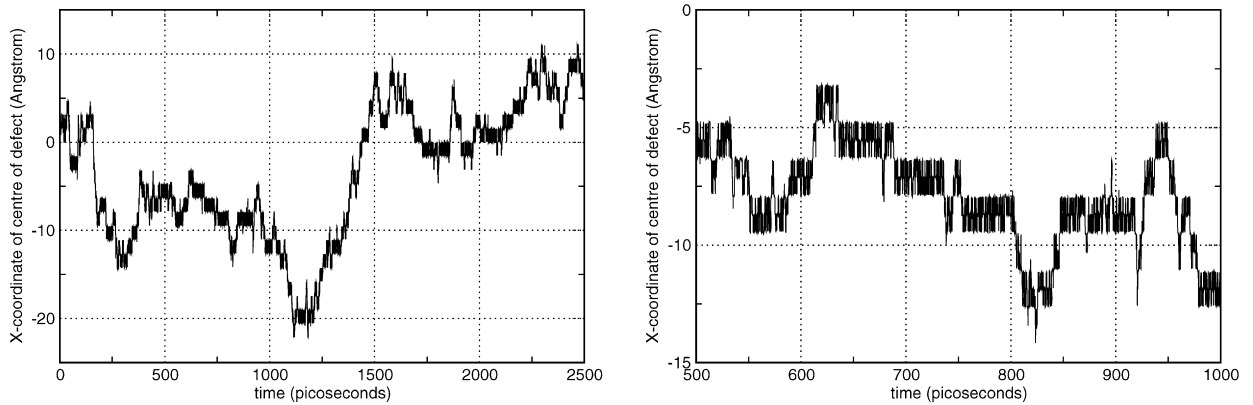


Fig. 3. The  $x$ -coordinate of the centre of the  $\langle 111 \rangle$  crowdion defect performing one-dimensional (in the direction of the axis of the defect) random Brownian walk in tungsten at  $T = 150$  K. The right panel shows the full simulated trajectory of the defect while the left panel shows a part of the same trajectory corresponding to the interval of time  $500 < t < 1000$  picoseconds.

on the defect. Eq. (4) does not include the effect of any non-random external potential on Brownian motion of a defect. This aspect of the problem has recently received attention and considerable progress was made in solving it [19,20,3]. Here we are interested in the treatment of diffusion of defects in the high-temperature limit  $k_B T / E_a \geq 1$  where the influence of the non-random component of the potential can be neglected.

Assuming that  $\overline{\mathbf{f}(t)} = 0$  or, equivalently, that migration of the defect is ergodic, in which case

$$\lim_{t_0 \rightarrow \infty} \frac{1}{t_0} \int_{t'}^{t'+t_0} \mathbf{f}(t) dt = 0$$

for any arbitrarily chosen  $t'$ , we find that  $\overline{\mathbf{v}(t)} = 0$  and that the average kinetic energy of a migrating defect is given by

$$\frac{m^* \overline{\mathbf{v}^2(t)}}{2} = \frac{1}{2m^*} \int_{-\infty}^t d\tau \int_{-\infty}^t d\tau' \exp\left[-\frac{\gamma}{m^*}(t-\tau)\right] \exp\left[-\frac{\gamma}{m^*}(t-\tau')\right] \overline{\mathbf{f}(\tau) \cdot \mathbf{f}(\tau')} \quad (5)$$

Assuming that the stochastic thermal force is delta-correlated

$$\overline{\mathbf{f}(\tau)\mathbf{f}(\tau')} = \overline{\mathbf{f}^2}\delta(\tau - \tau') \quad (6)$$

and applying the classical equipartition principle  $m^*\overline{\mathbf{v}^2(t)}/2 = (3/2)k_B T$ , from Eqs. (5) and (6) we find

$$\frac{m^*\overline{\mathbf{v}^2(t)}}{2} = \frac{3}{2}k_B T = \frac{\overline{\mathbf{f}^2}}{2m^*} \int_{-\infty}^t d\tau \exp\left[-\frac{2\gamma}{m^*}(t - \tau)\right] = \frac{\overline{\mathbf{f}^2}}{4\gamma} \quad (7)$$

This condition relates the amplitude of stochastic fluctuations of the thermal force and the coefficient of dissipative friction  $\gamma$ , namely

$$\overline{\mathbf{f}^2} = 6\gamma k_B T \quad (8)$$

Using this formula, it is a simple matter to show that the correlation function of velocities of a defect is

$$\begin{aligned} \overline{\mathbf{v}(t) \cdot \mathbf{v}(t')} &= \left(\frac{1}{m^*}\right)^2 \int_{-\infty}^t d\tau \int_{-\infty}^{t'} d\tau' \exp\left[-\frac{\gamma}{m^*}(t - \tau)\right] \exp\left[-\frac{\gamma}{m^*}(t' - \tau')\right] \overline{\mathbf{f}(\tau) \cdot \mathbf{f}(\tau')} \\ &= \frac{\overline{\mathbf{f}^2}}{2\gamma m^*} \exp\left[-\frac{\gamma}{m^*}|t - t'|\right] = \frac{3k_B T}{m^*} \exp\left[-\frac{\gamma}{m^*}|t - t'|\right] \end{aligned} \quad (9)$$

Integrating this correlation function over time we arrive at

$$\int_0^{\infty} \overline{\mathbf{v}(t) \cdot \mathbf{v}(0)} dt = \frac{3k_B T}{\gamma} \quad (10)$$

Defining the coordinate of the defect as an integral of its velocity

$$\mathbf{R}(t) = \int_0^t \mathbf{v}(\tau) d\tau$$

where  $\mathbf{R}(0) = 0$ , and evaluating the average square of this quantity using Eq. (9), we find an equation that was probably first derived by Chandrasekhar [18]

$$\begin{aligned} \overline{\mathbf{R}^2(t)} &= \int_0^t d\tau \int_0^t d\tau' \overline{\mathbf{v}(\tau) \cdot \mathbf{v}(\tau')} = \frac{3k_B m^* T}{\gamma^2} \int_0^{\frac{\gamma t}{m^*}} d\theta \int_0^{\frac{\gamma t}{m^*}} d\theta' \exp[-|\theta - \theta'|] \\ &= \frac{6k_B m^* T}{\gamma^2} \left\{ \frac{\gamma t}{m^*} - \left[1 - \exp\left(-\frac{\gamma t}{m^*}\right)\right] \right\} \end{aligned} \quad (11)$$

Combining (11) with the Einstein equation (3), we find a condition that relates the diffusion and the friction coefficients

$$D = \lim_{t \rightarrow \infty} \frac{\overline{\mathbf{R}^2(t)}}{6t} = \frac{k_B T}{\gamma} = \frac{6(k_B T)^2}{\overline{\mathbf{f}^2}} = \frac{1}{3} \int_0^{\infty} \overline{\mathbf{v}(t) \cdot \mathbf{v}(0)} dt \quad (12)$$

Comparing Eqs. (11) and (12) we see that taking the limit  $t \rightarrow \infty$  is equivalent to evaluating the right-hand side of Eq. (11) for  $\gamma t/m^* \gg 1$ . Estimates show that  $m^*/\gamma \sim 1$  ps and hence the minimum length of an interval of time required for evaluating the diffusion constant cannot be shorter than approximately 10 ps.

Eq. (12) shows that if we assume that the variance of the stochastic thermal force  $\overline{\mathbf{f}^2}$  varies linearly as a function of absolute temperature then the diffusion coefficient would also vary linearly as a function of  $T$ . The friction coefficient  $\gamma$  in this case is a constant quantity independent of absolute temperature  $T$ . In the next section we will prove this conjecture for the case of a linear crowdion defect migrating in bcc crystal lattice.

### 3. The Frenkel–Kontorova model for a migrating crowdion

We start by pointing out that the conventional one-dimensional Frenkel–Kontorova model [21,22], describing a linear string of atoms interacting by elastic forces and moving in an external periodic potential, does not provide a suitable starting point for the treatment of interaction of a crowdion defect with thermal vibrations of atoms in the lattice. The reason for this is that the conventional Frenkel–Kontorova model does not take into account displacements of atoms forming the lattice surrounding the defect. Hence it does not preserve the symmetry of the problem, where the displacement of an atom in a lattice surrounding the defect results in the same force as an equal in magnitude and opposite in sign displacement of an atom in the core of the defect itself.

An equation of motion for a crowdion moving in a vibrating lattice was derived in Refs. [23,10]. It has the form

$$\frac{d^2 Z(t)}{dt^2} = 4\omega^2 \sum_{n,\mathbf{h}} [\Phi_{n0}(t) - \Phi_{n\mathbf{h}}(t)] \frac{1}{\cosh^2[(n - Z(t)/a)/N]} \quad (13)$$

where  $Z(t)$  is the coordinate of the centre of a crowdion, index  $n$  refers to an atom in a string, and  $\mathbf{h}$  refers to a string.  $a$  is the distance between atoms in a string, and  $N$  is the dimensionless width of the strain field in the core of the crowdion defect.  $\Phi_{n0}(t)$  and  $\Phi_{n\mathbf{h}}(t)$  are the projections of thermal displacements of atoms in the string (0) containing the crowdion and in the strings ( $\mathbf{h}$ ) surrounding the crowdion, on the axes of the strings. The right-hand side of Eq. (13) is proportional to the force acting on a crowdion defect (to actually evaluate the force, the right-hand side of (13) needs to be multiplied by the mass of the defect).

The amplitude of the phonon force is linear in the atomic displacements. The force changes sign depending on whether a displaced atom belongs to the string (0) containing a crowdion or it belongs to one of the neighbouring atomic strings ( $\mathbf{h}$ ). The force is delta-correlated and its variance is proportional to the absolute temperature.

To prove this we first evaluate the correlation function of thermal displacements of atoms. The second-quantized operator of thermal displacements has the form [24]

$$\hat{\mathbf{u}}(t) = \sum_{\mathbf{f},\alpha} \sqrt{\frac{\hbar}{2M\omega(\mathbf{f},\alpha)N}} \{ \mathbf{e}(\mathbf{f},\alpha) \hat{a}(\mathbf{f},\alpha) \exp[i\mathbf{f} \cdot \mathbf{R}_n - i\omega(\mathbf{f},\alpha)t] + \text{h.c.} \} \quad (14)$$

where h.c. means Hermitian conjugate,  $\hat{a}(\mathbf{f},\alpha)$  is a phonon annihilation operator, and summation is performed over the wave vectors  $\mathbf{f}$  and branches  $\alpha$  of the phonon spectrum of the material. In Eq. (14)  $\mathbf{e}_j(\mathbf{f},\alpha)$  is the polarization vector of a phonon,  $M$  is the mass of an atom and  $N$  is the number of atoms per unit volume. The correlation function of projections of thermal displacements in the direction  $\xi$  of the axis of the crowdion in the classical limit is

$$\langle (\hat{\mathbf{u}}(t) \cdot \xi) (\hat{\mathbf{u}}(t') \cdot \xi) \rangle_T = \sum_{\mathbf{f},\alpha} \frac{k_B T}{M\omega^2(\mathbf{f},\alpha)N} |\mathbf{e}(\mathbf{f},\alpha) \cdot \xi|^2 \cos[\omega(\mathbf{f},\alpha)t] \quad (15)$$

In the isotropic acoustic approximation where  $\sum_{\alpha} |\mathbf{e}(\mathbf{f},\alpha) \cdot \xi|^2 = 1$ , and  $\omega(\mathbf{f},\alpha) = cf$ , where  $c$  is the average speed of sound in the material, we find that

$$\langle (\hat{\mathbf{u}}(t) \cdot \xi) (\hat{\mathbf{u}}(t') \cdot \xi) \rangle_T = \frac{\Omega k_B T}{4\pi^2 M c^3} \delta(t - t') \quad (16)$$

where  $\Omega$  is the volume per atom. Assuming that thermal vibrations of individual atoms are not correlated, and noting that each  $\langle 111 \rangle$  atomic string in bcc lattice is surrounded by six other strings, we find

$$\overline{\mathbf{f}(t) \cdot \mathbf{f}(t')} = \frac{64}{\pi^2} \Omega \frac{k_B T}{M c^3} (m^* \omega^2)^2 N \delta(t - t') \quad (17)$$

This equation shows that the phonon force acting on a defect is linear in absolute temperature and it is delta-correlated as a function of time. Combining this with the analysis given in the preceding section we see that the diffusion coefficient of crowdions migrating in a pure bcc metal is expected to vary linearly as a function of absolute temperature (as opposed to it approaching saturation in the high temperature limit as predicted by the Arrhenius equation (2))

$$D \sim T \quad (18)$$

We now show that the analysis of trajectories of migrating crowdions confirms this prediction.

#### 4. Numerical evaluation of the diffusion coefficient

A molecular dynamics simulation of a migrating defect predicts a trajectory of the defect  $\mathbf{R}(t)$  similar to that shown in Fig. 3. How can we estimate the magnitude of the diffusion coefficient  $D$  from this curve? An approach that is often used to evaluate  $D$  consists in splitting the trajectory into many independent sub-trajectories, for example by choosing arbitrarily defined starting points and time intervals, and evaluating the diffusion coefficient as a statistical average of [25]

$$D = \frac{\langle \mathbf{R}^2 \rangle}{6t} \quad (19)$$

While in some cases this approach gives satisfactory results, analysis shows that in the case of nearly freely migrating crowdions the statistics of values of  $D$  found using Eq. (19) may be relatively poor and the spread of calculated values may be large, making it difficult to draw a reliable conclusion about the temperature dependence of the diffusion coefficient.

One of the possible reasons responsible for the large statistical uncertainty in the value of the diffusion coefficient found from a given realization of the trajectory of the defect is that any simulated trajectory  $\mathbf{R}(t)$  does not satisfy the condition  $\overline{\mathbf{R}(t)} = 0$  required for the statistical interpretation of this function as a random process. In effect this means that a trajectory defined on a finite interval of time contains both the ‘random’ component  $\delta\mathbf{R}(t)$  that satisfies the requirement  $\overline{\delta\mathbf{R}(t)} = 0$ , as well as a part that can be interpreted as systematic regular drift of the defect over the duration of the simulation. The fact that for an infinitely long trajectory the drift term is expected to vanish is of no immediate significance here since any practical simulation generates a trajectory that is defined only on a finite interval of time.

To eliminate the effect of the effective drift we introduce a pseudo-trajectory  $\delta\mathbf{R}(t)$  defined as a real trajectory minus a drift term, which we take as a function linear in  $t$ , namely

$$\delta\mathbf{R}(t) = \mathbf{R}(t) - \frac{2t}{t_0^2} \int_0^{t_0} \mathbf{R}(t') dt' \quad (20)$$

At  $t = 0$  the pseudo-coordinate of a moving defect is the same as its actual coordinate, namely  $\delta\mathbf{R}(0) = \mathbf{R}(0)$ . Furthermore, if we associate taking an average over an ensemble with taking an average over time (which in this case is limited by the length of the interval of time considered in a simulation), we find that the pseudo-trajectory  $\delta\mathbf{R}(t)$  now satisfies the condition  $\overline{\delta\mathbf{R}(t)} = 0$  required for the statistical interpretation of the temporal variation of the position of the defect as a random process. Indeed

$$\int_0^{t_0} \delta\mathbf{R}(t) dt = \int_0^{t_0} \mathbf{R}(t) dt - \frac{2}{t_0^2} \int_0^{t_0} t dt \int_0^{t_0} \mathbf{R}(t') dt' = \int_0^{t_0} \mathbf{R}(t) dt - \frac{2}{t_0^2} \frac{t_0^2}{2} \int_0^{t_0} \mathbf{R}(t') dt' = 0 \quad (21)$$

and hence  $\delta\mathbf{R}(t)$  has zero mean on the interval of time  $[0, t_0]$ . Substituting the pseudo-coordinate of the defect given by (20) into Eq. (3), which defines the diffusion coefficient, we find that in the limit  $t \rightarrow \infty$  both the actual trajectory and the pseudo-trajectory result in the same calculated value of the diffusion coefficient (see Eq. (16) of Ref. [10])

$$D = \lim_{t \rightarrow \infty} \frac{\overline{[\mathbf{R}(t) - \mathbf{R}(0)]^2}}{6t} = \lim_{t \rightarrow \infty} \frac{\overline{[\delta\mathbf{R}(t) - \delta\mathbf{R}(0)]^2}}{6t} \quad (22)$$

Statistical analysis of results of numerical molecular dynamics simulations of migration of defects shows that the use of pseudo-trajectories instead of the actual trajectories reduces the statistical uncertainty of the calculated values of  $D$  and improves the numerical convergence of the method.

Fig. 4 shows plots of the diffusion coefficient evaluated in this way for a 19 self-interstitial atom cluster and a 37 self-interstitial atom cluster. In both cases diffusion coefficients vary approximately linearly as a function of absolute temperature, confirming the analysis given above. Also, data shown in Fig. 4 agree with simulations of diffusion of single interstitial defects and defect clusters performed recently by Zepeda-Ruiz et al. [26]. When analyzing the results of simulations, the authors of Ref. [26] noted that “...Although Arrhenius behavior is widely expected for diffusion in the solid state, it clearly does not occur here...” Analysis given in this paper explains the origin of the

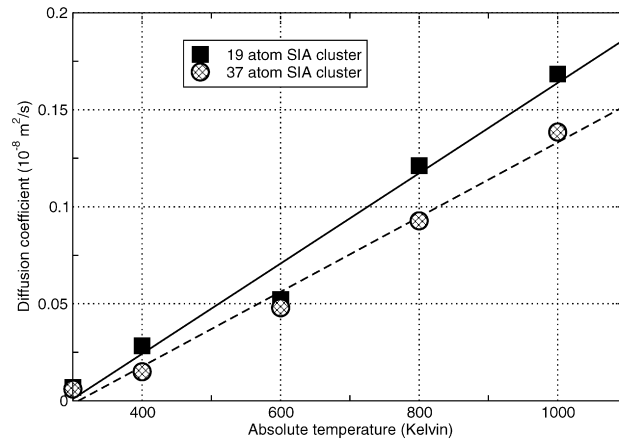


Fig. 4. Coefficients of thermal diffusion of a 19 self-interstitial atom cluster and a 37 self-interstitial atom cluster in tungsten evaluated by analyzing the statistics of trajectories of migration of mesoscopic defects in the crystal lattice, as described in the text. Straight lines are linear fits to the values found using molecular dynamics simulations.

non-Arrhenius diffusion of defects, and highlights the somewhat unexpectedly significant part played by the direct interaction between a migrating self-interstitial atom defect and the field of thermal phonons.

The fact that the diffusion coefficient of self-interstitial defects varies as a function of temperature in the way not consistent with the conventional Arrhenius law has significant implications for modelling microstructural evolution of materials under irradiation. Thermally activated mobility of defects is one of the main factors driving microstructural evolution. Correct quantitative understanding of mechanisms of migration of point defects, as well as defect clusters, represents an essential step in the development of quantitative models describing this evolution. The non-Arrhenius diffusion of defects occurring in the two most common bcc metals, vanadium [26] and tungsten, suggests that it probably also occurs in all the other bcc metals, including iron, where migration of clusters of self-interstitial defects obeys the same principles as migration of clusters of self-interstitial defects in vanadium or tungsten.

## 5. Summary and discussion

The activation energy for the migration of self-interstitial defects, and particularly self-interstitial atom clusters, is very low. Analysis given in this paper shows that a trajectory of a defect performing Brownian motion at or above room temperature *does not* follow the Arrhenius-like pattern of migration involving infrequent hops separated by the relatively long intervals of time during which a defect resides at a certain point in the crystal lattice. At high temperature the diffusion coefficient of a self-interstitial atom defect or a self-interstitial atom cluster varies linearly as a function of absolute temperature, in agreement with predictions of an analytical model for migration of crowdion defects involving interaction between point defects and phonons.

Concluding this investigation, I would like to highlight several significant outstanding questions that stem from the analysis given above. One of them is how to generalize the analytical model describing thermally activated migration of a single defect to the case of a cluster of defects, or in other words, to the case of a migrating mesoscopic dislocation loop. This question is closely related to the question about thermal fluctuations of dislocation lines, and dislocation dynamics at a finite temperature, see e.g. [27]. Another significant aspect of the treatment of diffusion of defects is related to the role played by disorder and interaction with solute atoms in dilute and concentrated alloys. There have been several interesting developments in this field including a study of migration of dislocation loops in the field of randomly distributed impurities [28], an investigation of the effect of solutes on migration of defects in concentrated FeCu and FeCr alloys [15,29,30] and the development of comprehensive kinetic Monte-Carlo models of migration of defects in alloys [31]. Further development of predictive models for migration of defects, mesoscopic defect clusters, and dislocations in technological alloys are required for the interpretation of experimental data and predictive modelling of behaviour of materials in the extreme environment of advanced nuclear and fusion power plants.



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