CONTINUOUS DIFFUSION MODEL FOR THE THERMODIFFUSION IN PERIODIC POTENTIAL

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We study the effect of temperature gradient on diffusion of an interstitial impurity in simple cubic lattice with the use of Langevin equation. Jump rate and diffusion coefficient as a function of temperature gradient at various temperatures are calculated.

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1. Introduction

Thermodiffusion (thermomigration) is a phenomenon far from being well understood. It is of some importance in ionic crystals, where thermomigration is at the origin of the thermoelectric power of these materials and eg. nuclear reactors, where material is subjected to a very strong temperature gradient. Phenomenological theory [1] of diffusion under the action of the temperature gradient predicts among others, that interstitials move toward the cold end and vacancies toward the hot end of the sample. Experiments on selfthermodiffusion in pure metals confirm to some extend predictions mentioned. It means that the material flux is toward the cold part, and the vacancies toward the hot end. In the case of interstitials, however, the material flux can have one or other direction with respect to temperature gradient.

In our recent paper [2] we studied dynamics of the system consisting of a single interstitial impurity atom in a simple cubic lattice which dynamics was described in harmonic approximation. We derived generalized Langevin equation which after some approximations was solved numerically yielding jump rate, jump lengths distribution and diffusion coefficient as a function of temperature.

In the present paper the same system is considered but in the presence of temperature gradient. There have been little work done on the dynamics

of the system coupled to the phonon bath which itself is not in equilibrium. Here we mention of Ref. [3] where dynamics of Brownian particles suspended In Section 2 the energy flux in terms of normal coordinates is derived. The Fokker–Planck equation for the case is derived among others.

In Section 2 the energy flux in terms of normal coordinates is derived. The problem how the temperature gradient modifies dynamics of the lattice is solved in Section 3. In Section 4 we derive the generalized Langevin equation for interstitial impurity which in the next Section is applied to one dimensional motion in cosine potential. Results of numerical solution of the Langevin equation as well as discussion are given in Section 6.

2. Flux of energy

The crucial problem is to incorporate temperature gradient into dynamics of the system. It is solved by taking into account a local constraint

$$\vec{j}\,(\vec{r}) + \sigma \nabla T = 0 \tag{1}$$

in a variational principle. There $\vec{j}\,(\vec{r})$ is energy flux through unit surface perpendicular to temperature gradient ∇T and σ stands for thermal conductivity of the lattice.

The energy of the lattice can be expressed as

$$H = \int d^3 r H(\vec{r}\,),$$

where density of energy operator is given by

$$H(\vec{r}) = \frac{1}{2} \sum_l \left[m\, \dot{\vec{R}}_l^{\,2} + \sum_{p \neq l} U\left(\left| \vec{R}_l - \vec{R} \right| \right) \right] \delta\left(\vec{r} - \vec{R}_l \right) . \tag{2}$$

Obviously m and $\vec{R}_l$ denotes mass and radius vector of the lattice atom respectively. According to *e.g.* Zubariev [4] density of the energy flux of the field represented by Eq. (2) is

$$\begin{aligned} \vec{j}\,(\vec{r}) \;=\; & \frac{1}{2} \sum_l \left[m\, \dot{\vec{R}}_l^{\,2} + \sum_{p \neq l} U\left(\left| \vec{R}_l - \vec{R}_p \right| \right) \right] \dot{\vec{R}}_l\, \delta\left(\vec{r} - \vec{R}_l \right) \\ + \; & \frac{1}{4} \sum_{l,p} \left[\left(\dot{\vec{R}}_l + \dot{\vec{R}}_p \right) \cdot \vec{F}_{lp} \right] \left(\vec{R}_l - \vec{R}_p \right) \delta\left(\vec{r} - \vec{R}_l \right) , \end{aligned} \tag{3}$$

where

$$\vec{F}_{lp} = -\vec{F}_{pl} = -\nabla_{\vec{R}_l} U\left(\left|\vec{R}_l - \vec{R}_p\right|\right),$$

and $\delta(\vec{r})$ stands for the product $\delta(x)\,\delta(y)\delta(z)$ of Dirac delta functions.

We want to express $\vec{j}\,(\vec{r})$ in terms of small deviations $\vec{u}_l$ of the lattice atoms from their equilibrium positions $\vec{r}_l$

$$\vec{R}_l = \vec{r}_l + \vec{u}_l\ .$$

Neglecting terms of third and higher orders in $\vec{u}_l$ we get for energy flux density

$$\vec{j}\,(\vec{r}) = \frac{1}{4}\sum_{l,p}\left[\sum_{\alpha,\beta}\left(\dot{u}_l^{\alpha} + \dot{u}_p^{\alpha}\right)\Phi_{lp}^{\alpha\beta}\left(u_l^{\beta} - u_p^{\beta}\right)\right]\left(\vec{r}_l - \vec{r}_p\right)\delta\left(\vec{r} - \vec{r}_l\right), \quad (4)$$

where

$$\Phi_{lp}^{\alpha\beta} = \frac{\partial^2 U\left(\left|\vec{r}_l - \vec{r}_p\right|\right)}{\partial r_l^{\alpha}\partial r_p^{\beta}}$$

satisfies the equation

$$\sum_l \Phi_{lp}^{\alpha\beta} = 0\,.$$

Because there is no sources or sinks of the energy flux inside the crystal and because of translational symmetry of the lattice the vector field $\vec{j}\,(\vec{r})$ is also translationally invariant in the bulk of material. To make $\vec{j}\,(\vec{r})$ continuous function of $\vec{r}$ we average it over the crystal volume

$$\vec{j}_{\mathrm{av}} = \frac{1}{\Omega}\iiint \vec{j}\,(\vec{r})dV$$

with the result

$$\vec{j}_{\mathrm{av}} = \frac{1}{4m\Omega}\sum_{l,p}\sum_{\alpha,\beta}\left(\dot{u}_l^{\alpha} + \dot{u}_p^{\alpha}\right)\Phi_{lp}^{\alpha\beta}\left(u_l^{\beta} - u_p^{\beta}\right)\left(\vec{r}_l - \vec{r}_p\right).$$

For simplicity we consider one mode of vibrations only, and express deviations $\vec{u}_l$ in terms of normal coordinates $a_{\vec{q}}$

$$\vec{u}_l = \frac{1}{\sqrt{Nm}}\sum_{\vec{q}} \vec{e}_{\vec{q}}\; a_{\vec{q}}\, \mathrm{e}^{i\vec{q}\cdot\vec{r}_l}\,.$$

Averaged energy flux density which we call simply $\vec{j}$ from now on reads

$$\vec{j} = -i\sum_{\vec{q}} \vec{I}\,(\vec{q})\dot{a}_{\vec{q}}a^*_{\vec{q}} = \sum_{\vec{q}} \vec{I}\,(\vec{q})\left(a^{(1)}_{\vec{q}}\,\dot{a}^{(2)}_{\vec{q}} - a^{(2)}_{\vec{q}}\,\dot{a}^{(1)}_{\vec{q}}\right), \tag{5}$$

where

$$\vec{I}\,(\vec{q}) = -\frac{1}{2m\Omega}\sum_n \vec{r}_n \sin(\vec{q}\cdot\vec{r}_n)\sum_{\alpha,\beta} e^{\alpha}_{\vec{q}}\Phi^{\alpha\beta}_n e^{\beta}_{\vec{q}} \tag{6}$$

and

$$a_{\vec{q}} = a^{(1)}_{\vec{q}} + ia^{(2)}_{\vec{q}}\,.$$

Because

$$\omega^2(\vec{q}) = \frac{1}{m}\sum_n \cos(\vec{q}\cdot\vec{r}_n)\sum_{\alpha,\beta} e^{\alpha}_{\vec{q}}\Phi^{\alpha\beta}_n e^{\beta}_{\vec{q}}$$

then under approximation

$$\sum_n \cos(\vec{q}\cdot\vec{r}_n)\sum_{\alpha,\beta}\Phi^{\alpha\beta}_n\nabla_{\vec{q}}\left(e^{\alpha}_{\vec{q}}e^{\beta}_{\vec{q}}\right) = 0$$

it follows from Eq. (6) that

$$\vec{I}\,(\vec{q}) = -\frac{1}{2\Omega}\nabla_{\vec{q}}\omega^2(\vec{q}). \tag{7}$$

3. Lattice dynamics in presence of temperature gradient

Now we are ready to derive time dependence of normal coordinates $a_{\vec{q}}(t)$.The energy of the lattice per one mode of vibrations when expressed in terms of normal coordinates reads

$$H_l = \sum_{\vec{q}}\left(\dot{a}_{\vec{q}}\dot{a}^*_{\vec{q}} + \omega^2(\vec{q})a_{\vec{q}}a^*_{\vec{q}}\right).$$

Corresponding Lagrangian L can be derived and when constraint Eq. (1) is taken into account the following function have to be minimized with respect to real and imaginary part of $a_{\vec{q}}(t)$ and $\dot{a}_{\vec{q}}(t)$

$$\begin{aligned}\widetilde{L} \;=\; \frac{1}{2}\sum_{\vec{q}}\Bigg[&\dot{a}^{(1)2}_{\vec{q}} + \dot{a}^{(2)2}_{\vec{q}} - \omega^2(\vec{q})\left(a^{(2)2}_{\vec{q}} + \dot{a}^{(1)2}_{\vec{q}}\right)\\ &+2\,\vec{\lambda}\cdot\vec{I}\,(\vec{q})\left(a^{(1)}_{\vec{q}}\dot{a}^{(2)}_{\vec{q}} - a^{(2)}_{\vec{q}}\dot{a}^{(1)}_{\vec{q}}\right)\Bigg] + \sigma\,\vec{\lambda}\cdot\nabla T\,.\end{aligned}$$

To find time dependence of normal coordinates when temperature gradient is applied to the lattice we use the variational principle

$$\delta \int \widetilde{L} dt = 0 \,. \tag{8}$$

The components of the vector $\vec{\lambda}$ constitute a set of three Lagrange multipliers, which in general depend on time. The equations of motion of the system we are looking for in terms of complex normal coordinates are

$$\ddot{a}_{\vec{q}} + 2i\,\vec{\lambda}\cdot\vec{I}\,\vec{a}(\vec{q})\dot{a}_{\vec{q}} + i\,\dot{\vec{\lambda}}\cdot\vec{I}\,(\vec{q})a_{\vec{q}} + \omega^2(\vec{q})a_{\vec{q}} = 0\,,$$

and its approximate (accurate when $\dot{\vec{\lambda}}\cdot\vec{I}\,(\vec{q})/\omega^2(\vec{q}) \ll 1$ which is usually fulfilled) solution is

$$a_{\vec{q}}(t) = A(\vec{q})\mathrm{e}^{-i\vec{I}(\vec{q})\cdot\int\vec{\lambda}(t)dt}\cos(\omega(\vec{q})t - \delta(\vec{q}))\,. \tag{9}$$

At each $\vec{q}$ within the first Brillouin zone both $A(\vec{q})$ and $\delta(\vec{q})$ are random numbers, their statistical properties are given under assumption of local statistical equilibrium by the Maxwell–Boltzmann distribution

$$p(A)dA = \frac{A\omega^2(\vec{q})}{k_{\mathrm{B}}T}\exp\left(-\frac{A^2\omega^2(\vec{q})}{2k_{\mathrm{B}}T}\right)dA$$

for the amplitude and uniform distribution within $[0, 2\pi]$ range for the phase $\delta(\vec{q})$.

Having found time dependence of normal coordinates Eq. (9) we insert them into Eq. (5). However the energy flux density becomes then a random number and will be difficult to deal with. Therefore it seems that there is no choice but to average the energy flux density Eq. (5) over amplitudes $A(\vec{q})$ and phases $\delta(\vec{q})$. It becomes then

$$\langle\vec{j}\rangle = k_{\mathrm{B}}T\sum_{\vec{q}}\frac{\vec{I}\,(\vec{q})}{\omega^2(\vec{q})}\left(\vec{\lambda}\,(t)\cdot\vec{I}\,(\vec{q})\right),$$

$\langle\ \rangle$ means "statistical average of" with T being local equilibrium temperature and the constraint Eq. (1), when averaged over volume and random amplitudes and phases reduces to

$$\sum_{\vec{q}}\frac{\vec{I}\,(\vec{q})}{\omega^2(\vec{q})}\left(\vec{\lambda}\cdot\vec{I}\,(\vec{q})\right) - \frac{\sigma}{k_{\mathrm{B}}}\frac{\nabla T}{T} = 0\,. \tag{10}$$

Equation (10) serves for determination of the Lagrange multipliers λ_i, it is seen that as a result of approximations made they do not depend on time. Once $\vec{\lambda}$ is known the normal coordinates of the lattice are uniquely (besides random amplitudes and phases) determined by

$$a_{\vec{q}}(t) = A(\vec{q})\mathrm{e}^{-i\vec{\lambda}\cdot\vec{I}(\vec{q})t}\cos(\omega(\vec{q})t - \delta(\vec{q}))\,. \tag{11}$$

Equations (10) and (11) constitute dynamics of the lattice in the presence of temperature gradient.

4. Dynamics of the interstitial impurity

The system we are interested in consists of single impurity atom in a simple cubic lattice of the lattice constant a. The lattice dynamics is described in approximation discussed in previous parts of the paper. Impurity energy when expanded with respect to deviation of the lattice atoms from their equilibrium positions $\vec{r}_l$ takes the form [2]

$$H_i = \frac{1}{2}M\dot{\vec{r}}^{\,2} + V(\vec{r}\,) + \sum_{\vec{q}} f_{\vec{q}}(\vec{r}\,)\, a_{\vec{q}}\,,$$

here potential energy of the impurity

$$V(\vec{r}\,) = \sum_l v(\vec{r} - \vec{r}_l)\,,$$

$$f_{\vec{q}}(\vec{r}\,) = -\frac{1}{\sqrt{Nm}}\sum_l \vec{e}_{\vec{q}}\cdot\nabla v(\vec{r} - \vec{r}_l)\,\mathrm{e}^{i\vec{q}\cdot\vec{r}_l}$$

and $\vec{e}$ denotes polarization vector of the lattice wave, $m(M)$ is mass of the lattice (impurity) atom. Radius vector of the interstitial atom $\vec{r}$ and normal coordinates of lattice vibration $a_{\vec{q}}$ constitute set of dynamical variables of the total system. The equations of motion of the system follow from the variational principle Eq. (7) with $\widetilde{L}$ of the form of Eq. (8) but supplemented by the term

$$\frac{1}{2}M\dot{\vec{r}}^{\,2} - V(\vec{r}\,) - \sum_{\vec{q}} f_{\vec{q}}(\vec{r}\,)\, a_{\vec{q}}$$

due to the interstitial atom.

The equations of motion that follow are

$$\ddot{a}_{\vec{q}} + 2i\,\vec{\lambda}\cdot\vec{I}\,(\vec{q})\,\dot{a}_{\vec{q}} + i\,\vec{\lambda}\cdot\vec{I}\,(\vec{q})\,a_{\vec{q}} + \omega^2(\vec{q})\,a_{\vec{q}} + f^*_{\vec{q}}(\vec{r}\,) = 0\,, \tag{12}$$

and

$$M\ddot{\vec{r}} + \nabla V(\vec{r}) + \sum_{\vec{q}} a_{\vec{q}} \nabla f_{\vec{q}}(\vec{r}) = 0 \tag{13}$$

with initial conditions $a_{\vec{q}}(0) = A(\vec{q})\cos(\delta(\vec{q}))$ and $\dot{a}_{\vec{q}}(0) = A(\vec{q})\sin(\delta(\vec{q}))$.

The solution of the first one, when $\vec{\lambda}$ does not depend on time and $\vec{\lambda} \cdot \vec{I}\ \langle\langle\omega^2(\vec{q})$ reads

$$\begin{aligned} a_{\vec{q}}(t) \ &= \ A(\vec{q})\,\mathrm{e}^{-i\gamma(\vec{q})t}\cos\left[\omega(\vec{q})t - \delta(\vec{q})\right] \\ &\quad - \frac{1}{\omega(\vec{q})}\int_0^t f^*_{\vec{q}}(\vec{r}\ (s))\,\mathrm{e}^{-i\gamma(\vec{q})(t-s)}\sin\left[\omega(\vec{q}\ )(t-s)\right] ds\,, \end{aligned} \tag{14}$$

where notation $\gamma(\vec{q}) = \vec{\lambda} \cdot \vec{I}\ (\vec{q})$ was introduced. With the use of Eq. (14) the lattice degrees of freedom can be eliminated, then from Eq. (13) the generalized Langevin equation follows

$$M\ddot{\vec{r}} = \vec{F}_0\ (\vec{r}\ ) + \vec{F}_d\ (t) + \vec{F}_s\ (t)\,. \tag{15}$$

On the right hand side of Eq. (15) there are three forces:

$$\vec{F}_0\ (\vec{r}\ ) = -\nabla V(\vec{r}\ )$$

comes from static periodic potential,

$$\vec{F}_d\ (t) = \sum_{\vec{q}} \frac{1}{\omega(\vec{q}\ )} \nabla f_{\vec{q}}(\vec{r}\ ) \int_0^t \mathrm{e}^{-i\gamma(\vec{q})(t-s)} f^*_{\vec{q}}(\vec{r}\ (s))\sin\left[\omega(\vec{q}\ )(t-s)\right] ds \tag{16}$$

represents dumping force, which after integrating by parts is rewritten as follows

$$\begin{aligned} \vec{F}_d\ (t) = &- \sum_{\vec{q}} \frac{1}{\omega^3(\vec{q}\ )} \nabla f_{\vec{q}}(\vec{r}\ ) \int_0^t \mathrm{e}^{-i\gamma(\vec{q})(t-s)} \nabla f^*_{\vec{q}}(\vec{r}\ (s)) \cdot \dot{\vec{r}}\ (s) \\ &\times \left\{ i\gamma(\vec{q})\sin\left[\gamma(\vec{q})(t-s)\right] + \omega(\vec{q}\ )\cos\left[\omega(\vec{q}\ )(t-s)\right] \right\} ds + \vec{F}_d^{\,(1)}\ (t). \end{aligned} \tag{17}$$

In the following we neglect the term $\vec{F}_d^{(1)}$, which stands for correction of the second order in $V(\vec{r})$ to the periodic force $\vec{F}_0(\vec{r})$. The last term on the right hand side of Eq. (15)

$$\vec{F}_s(t) = -\sum_{\vec{q}} A(\vec{q}) \mathrm{e}^{-i\gamma(\vec{q})t} \nabla f_{\vec{q}}(\vec{r}) \cos\left[\omega(\vec{q})t - \delta(\vec{q})\right] \tag{18}$$

is stochastic force. That kind of generalized Langevin equation of motion for impurity has already been derived in Ref. [2].

5. One dimensional motion in cosine potential

To proceed further we will follow Ref. [2] and consider simple case of motion along $y = a/2$, $z = a/2$ line in the cosine potential with $x = a/2$ as the origin of x-coordinate. When temperature gradient is

$$V(\vec{r}) = V_0 \left[1 - \cos\left(\frac{2\pi x}{a}\right)\right]$$

with $x = a/2$ as the origin of x-coordinate. When temperature gradient is along x-axis then energy flux vector and Lagrangian multiplicator $\vec{\lambda}$ are also along x-axis. From Eq. (11) it follows then that single Lagrangian multiplicator

$$\lambda_x(t) \equiv \lambda = \frac{\frac{\sigma}{k_\mathrm{B}} \frac{dT/dx}{T}}{\sum\limits_{\vec{q}} \left(\frac{I(\vec{q})}{\omega(\vec{q})}\right)^2}$$

with Eq. (7) yields for constant $\gamma = -\rho q_x$, where

$$\rho = \frac{18\pi^2 \sigma}{k_\mathrm{B} q_\mathrm{D}^3 T} \frac{dT}{dx}, \tag{19}$$

for longitudinal phonons in Debye model.

Now we are ready to calculate x-components of the forces on the right hand side of Eq. (15). The periodic force becomes simply

$$F_0(x) = -\frac{2\pi V_0}{a} \sin\left(\frac{2\pi x}{a}\right), \tag{20}$$

the dumping force can be expressed as

$$F_d(t) = -\left(\frac{2\pi}{a}\right)^4 \frac{V_0^2}{m} \int_0^t \cos\left(\frac{2\pi}{a} x(t)\right) \cos\left(\frac{2\pi}{a} x(t')\right)$$

$$\times\frac{1}{N}\sum_{\vec{q}}\frac{1}{\omega^2(\vec{q}\,)}\mathrm{e}^{iq_x\Delta(t,t')}\cos\left[\omega(\vec{q}\,)(t-t')\right]\dot{x}\,(t')dt'\,, \quad (21)$$

where

$$\Delta(t,t') = a\left\{E\left[\frac{x(t)}{a}\right] - E\left[\frac{x(t')}{a}\right]\right\} + \rho(t-t')$$

and $E(x)$ stands for integer part of x. And finally the stochastic force, Eq. (18) now reads

$$F_s(t)=\left(\frac{2\pi}{a}\right)^2\frac{V_0}{\sqrt{Nm}}\cos\left(\frac{2\pi x}{a}\right)\sum_{\vec{q}}A(\vec{q})\mathrm{e}^{i[aE(x/a)+\rho t]q_x}\cos\left[\omega(\vec{q}\,)t-\delta(\vec{q})\right]. \quad (22)$$

To perform summation over wave vector $\vec{q}$ we again assume isotropic Debye model for a longitudinal acoustic phonons *i.e.* $\omega(\vec{q}\,) = v_s\left|\vec{q}\right|$, v_s being sound velocity in crystal.

Summation over $\vec{q}$ within Debye sphere of radius $q_{\mathrm{D}} = (6\pi^2)^{1/3}/a$ yields

$$\begin{aligned} F_d(t) \;=\; & \left(\frac{2\pi}{a}\right)^2\frac{aV_0^2}{mv_s^3}\int_0^t\cos\left(\frac{2\pi}{a}x(t)\right)\cos\left(\frac{2\pi}{a}x(t')\right) \\ & \times\left\{\frac{2\rho}{v_s}\frac{\sin(q_{\mathrm{D}}\Delta(t,t'))}{q_{\mathrm{D}}\Delta(t,t')}\sin(q_{\mathrm{D}}v_s(t-t')) + \left[1-\frac{\rho(t-t')}{\Delta(t,t')}\right]S(t,t')\right\} \\ & \times\frac{v_s}{\Delta(t,t')}\,\dot{x}\,(t')dt'\,, \end{aligned} \quad (23)$$

where $S(t,t') = \mathrm{Si}[q_{\mathrm{D}}(\Delta(t,t') - v_s(t-t'))] + \mathrm{Si}[q_{\mathrm{D}}(\Delta(t,t') + v_s(t-t'))]$ and $\mathrm{Si}(t) = \int_0^t\frac{\sin(x)}{x}dx$ stands for integral sine function. Eq. (21) can be rewritten as

$$F_d(t) = -\int_0^t\Phi(t,t')\,\dot{x}\,(t')dt'$$

with the friction kernel $\Phi(t,t')$obeying the fluctuation dissipation theorem

$$\langle\, F_s(t)F_s(t')\rangle \;= k_{\mathrm{B}}T\Phi(t,t')\,. \quad (24)$$

The forces mentioned enter the one dimensional generalized Langevin equation (15)

$$M\,\ddot{x} = F_0(x) + F_d(t) + F_s(t)\,. \quad (25)$$

There is no method to solve stochastic equation (25). However if the thermal energy $k_{\mathrm{B}}T$ of the impurity is smaller than the height of the potential barriers significant simplification is possible. It is because usually the motion of the impurity is confined to a single interstitial. If t and $t^{'}$ are within that time then $\Delta(t,t^{'}) = \rho(t-t^{'})$. Only after a time long enough to accumulate action of the random force the impurity will drive over the barrier into another interstitial. Therefore one can say that $\Delta(t,t^{'}) \ll v_s(t-t^{'})$ (because $\rho \ll v_s$) holds for most of the time , so we can set approximately

$$\frac{1}{\Delta(t,t^{'})}\left\{\mathrm{Si}[q_{\mathrm{D}}(\Delta(t,t^{'})-v_s(t-t^{'}))]+\mathrm{Si}[q_{\mathrm{D}}(\Delta(t,t^{'})+v_s(t-t^{'}))]\right\}$$
$$\underset{\Delta(t,s)\to 0}{\longrightarrow} 2q_{\mathrm{D}}\frac{\sin(q_{\mathrm{D}}v_s(t-t^{'}))}{q_{\mathrm{D}}v_s(t-t^{'})}\,.$$

With the above approximation dissipative force Eq. (23) becomes

$$\begin{aligned} F_d(t) &= -2a\left(\frac{2\pi}{a}\right)^2\frac{V_0^2}{mv_s^3}\int_0^t\cos(\frac{2\pi}{a}x(t))\cos\left(\frac{2\pi}{a}x(t^{'})\right) \\ &\quad\times\frac{\sin(q_{\mathrm{D}}\Delta(t,t^{'}))}{q_{\mathrm{D}}\Delta(t,t^{'})}\frac{\sin(q_{\mathrm{D}}v_s(t-t^{'}))}{(t-t^{'})}\dot{x}(t^{'})dt^{'}\,. \end{aligned} \tag{26}$$

Still stochastic force in the form of Eq. (22) precludes numerical solution of Eq. (25) because of a large number $(2N)$ of random numbers needed and sum over $\vec{q}$ as well. The remedy is to model $F_s(t)$ by the random process

$$\begin{aligned} F_s(t) &= 2V_0\left(\frac{2\pi}{a}\right)\sqrt{\frac{2aq_{\mathrm{D}}k_{\mathrm{B}}T}{mv_s^2}}\cos(\frac{2\pi x}{a})\cos\left[\alpha q_{\mathrm{D}}\left(aE\left(\frac{x}{a}\right)+\rho t\right)-2\pi\gamma\right] \\ &\quad\times\cos\left(\eta q_{\mathrm{D}}v_s t-2\pi\delta\right)\,, \end{aligned} \tag{27}$$

where α, γ, δ and η stand for random numbers of uniform distribution within $[0,1]$ range. The random quantity ηq_{D} mimics variety of phonon wave numbers. Dissipative force, Eq. (26) and stochastic force, Eq. (27) are consistent with the fluctuation dissipation theorem Eq. (24). Damping force as given by Eq. (26) is still, due to finite memory kernel, hardly tractable. Further approximation is, therefore, needed $\frac{\sin(q_{\mathrm{D}}v_s\tau)}{\tau}\cong\pi\delta(\tau)$, which becomes correct for $q_{\mathrm{D}}v_s\to\infty$. As a result we get position dependent and memory-free damping

$$F_d(t) = -\pi a\left(\frac{2\pi}{a}\right)^2\frac{V_0^2}{mv_s^3}\cos^2\left(\frac{2\pi}{a}x(t)\right)\dot{x}\,(t)\,. \tag{28}$$

There is also convenient to express Eq. (25) in terms of dimensionless variables; coordinate $x^{'} = 2\pi x/a$ and time $t^{'} = 2\pi t/T_0$, where $T_0 = a\sqrt{M/V_0}$ is a period of small oscillations of the interstitial atom. With that and after dropping prime sign we can summarize up the results in the form of the following stochastic equation

$$\ddot{x} = -\sin x - R\cos^2 x\,\dot{x} + F\cos x\cos(\alpha(k_{\mathrm{D}}x + \omega_\rho t) - 2\pi\gamma)\cos(\eta\omega_v t - 2\pi\delta)\,, \tag{29}$$

where amplitudes of dissipative and random forces are

$R = 2\pi^2\frac{V_0}{mv_s^2}\sqrt{\frac{V_0}{Mv_s^2}}$ and $F = 2\left(6\pi^2\right)^{1/6}\sqrt{\frac{2k_{\mathrm{B}}T}{mv_s^2}}$ respectively,

and $\omega_\rho = k_{\mathrm{D}}\sqrt{\frac{M\rho^2}{V_0}}$, $\omega_v = k_{\mathrm{D}}\sqrt{\frac{Mv_s^2}{V_0}}$ with $k_{\mathrm{D}} = \left(\frac{3}{4\pi}\right)^{1/3}$.

6. Results and discussion

Because of complex structure of Langevin equation (29) the numerical simulation is the unique tool in the investigation of dynamics of impurity atom. As a method of integration Eq. (29) we assume a standard Runge–Kutta procedure. To deal with stochastic term in the equation we independently choose and keep constant the random numbers at each time step. The time steps are relatively long to give the impurity enough time to gain energy from the thermal bath when a frequency of the stochastic force is close to impurity's own frequency. It is the case when the impurity has a high probability of being resonantly activated over potential barrier.

Once solution $x(t)$ of Eq. (29) is known it can be rewritten as a sum of lattice constant (equal to 2π) times cell number $l(t)$ and relative coordinate $-\pi \le x_r(t) \le \pi$, *i.e.* $x(t) = 2\pi l(t) + x_r(t)$.

When impurity hopes out of the cell l_1 and then thermalizes in another cell l_2 we say that the impurity makes a jump of multiplicity $n = l_2 - l_1$. When the total number N_n of jumps of length n in time t is known the jump rate (*i.e.* number of jumps per $T_0/2\pi$ seconds) to the right r_j^+ and to the left r_j^-

$$r_j^+ = \frac{1}{t}\sum_{n=1}^{\infty} N_n, \qquad r_j^- = \frac{1}{t}\sum_{n=1}^{\infty} N_{-n}\,.$$

Corresponding probabilities of a jump of length of $2\pi n$ are

$$P_{\pm n} = \frac{N_{\pm n}}{\sum\limits_{n=1}^{\infty}(N_n + N_{-n})}\,. \tag{30}$$

Having known probabilities $P_{\pm n}$ we can find dimensionless mean square jump length

$$\langle\, l^2\rangle \;= (2\pi)^2 \sum_{n=1}^{\infty} n^2 (P_{+n} + P_{-n})\,. \tag{31}$$

Diffusion coefficient is D defined as

$$D = \lim_{t\to\infty} \frac{\langle\, l^2\rangle}{2t} \tag{32}$$

which have to be multiplied by $a^2/2\pi T_0$ in order to get D in m^2/s units.

We have followed evolution of $x(t)$ as given by Eq. (29) for as long as 10^9 time units and different temperatures. Three cases of temperature gradient were considered *i.e.* $\mathrm{grad}T = 0, \pm 10000\mathrm{K/m}$. In Fig. 1 we show time

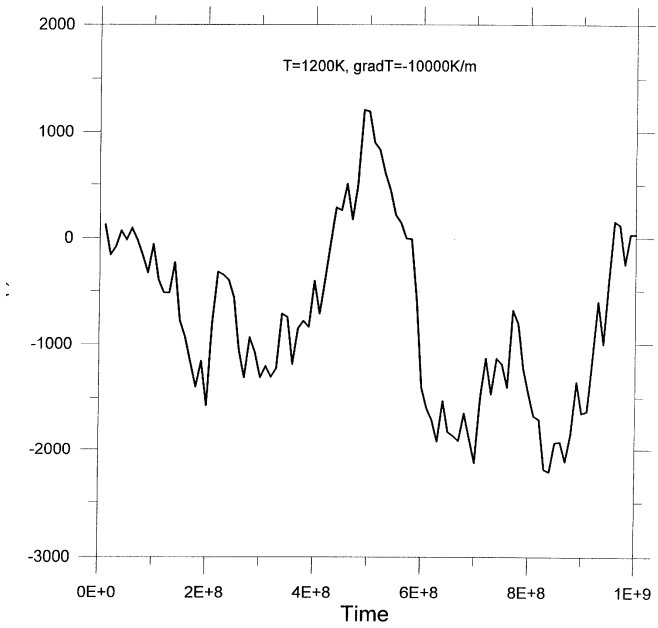

Fig. 1. An example of time evolution of the cell number occupied by the interstitial atom.

dependence of cell number $l(t)$ occupied by interstitial atom following from a particular evolution of the coordinate $x(t)$. We however do not detect a systematic drift in motion of the interstitial atom. Therefore the model does not predict a definite relationship between direction of material flux and the temperature gradient. In Fig. 2 an example of mean square jump length is reported. We notice that it depends linearly on time with high accuracy so

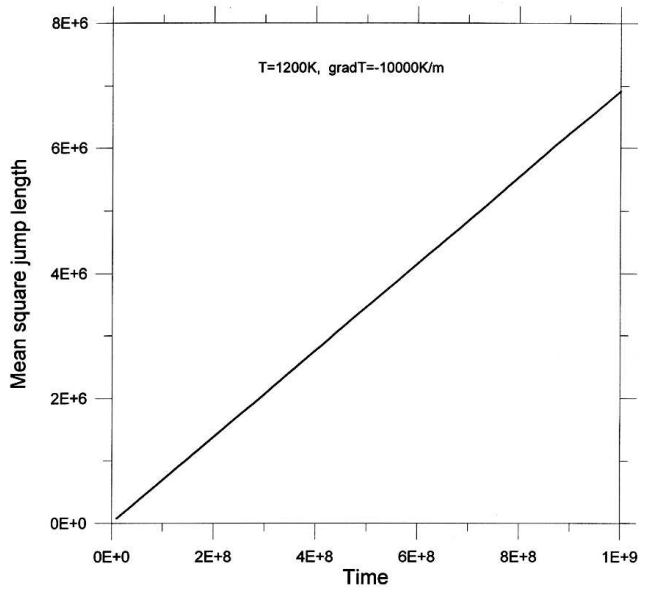

Fig. 2. The time evolution of the mean square jump length

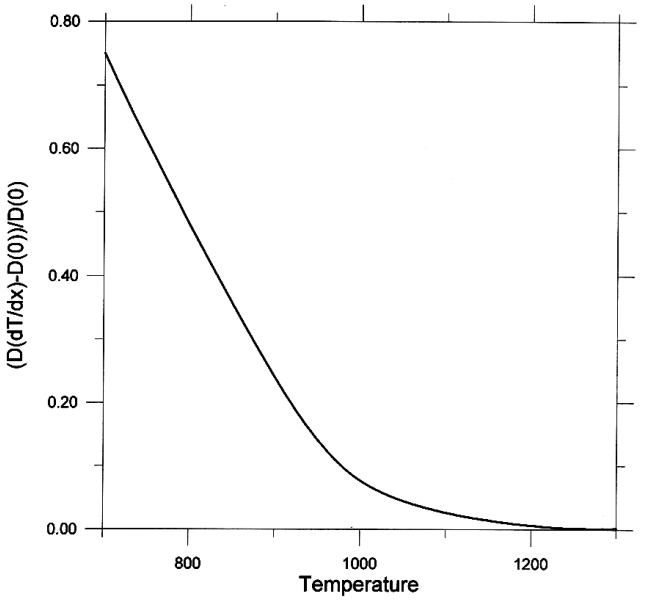

Fig. 3. The temperature dependence of thermodiffusion at grad$T = 10^4$K/m

Eq. (32) defines diffusion coefficient univocally. Its temperature dependence when fitted to Arrhenius law

$$D = D_0 \mathrm{e}^{\frac{E_f}{k_\mathrm{B} T}}$$

yields $D_0 = 0.48\mathrm{x}10^{-2}\mathrm{cm}^2/\mathrm{s}$ and $E_f = 0.77\mathrm{eV}$ in the absence of temperature gradient, which can be compared with $D_0 = 2\mathrm{x}10^{-2}\mathrm{cm}^2/\mathrm{s}$ and $E_f = 0.9\mathrm{eV}$ for C interstitials in Fe [5]. Our calculations show that the diffusion coefficient increases when temperature gradient $\mathrm{d}T/\mathrm{d}x = 10^4\mathrm{K/m}$ is applied. Relative increase $(D(\mathrm{d}T/\mathrm{d}x) - D(0))/D(0)$ depends on temperature and becomes very low above 1200K, as shown in Fig. 3. Our approach however fails to explain nonzero drift (a particle current) due to the temperature gradient. The potential reason which needs examination is neglection of temperature dependence of the lattice constant and sound velocity as well.

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