

DIFFUSION IN PERIODIC POTENTIAL LANGEVIN VERSUS FOKKER–PLANCK EQUATION APPROACH

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Phonon activated diffusion of an interstitial impurity in one dimensional cosine potential is discussed with the use both of Langevin (continuous diffusion model) and Fokker–Planck (jump-diffusion model) equations. Jump rate, jump length and diffusion coefficient as a function of temperature at various barrier heights are calculated. There is some difference between results provided by these two models. Therefore the question arises to what extent these two models of diffusion are equivalent.

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1. Introduction

Thermally activated transition between local minima of the potential energy is a process of great importance in diffusion in solids. The problem has been studied by many investigators to retrieve various features of the diffusion process.

Among others a continuous diffusion model was proposed and intensively studied [1]. The continuous diffusion approach rests on the generalized Langevin equation. From a microscopic point of view impurity diffusion results from complex interplay between impurity atom and the surrounding crystalline lattice. Therefore many attempts have been made to derive the Langevin equation from first principles. The one we mention here is due to Tsekov *et al.* [2].

An independent and widely employed microscopic study of diffusion in solids rests on the Fokker-Planck equation in an external field (also called Klein–Kramers equation). Under assumption of simple periodic potential and uniform dumping Ferrando *et al.*, Ref. [3], calculated the jump rate and jump length distribution.

The diffusion in crystal consists of jumps from well to well under influence of a phonon bath. The aim of the present paper is: First to rederive generalized Langevin equation for interstitial atom in simple cubic lattice. The method we use is very close to that of Tsekov *et al.* [2]. Then we make some approximations concerning dumping as well as stochastic force and solve resulting stochastic equation numerically obtaining jump rate and jump length distribution. Secondly, we derive the Fokker–Planck equation for probability density. We solve it numerically and generalizing results of Ferrando *et al.* results to more realistic potential and damping, once more calculate jump rate and jump length distribution. Results provided by both methods are compared for various values of friction and temperature.

2. Generalized Langevin equation

Our system consists of a single interstitial impurity atom in a simple cubic lattice of lattice constant a . The lattice dynamics is described in the harmonic approximation. Its energy per one mode of vibrations in terms of normal coordinates $a_{\vec{q}}$ is

$$H_l = \frac{1}{2} \sum_{\vec{q}} \dot{a}_{\vec{q}} \dot{a}_{\vec{q}}^* + \frac{1}{2} \sum_{\vec{q}} \omega^2(\vec{q}) a_{\vec{q}} a_{\vec{q}}^*. \quad (1)$$

Impurity energy when expanded with respect to deviation of the lattice atoms from their equilibrium positions \vec{r}_l , takes the form [4]

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

where potential energy of the impurity

$$\begin{aligned} V(\vec{r}) &= \sum_l v(\vec{r} - \vec{r}_l), \\ f_{\vec{q}}(\vec{r}) &= -\frac{1}{\sqrt{Nm}} \sum_l \vec{e} \cdot \nabla v(\vec{r} - \vec{r}_l) e^{i\vec{q} \cdot \vec{r}_l} \end{aligned} \quad (3)$$

and \vec{e} denotes polarization vector of the lattice wave, $m(M)$ is the 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 whole system. They satisfy the following equations of motion (*e.g.* Lagrange equations)

$$\ddot{a}_{\vec{q}} + \omega^2(\vec{q}) a_{\vec{q}} + f_{\vec{q}}^*(\vec{r}) = 0, \quad (4)$$

$$M \ddot{\vec{r}} + \nabla V(\vec{r}) + \sum_{\vec{q}} a_{\vec{q}} \nabla f_{\vec{q}}(\vec{r}) = 0. \quad (5)$$

Under 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 reads

$$a_{\vec{q}}(t) = A(\vec{q}) \cos[\omega(\vec{q})t - \delta(\vec{q})] - \frac{1}{\omega(\vec{q})} \int_0^t f_{\vec{q}}^*(\vec{r}(s)) \sin[\omega(\vec{q})(t - s)] ds.$$

After substitution into Eq. (5) we obtain the generalized Langevin equation

$$M\ddot{\vec{r}} = \vec{F}_0(\vec{r}) + \vec{F}_d(t) + \vec{F}_s(t). \tag{6}$$

On the right hand side of Eq. (6) there are three forces; $\vec{F}_0(\vec{r}) = -\nabla V(\vec{r})$ comes from static periodic potential,

$$\vec{F}_d(t) = \sum_{\vec{q}} \frac{1}{\omega(\vec{q})} \nabla f_{\vec{q}}(\vec{r}) \int_0^t f_{\vec{q}}^*(\vec{r}(s)) \sin[\omega(\vec{q})(t - s)] ds \tag{7}$$

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

$$\vec{F}_d(t) = - \sum_{\vec{q}} \frac{1}{\omega^2(\vec{q})} \nabla f_{\vec{q}}(\vec{r}) \int_0^t \nabla f_{\vec{q}}^*(\vec{r}(s)) \cdot \dot{\vec{r}}(s) \cos[\omega(\vec{q})(t - s)] ds + \vec{F}_d^{(1)}(t). \tag{8}$$

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.(6)

$$\vec{F}_s(t) = - \sum_{\vec{q}} A(\vec{q}) \nabla f_{\vec{q}}(\vec{r}) \cos[\omega(\vec{q})t - \delta(\vec{q})] \tag{9}$$

is the stochastic force. That kind of generalized Langevin equation of motion for impurity has already been derived in Refs [2] and [5]. At each \vec{q} within the first Brillouin zone both $A(\vec{q})$ and $\delta(\vec{q})$ are random numbers, $A(\vec{q})$ having the Maxwell–Boltzmann distribution function and $\delta(\vec{q})$ uniform distribution function within $[0, 2\pi]$ range.

3. One dimensional motion in cosine potential

To proceed further we have to specialize potential energy function. From a general Fourier expansion of a periodic potential

$$V(\vec{r}) = \sum_{\vec{G}} V_{\vec{G}} e^{i\vec{G} \cdot \vec{r}},$$

where \vec{G} is a reciprocal lattice vector, we consider four lowest order terms

$$V(\vec{r}) = C + V_0 \left[\left(\frac{2\pi x}{a} \right) + \cos \left(\frac{2\pi y}{a} \right) + \cos \left(\frac{2\pi z}{a} \right) \right].$$

As sooner or latter we will not avoid reduction of the problem to one dimension, we can do it now as well by assuming that the interstitial atom can visit interstitials along $y = a/2$, $z = a/2$ line only. It is also convenient to take the interstitial at $x = a/2$ as the origin of x - coordinate. In that case conventional form of the potential is

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

and

$$f_{\vec{q}}(x) = \frac{2\pi V_0}{a\sqrt{Nm}} e_x \sin \left(\frac{2\pi x}{a} \right) e^{iaq_x E(x/a)},$$

where $E(x)$ stands for integer part of x . Now we are ready to calculate x -components of the forces mentioned explicitly. The periodic force becomes simply

$$F_0(x) = -\frac{2\pi V_0}{a} \sin \left(\frac{2\pi x}{a} \right). \quad (10)$$

The stochastic force in Eq. (9) now reads

$$F_s(t) = \left(\frac{2\pi}{a} \right)^2 \frac{V_0}{\sqrt{Nm}} \cos \left(\frac{2\pi x}{a} \right) \sum_{\vec{q}} A(\vec{q}) e^{iaq_x E(x/a)} \cos[\omega(\vec{q})t - \delta(\vec{q})]. \quad (11)$$

Finally after substituting $f_{\vec{q}}(x)$ into Eq. (8) the dumping force can be expressed as

$$F_d(t) = -\left(\frac{2\pi}{a} \right)^4 \frac{V_0^2}{m} \int_0^t \cos \left(\frac{2\pi}{a} x(t) \right) \cos \left(\frac{2\pi}{a} x(s) \right) \\ \times \frac{1}{N} \sum_{\vec{q}} \frac{1}{\omega^2(\vec{q})} e^{iaq_x \Delta(t,s)} \cos[\omega(\vec{q})(t-s)] \dot{x}(s) ds,$$

where $\Delta(t, s) = E \left[\frac{x(t)}{a} \right] - E \left[\frac{x(s)}{a} \right]$.

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

$$F_d(t) = \left(\frac{2\pi}{a} \right)^2 \frac{V_0^2}{mv_s^2} \int_0^t \cos \left(\frac{2\pi}{a} x(t) \right) \cos \left(\frac{2\pi}{a} x(s) \right) \frac{1}{\Delta(t,s)} \\ \times \{ \text{Si}[q_D(a\Delta(t,s) - v_s(t-s))] + \text{Si}[q_D(a\Delta(t,s) + v_s(t-s))] \} \dot{x}(s) ds, \quad (12)$$

where $\text{Si}(t) = \int_0^t \frac{\sin(x)}{x} dx$ stands for integral sine function. Eq. (12) can be rewritten in terms of friction kernel $\Phi(t, s)$ as

$$F_d(t) = - \int_0^t \Phi(t, s) \dot{x}(s) ds,$$

obeying the fluctuation dissipation theorem

$$\langle F_s(t) F_s(s) \rangle = k_B T \Phi(t, s). \tag{13}$$

Under above mentioned restrictions it is enough to consider x -component of Eq. (6) only. As a result we obtain one dimensional generalized Langevin equation

$$M \ddot{x} = F_0(x) + F_d(t) + F_s(t). \tag{14}$$

4. Langevin equation

Available methods of solution of stochastic equations fail to treat Eq. (14). However, if the thermal energy $k_B T$ 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 s are within that time then $\Delta(t, s) = 0$. 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 $a\Delta(t, s) \ll v_s(t-s)$ holds for most of the time, so we can set approximately

$$\begin{aligned} & \frac{1}{\Delta(t, s)} \{ \text{Si}[q_D(a\Delta(t, s) - v_s(t-s))] + \text{Si}[q_D(a\Delta(t, s) + v_s(t-s))] \} \\ & \xrightarrow{\Delta(t, s) \rightarrow 0} 2aq_D \frac{\sin(q_D v_s(t-s))}{q_D v_s(t-s)}. \end{aligned}$$

With the above approximation dissipative force from Eq. (12) becomes

$$\begin{aligned} F_d(t) = & -2a \left(\frac{2\pi}{a} \right)^2 \frac{V_0^2}{m v_s^3} \\ & \times \int_0^t \cos \left(\frac{2\pi}{a} x(t) \right) \cos \left(\frac{2\pi}{a} x(s) \right) \frac{\sin(q_D v_s(t-s))}{(t-s)} \dot{x}(s) ds. \tag{15} \end{aligned}$$

Also stochastic force in the form of Eq. (11) precludes numerical solution of Eq. (14) because of a large number ($2N$) of random numbers needed and sum over \vec{q} as well. The remedy is to replace $F_s(t)$ as given by Eq. (11) with

$$F_s(t) = 2V_0 \left(\frac{2\pi}{a} \right) \sqrt{\frac{aq_D k_B T}{mv_s^2}} \cos \left(\frac{2\pi x}{a} \right) \cos(\eta q_D v_s t - 2\pi\delta), \quad (16)$$

where η and δ stand for random numbers of uniform distribution within $[0, 1]$ range. The random quantity $\eta q_D v_s$ mimicks variety of phonon frequencies. Dissipative force, Eq. (15) and stochastic force, Eq. (16) are consistent with the fluctuation dissipation theorem, Eq. (13). Damping force as given by Eq. (15) is still, due to finite memory kernel, hardly tractable. Further approximation is, therefore, needed, it is $\sin(q_D v_s \tau)/\tau \cong \pi\delta(\tau)$, which becomes correct for $q_D v_s \rightarrow \infty$. As a result we get position dependent and memory-free damping

$$F_d(t) = -\pi a \left(\frac{2\pi}{a} \right)^2 \frac{V_0^2}{mv_s^3} \cos^2 \left(\frac{2\pi}{a} x(t) \right) \dot{x}(t). \quad (17)$$

It is now convenient to express Eq. (14) 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 in mind (and after dropping prime sign) we can summarize the results in the form of the following stochastic equation

$$\ddot{x} = -\sin x - R \cos^2 x \dot{x} + F \cos x \cos(\eta\omega t - 2\pi\delta), \quad (18)$$

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

$$F = 2(6\pi^2)^{1/6} \sqrt{\frac{k_B T}{mv_s^2}},$$

respectively and $\omega = (3/4\pi)^{1/3} \sqrt{Mv_s^2/V_0}$.

Let us stress that in Eq. (18) dissipative force is evaluated as if stochastic force were delta-correlated in time which is an approximation. Now the problem of numerical solution of Eq. (18) arises. Several algorithms to integrate stochastic differential equations have been proposed. For a list of references Ref. [7] should be consulted, see also Ref. [8]. In particular Mannella in Ref. [7] developed an one step collocation algorithm to solve system of autonomous equations with stochastic force being white or colored

Gaussian process. He quotes some objection against other methods like predictor-corrector method or Runge–Kutta algorithm. The crucial point in solution procedure is to deal with stochastic term in the equation. The most straightforward method one can imagine is to apply any procedure of solving differential equation with a particular realization of the stochastic process kept unchanged and then averaging over all (at least many) realizations. It is, however, extremely time consuming. A simple and realistic approach is by discretizing time and using any algorithm for advancing solution from t_n to t_{n+1} . At each time step one particular realization of the random process is independently chosen. In general it is believed that the shorter the time step assumed the better approximation for solution is obtained.

We will follow that method with the Runge–Kutta algorithm, however, we choose the time step relatively long. The reason is that resonance between the own frequency of impurity and some frequencies of a stochastic force in Eq. (18) may result in gaining energy very efficiently from the thermal bath. If it happens and lasts for a time not small in comparison with the period $2\pi/\eta\omega$ then the impurity has a high probability of being resonantly activated over barrier.

At any time the solution can be split in two terms $x(t) = 2\pi l(t) + x_c(t)$, $l(t)$ stands for cell number (lattice constant in the present units is 2π) and $-\pi \leq x_c(t) \leq \pi$. We are interested in events when impurity hops out of the cell l_1 and then thermalizes in another cell l_2 . We count the event as jump of multiplicity $n = l_2 - l_1$. Having known number N_n of jumps of length n in time t we obtain the total jump rate (*i.e.* number of jumps per $\sqrt{a^2 M/V_0}/2\pi$ seconds)

$$r_j = \frac{1}{t} \sum_{n=1}^{\infty} (N_n + N_{-n}) \quad (19)$$

and the probability P_n of a jump of length of $2\pi n$ lattice constant ($n = 1, 2, 3, \dots$)

$$P_n = \frac{(N_n + N_{-n})}{\sum_{n=1}^{\infty} (N_n + N_{-n})}. \quad (20)$$

Diffusion coefficient, when expressed in $a\sqrt{V_0/M}/2\pi$ units, is related to jump rate and jump length probability given above through

$$D = (2\pi)^2 r_j \sum_{n=1}^{\infty} n^2 P_n. \quad (21)$$

5. Fokker–Planck equation

A description, under some assumptions, equivalent to Eq. (14) is given in terms of the probability $P(x, v, t)dx dv$ that the dynamical variables $x, v = \dot{x}$ (the same that were used in Eq. (18)) are in the intervals $(x, x + dx)$ and $(v, v + dv)$ respectively. Following van Kampen [6] an equation of evolution for the probability density $P(x, v, t)$ in terms of correlation function of stochastic force reads

$$\frac{\partial P(x, v, t)}{\partial t} = L_0 P(x, v, t) + F^2 \int_0^\infty \cos x \frac{\partial}{\partial v} e^{\tau L_0} \cos x \langle f(t) f(t - \tau) \rangle \frac{\partial}{\partial v} e^{-\tau L_0} d\tau P(x, v, t).$$

The operator

$$L_0 = -v \frac{\partial}{\partial x} + \sin x \frac{\partial}{\partial v} + R \cos^2 x \frac{\partial}{\partial v} v$$

is associated with the deterministic evolution of the system and $f(t) = \cos(\eta\omega t - 2\pi\delta)$ is (because of random numbers η and δ) the stochastic function of time. To proceed further we must, like before, approximate correlation function $\langle f(t) f(t - \tau) \rangle \cong \frac{\pi}{2\omega} \pi\delta(\tau)$. The above equation of evolution reduces then to the well known Fokker–Planck equation

$$\frac{\partial P(x, v, t)}{\partial t} = -v \frac{\partial P(x, v, t)}{\partial x} + \sin x \frac{\partial P(x, v, t)}{\partial v} + R \cos^2 x \frac{\partial}{\partial v} \left(v + \frac{k_B T}{V_0} \frac{\partial}{\partial v} \right) P(x, v, t). \quad (22)$$

The most efficient numerical method to solve the Fokker–Planck equation (22) is the matrix continued fraction method (MCFM), developed by Risken, Ref. [9]. As shown by Ferrando *et al.* in Ref. [3] MCFM allows to calculate the dynamic structure factor

$$S(q', \omega') = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dt e^{-i(\omega' t - q' x)}$$

expressed in terms of dimensionless wavenumber $q' = aq/2\pi$ and frequency $\omega' = \omega \sqrt{Ma^2/k_B T}/2\pi$ (in the following we will omit prime sign). Note that the Fokker–Planck equation in Ref. [3] is written in terms of time we call t_F which is related to ours time t_O in *e.g.* Eq. (18) and to real time t_R through

$$t_F = \sqrt{\frac{k_B T}{V_0}} t_O = 2\pi \sqrt{\frac{k_B T}{Ma^2}} t_R. \quad (23)$$

In the case of sufficiently high barriers $S(q, \omega)$ is related to jump rate r_j (number of jumps per time $\sqrt{Ma^2/k_B T}/2\pi$ seconds) and jump length probability P_n through

$$r_j = 2 \int_0^{1/2} f(q) dq, \quad (24)$$

and

$$P_n = -\frac{4}{r_j} \int_0^{1/2} f(q) \cos(2\pi nq) dq, \quad (25)$$

where

$$f(q) = \sqrt{\frac{2S(q, \omega)}{-\frac{\partial^2 S(q, \omega)}{\partial \omega^2} \Big|_{\omega=0}}}. \quad (26)$$

From equations (21), (24) and (25) it follows that the diffusion coefficient can be expressed as

$$D = (2\pi)^2 \frac{d^2 f(q)}{dq^2} \Big|_{q=0},$$

which in turn, due to Eq. (26), gives the following relation

$$D = \frac{(2\pi)^2 \lim_{\omega \rightarrow 0} \omega^2 \frac{\partial^2 S(q, \omega)}{\partial q^2} \Big|_{q=0}}{\lim_{\omega \rightarrow 0} \omega^2 \sqrt{-\frac{1}{2} S(q, \omega) \frac{\partial^2 S(q, \omega)}{\partial \omega^2} \Big|_{q=0}}} \quad (27)$$

between dynamic structure factor and diffusion coefficient. There is a difference between Eq. (27) and corresponding incorrect relationship (43) from Ref. [10]. For more details one should consult Appendix.

6. Results and discussion

Here we present some results of preliminary numerical calculations. First of all we consider the model of Ferrando *et al.* [3] which corresponds to the following Langevin equation

$$\ddot{x} = -\sin x - \gamma \dot{x} + F \cos x \cos(\eta \omega t - 2\pi \delta), \quad (28)$$

with homogeneous friction. In Fig. 1 the jump rate is plotted as a function of friction parameter γ for medium barrier height ($2V_0 = 6k_B T$ or $g = 1.5$ in terms of Ferrando parameters). The full lines (here and in the following)

represent results which follow from solution of the Fokker–Planck (Kramers) equation. It reproduces exactly the corresponding the line of Ref. [3] for the whole range $0 \leq \gamma \leq 10$ considered there. The jump rate following from solution of the Langevin equation (28) is given by the dashed line. There is a substantial difference between the lines. Jump rate given by the Langevin equation is of one order of magnitude larger for low friction but decreases rapidly when γ crosses about 0.2 in contrast to jump rate given by the Fokker–Planck equation which even for $\gamma = 10$ is quite large of order of 0.02. In Figs 2 and 3 single-jump (double-jump) probability versus friction parameter is shown. It is quite clear that our solution of the Langevin equation predicts much lower probability of jumps longer than single lattice spacing in comparison with solution of the Fokker–Planck equation.

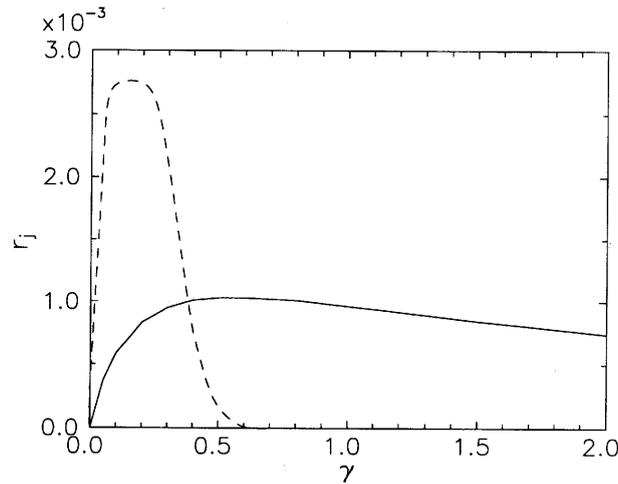


Fig. 1. Results for model of Ferrando *et al.*. The full and dashed lines represent solution of the Fokker–Planck and Langevin equations respectively. The jump rate r_j versus friction γ is plotted.

Now we proceed to our model represented by stochastic equation (18) and the Fokker–Planck equation (22). We will choose the following three dimensionless parameters to describe our model. They are $\tau = k_B T / 2V_0$, *i.e.* a ratio of thermal energy of the particle to height of the potential barrier, $\gamma = 4V_0 / Mv_s^2$, which is a ratio of barrier height to kinetic energy of the impurity if it moved with the velocity of sound, γ is related to the amplitude of friction coefficient R in Eqs (18) and (22). The last one is $\mu = M/m$ — ratio of masses of impurity and lattice atoms, μ will be kept constant equal to 12/56 which roughly corresponds to carbon impurity atom in Fe lattice. We will consider the case of intermediate ($\gamma = 0.49$) barrier height. Let us first

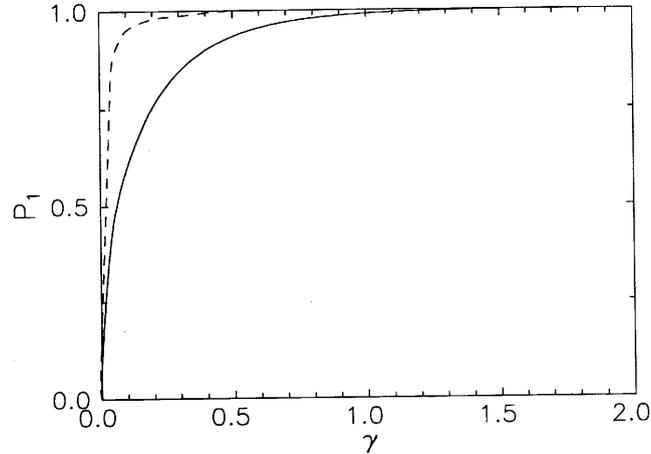


Fig. 2. The same as in Fig. 1, but now single-jump probability is plotted

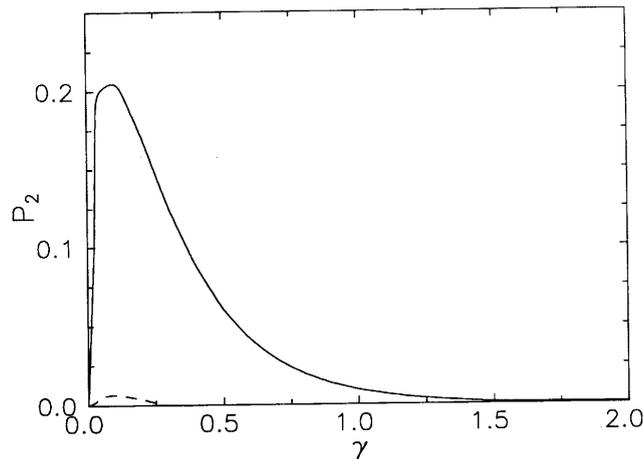


Fig. 3. The same as in Fig. 1, but now double-jump probability is plotted

note that our results that follow from the Fokker–Planck equation do not differ much from corresponding results of Ferrando *et al.* [3] for homogeneous friction when the same set of parameters is assumed.

We have calculated jump rate and jump length probabilities versus dimensionless temperature τ from 0 to 0.3 range which roughly corresponds to $0 \leq T \leq 2000$ K. Like before, full and dashed lines represent Fokker–Planck and Langevin solution respectively. Jump rates do not differ very much as is seen from Fig. 4. It does not hold for jump length probabilities, however. The Fokker–Planck equation predicts rather high probability of

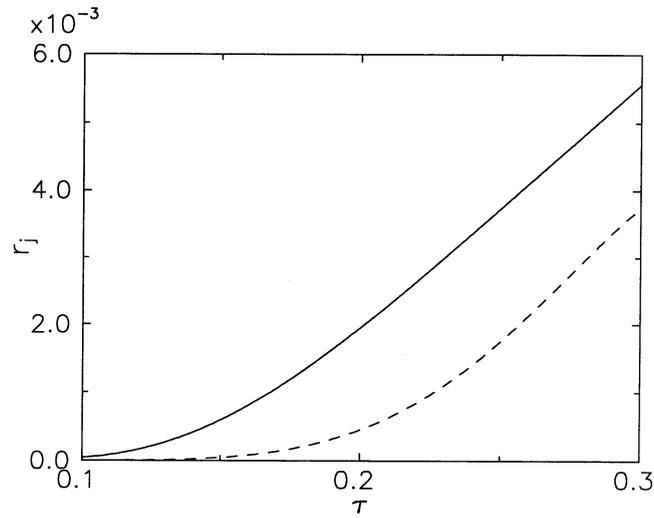


Fig. 4. Results for model given by stochastic equation (18). The full and dashed lines represent solutions of the Fokker-Planck (Eq. (22)) and the Langevin (Eq. (18)) equations respectively. The jump rate r_j versus temperature τ is plotted.

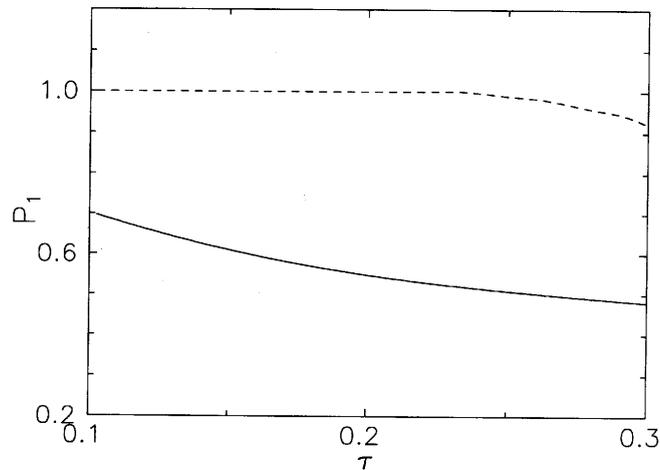


Fig. 5. The same as in Fig. 4, but now single-jump probability is plotted

double jumps Fig. 6, while according to our solution of the Langevin equation double jumps constitute only about 0.01% even at highest temperatures considered. At $\tau = 1.5$ we have $P_1 + P_2 + P_3 \simeq 0.9$, so according to the Fokker-Planck equation about 10% of jumps is longer than three lattice spacings. A final remark is concerned with diffusion coefficient D . Within

the Fokker–Planck equation approach we could, in principle, use an exact relation, Eq. (27), between D and dynamic structure factor $S(q, \omega)$. However due to numerical problems with calculation of derivatives of $S(q, \omega)$ we used Eq. (21) instead. Bearing preceding results in mind one can guess that the Fokker–Planck equation predicts much larger diffusion coefficient than the Langevin equation. Fig. 7 shows that it is the case, in particular at $\tau \simeq 0.3$ the former is of one order of magnitude greater than the latter one.

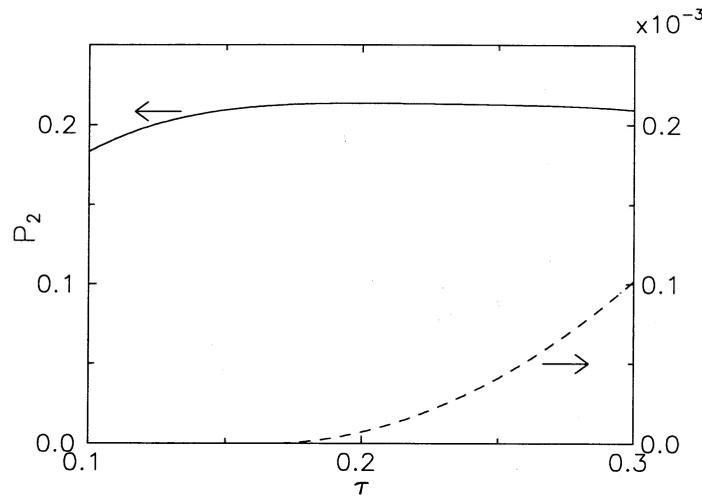


Fig. 6. The same as in Fig. 4, but now double-jump probability is plotted

It is not clear to the author what is the reason of differences encountered. We can only argue that the separation of the intracell from intercell dynamics is an unavoidable approximation of the jump-diffusion theory. It can be justified only in the case of sufficiently high potential barriers. On the contrary the continuous diffusion approach which rests on the Langevin equation, Eq. (18), is not affected by need of such a separation. Therefore results provided by it seem more reliable. To get some numbers concerning diffusion coefficient let us note that in the case of C atom in Fe lattice $\gamma = 0.49$ corresponds to barrier height $2V_0 = 0.76$ eV, then, dimensionless temperature, for example $\tau = 0.14$ is equivalent $T = 1200$ K. At that temperature the diffusion coefficient, as given by solution of the Langevin equation $D \approx 6 \times 10^{-11} \text{m}^2/\text{s}$, can be compared with experimental value [11] of $3 \times 10^{-11} \text{m}^2/\text{s}$.

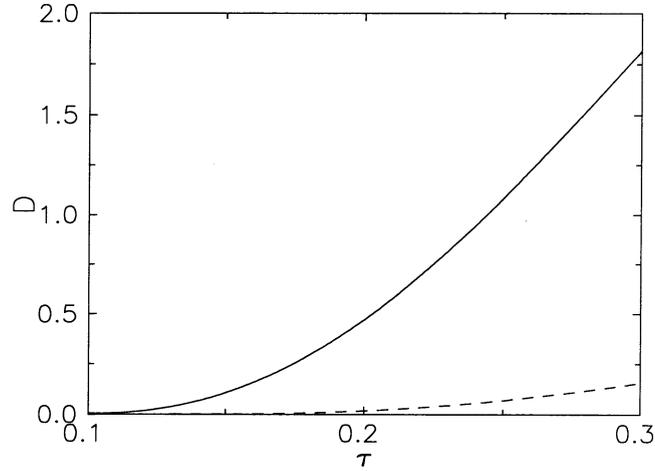


Fig. 7. The same as in Fig. 4, but now results for diffusion coefficient are compared.

Appendix A

In Ref. [10] it was shown that dynamic structure factor can be expressed through matrix Green function $G(q, z)$ of the Fokker–Planck equation

$$S(q, \omega) = 2\text{Re} \sum_{p, l=-\infty}^{\infty} M_p G_{pl}(q, i\omega) M_l, \quad (\text{A.1})$$

which is given by matrix continued fraction

$$G(q, z) = \left(zI + B^+ (zI + 2B^+ [zI + 2\Gamma + 3B^+ \{zI + 3\Gamma + \dots\}^{-1} B^-]^{-1} B^-)^{-1} B^- \right)^{-1} \quad (\text{A.2})$$

The matrices Γ and B^\pm , in the case of friction $R \cos^2 x$ and force $-V_0 \sin x$ are given by

$$\Gamma_{l,p} = \frac{1}{2} R \sqrt{\bar{V}} [\delta_{l,p} + \frac{1}{2} (\delta_{l,p-2} + \delta_{l,p+2})], \quad (\text{A.3})$$

$$B_{l,p}^\pm = (l+q) \delta_{l,p} \mp \frac{\bar{V}}{4} (\delta_{l,p-1} - \delta_{l,p+1}), \quad (\text{A.4})$$

with $\bar{V} = V_0/k_B T$, and

$$M_p = \frac{I_p(\bar{V}/2)}{\sqrt{\pi I_0(\bar{V})}}. \quad (\text{A.5})$$

Here $I_p(x)$ stands for modified Bessel function. From Eq. (A1) one can derive a set of matrix recursion relations

$$\begin{aligned} K_n &= [(n-1)\Gamma + nB^+K_{n+1}B^-]^{-1}, \\ L_n &= K_n[I - nB^+L_{n+1}B^-]K_n, \\ P_n &= -2L_nK_n^{-1}L_n - nK_nB^+P_{n+1}B^-K_n, \end{aligned} \quad (\text{A.6})$$

with starting values $K_{N+1} = \Gamma^{-1}/N$ and $L_{n+1} = P_{n+1} = O(1/N^2)$ for $N \rightarrow \infty$. Of course size of matrix and number of iterations N in numerical calculations must be finite. Dynamic structure factor and its second derivative at $\omega = 0$ depend on matrix Green function via Eq. (A1) which in turn is related to matrices K_1 and P_1 in the following way $G(q, 0) = K_1(q)$ and $\partial^2 G(q, \omega)/\partial \omega^2|_{\omega=0} = P_1(q)$.

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