

Diffusion in symmetric metastable periodic potential: the Fokker-Planck equation

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We investigate the dynamic properties of Brownian particle subject to a metastable periodic potential. By employing the Fokker-Planck equation, which we solve numerically by the matrix continued fraction method, we have calculated the full width at half-maximum (FWHM) $\lambda(q)$ of the quasi-elastic peak of the dynamic structure factor, for large range of values of the wave-vectors q and for different temperature. Our results show that at low temperature and for different values of the ratio of the barriers $\Delta = V_2/V_1$ the diffusion process can be described by a simple jump motion with the jump length equal to $a/2$ for $\Delta=1$ and equal a for $0 \leq \Delta \leq 1/2$. While for the other cases, the diffusion process consists of a superposition of both of them. At high temperature, the Fokker-Planck equation describes a diffusion process, which has some characteristic of jump and liquid-like regimes.

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1- INTRODUCTION:

Diffusion of particles in a periodic potential is a very interesting problem from technological, experimental and theoretical point of view. It has been extensively studied in connection with so-called superionic conductors. These materials form a particular class of ionic solids characterised by ionic conductivities of an order of magnitude as usually found for molten salts [1,2]. This phenomenon of fast ionic transport in solids has been observed in a variety of materials with different kinds of structure. Well-known examples are the AgI -type materials, e.g., the Ag^+ conductors AgI , Ag_2S , Ag_3SI or the Cu^+ conductors CuI , $CuBr$, ...etc., which have been studied extensively in the past. Another interesting group of substances includes anionic conductors like CaF_2 or PbF_2 . Examples, where the conduction process is confined to a lower dimensionality are the β -alumina ($d=2$) or k -hollandite ($d=1$). The superionic conductors are characterised structurally in terms of the mobile and immobile sublattices. The immobile ions form a complex structure through which the mobile ions move, this structure is not rigid since these ions execute large vibrations about their lattices sites; nonetheless, they do not leave those sites and so do not contribute to the ionic conductivity, the positions of the immobile ions define characteristic voids which are populated to varying degrees by the mobile ions and through which these ions move. In this paper the diffusion particle is studied in the framework of the continuous Brownian model and some kind of transport equation, in general a Fokker-Planck equation (FPE) in two-vector variables (position and velocity of the diffusing particle) must be solved. The stochastic theory based on the FPE is able to describe different diffusion mechanisms. Quasi-continuous diffusion and hopping mechanisms (by single or multiple jumps) correspond to different ranges of the friction and of the potential barrier or, more physically to different ratios between some typical time scales. Long- and short- time dynamics can be quantitatively investigated by

calculating the diffusion coefficient and the relevant correlation functions respectively. Thus, the most complete statistical information about the diffusing particles is contained in the dynamic structure factor $S(q, \omega)$, which is proportional to the quasi-elastic scattering intensity both in neutron and in atom scattering experiments. The full width at half maximum (fwhm) $\lambda(q)$ of the quasi-elastic peak of $S(q, \omega)$, at small momentum transfer q , is proportional to the diffusion constant, while its behaviour at larger q depends on the diffusion mechanism.

Our aim is to employ the Fokker-Planck equation in order to calculate the dynamic structure factor and its FWHM up to large q values, extending in several Brillouin zones. The Fokker-Planck equation cannot be analytically solved in every regime, i.e. at every friction and at every value of the potential barrier. In this work, we use the matrix continued fraction method (MCFM) which seems to be very effective for treating the FPE for two variables without detailed balance [3]. In several papers, Ferrando et al [4,5] have applied this method, in order to study the dynamic of a classical Brownian particle in simple potential. The MCFM yields accurate results for the experimentally relevant dynamic correlation functions and also for the non-equilibrium response. In the periodic case, the MCFM introduced by Risken et al [6] is based on the expansion of the solution into a basis set of plane wave for the position variable and of hermit functions for the velocity variable which form together a complete system and have the correct natural boundary conditions in velocity space $-\infty < v < +\infty$.

In the following we sketch the essential features of the Brownian theory, which can give a complete treatment of the diffusive process of particle and discuss the influence of different shapes of the external potential on the diffusion process.

II- MODEL AND METHOD OF CALCULATION

Both from a theoretical and an experimental point of view, the quantity carrying the most complete information on the correlation effects between the diffusing ions in space and time is the coherent dynamic structure factor $S(q, \omega)$ defined (in 1D notation) as the time Fourier transform of the characteristic function $F(q, t)$:

$$S(q, \omega) = \frac{1}{2\pi} \int e^{i\omega t} F(q, t) dt \quad (1)$$

with

$$F(q, t) = \langle \exp -iq(x(t) - x(0)) \rangle \quad (2)$$

where the angle brackets refer to the thermal average. $x(t)$ and $x(0)$ refer to the same particle. The derivatives of $F(q, t)$ with respects to q , evaluated in $q=0$, give the moments of the displacements distribution (even moments only differing from zero) and all the self-correlation functions can be deduced from $S(q, \omega)$, via the Green-Kubo relation [7], by doing suitable limits. Let us illustrate how the average in equation (2) can be calculated. The starting point is the Fokker-Planck equation (FPE), which describes the diffusive motion of a Brownian particle

$$\frac{\partial W(x, v, t)}{\partial t} = L_{FP} W(x, v, t) \quad (3)$$

with the Fokker-Planck operator L_{FP}

$$L_{FP} = -v \frac{\partial}{\partial x} - \frac{1}{m} \frac{\partial V(x)}{\partial x} \frac{\partial}{\partial v} + \gamma \frac{\partial}{\partial v} \left(v + \frac{k_B T}{m} \frac{\partial}{\partial v} \right)$$

where m and x represent respectively the mass and the position of the particle. γ is the friction coefficient, T is the temperature of the thermal bath. $W(x, v, t)$ is the transition probability density in the phase space (x, v) of all mobile particles. This function determines the probability that a particle initially prepared at position x'

$$F(q, t) = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dv \int_{-\infty}^{+\infty} dx' \int_{-\infty}^{+\infty} dv' e^{-iq(x-x')} P(x, v, t / x', v', 0) W_{st}(x', v') \quad (5)$$

W_{st} is the stationary probability given by the Maxwell-Boltzman distribution and normalized to one particle per cell. The conditional probability $P(x, v, t / x', v', 0)$ (i.e. The probability of having the particle in x and v at time t if it was x' and v' at time 0) is the Green function of the FPE and is then obtained by solving Eq(3) with initial δ -condition in the variable x and v .

The Fokker-Planck equation cannot be solved analytically in every regime of frictions and potential barriers, but it can be solved numerically without

and velocity v' will be found at x and v after a time t . $V(x)$ is the metastable periodic potential and we choose it in the following form:

$$V(x) = A \cos(q_0 x) + B \cos(2q_0 x) \quad (4)$$

where $q_0 = 2\pi/a$ denotes the reciprocal lattice vector and a is the lattice constant. The metastable potential depends on two parameters, A and B , which determine the amplitudes of both two potential barriers (V_1 and V_2). Our investigations were performed using the potential (4) for various values of Δ , we vary only the second barrier V_2 . the first one is chosen to be constant and equal to 0.1eV (see fig.1)

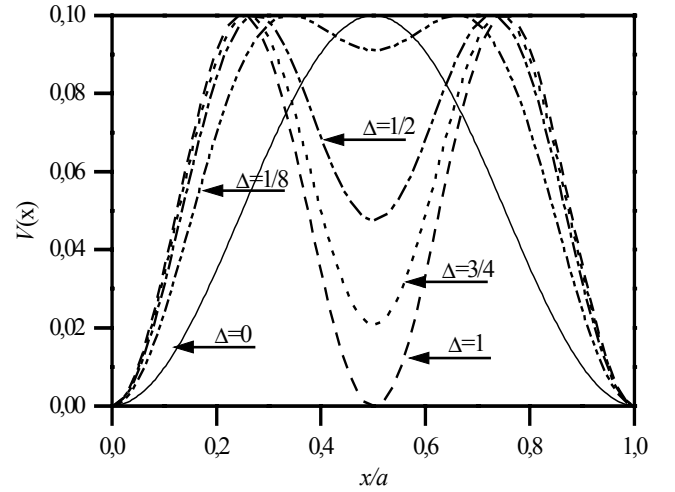


Fig. 1 : Structure of the symmetric metastable potential $V(x)$ for different values of the ratio of the two potential barriers Δ ($\Delta = V_2/V_1$).

If the Fokker-Planck equation is solved, the characteristic function (2) is found as:

restriction of parameters of system by using the MCFM. This numerical method developed by Risken [6], has been already presented elsewhere with more details [8] ; so here only the final result for $S(q, \omega)$ is recalled.

The result for the dynamic structure factor is

$$S(q, \omega) = N \text{Re} \left\{ \sum_{p, q=-\infty}^{\infty} \tilde{G}_{0,0}^{p,q}(k, i\omega) M_{p-1} M_{q-1}^* \right\} \quad (6)$$

where M_r is the modified Bessel function depending on the potential

$$M_r = \frac{1}{2\pi} \int_{-\pi}^{\pi} \exp(-V(x) + irx) dx$$

$q=2\pi/a(k+l)$ with $-1/2 < k < 1/2$; (k is restricted to the first Brillouin zone), l integer and N is a normalization factors.

$\tilde{G}_{0,0}^{p,q}(k, i\omega)$ are the Laplace transforms of the matrix elements $G_{0,0}^{p,q}(k, t)$, and can be expressed as a continuous fraction of some matrix depending on the potential and the friction.

(7)

$$\tilde{G}(k, i\omega) = \frac{I}{i \frac{a}{2\pi} \sqrt{\frac{m}{k_B T}} \omega I + D - \frac{a}{2\pi} \sqrt{\frac{m}{k_B T}} (i\omega + \gamma) I + 2D - \frac{a}{2\pi} \sqrt{\frac{m}{k_B T}} (i\omega + 2\gamma) + \dots \tilde{D}}$$

where I is the identity matrix elements of D and \tilde{D} are given by

$$\begin{aligned} D^{p,q}(k) &= (p+k)\delta^{p,q} + \frac{A}{4k_B T} (\delta^{p,q-1} - \delta^{p,q+1}) \\ &\quad + \frac{B}{2k_B T} (\delta^{p,q-2} - \delta^{p,q+2}) \\ \tilde{D}^{p,q}(k) &= (p+k)\delta^{p,q} - \frac{A}{4k_B T} (\delta^{p,q-1} - \delta^{p,q+1}) \\ &\quad - \frac{B}{2k_B T} (\delta^{p,q-2} - \delta^{p,q+2}) \end{aligned}$$

In writing Eq. (7) the same notations of Ref. [8] have been used.

The coherent dynamic structure factor $S(q, \omega)$ can now be numerically solved without too much effort for a wide range of the parameters. The matrix continued fraction must be truncated at a certain number of iterations and matrices of finite size must be used.

III- HALF-WIDTH OF THE QUASIELASTIC LINE

We present here some results of the half-width $\lambda(q)$ as a function of the scattering wave-vector q , for different values of Δ . Thus, for $0 \leq \Delta \leq 1/2$ and at low temperature ($k_B T/V_l \ll 1$), $\lambda(q)$ approaches the shape of cosine as can be seen in fig.2. The function $\lambda(q)$ is a periodic function of q . For reciprocal lattice vectors ($q/q_0 = 1, 2, 3, \dots$) the half-width vanishes and reaches its maxima at $q/q_0 = 1, 2, 3 \dots$. We rejoin the calculations performed by Ferrando et al [9] for the cosine potential (simple potential). The mechanism is described by jump process and the jump length is close to the lattice constant a . We make clear that all our calculation are done for high friction limit $\Gamma = 2\pi\gamma/\omega_0 \gg 1$ where $\omega_0 = (2\pi/a)(V_l/2m)^{1/2}$ is the characteristic frequency

for vibration at the bottom of the well when $\Delta = 0$). This behaviour can be derived exactly from the hopping model where the only jumps considered are those connecting nearest-neighbour sites and the half-width takes the following form:

$$\lambda(q) = \tau^{-1} (1 - \cos(qa))$$

τ is the residence time of the diffusing particle potential and a is the lattice constant.

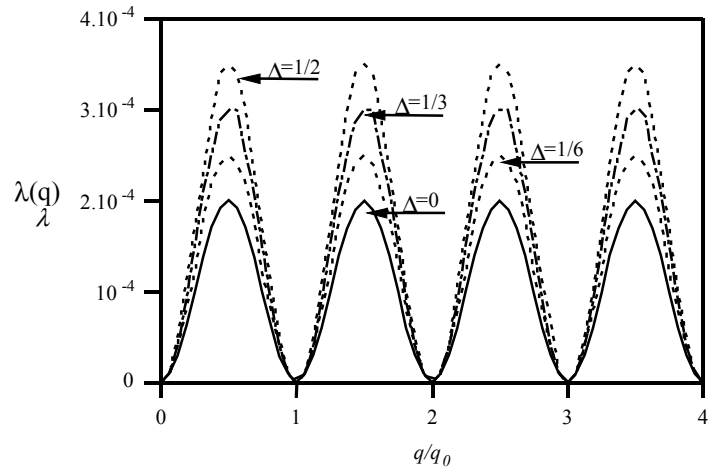


Fig. 2 : The q -dependence of $\lambda(q)$ associated with different low values of Δ . The parameters for this figure are $V_l = 0.1eV$, $k_B T = V_l/6$, $\Gamma \gg 1$

Let us analyse now the behaviour of $\lambda(q)$ for large values of Δ (fig.3). For $3/4 \leq \Delta \leq 9/10$ and at low temperature, we notice that the $\lambda(q)$ presents a complicated structure, which different from a cosine-like. For this range of Δ , the diffusion mechanism results from a combination of two types of jumps differing by the jump lengths (a and $a/2$). By increasing still more the value of Δ , we not clearly that the width of minima at q_0 and $3q_0$ becomes narrower, this implies that the jump of length a is practically forbidden. The diffusion mechanism is essentially dominated by jump of length $a/2$, inside and between

the unit cell. While for $\Delta = 1$ ($V_1 = V_2$), the potential becomes simple with one barrier and with a period $a/2$. the half width $\lambda(q)$ coincides with the cosine shape. The diffusion mechanism, in this case, is entirely represented by instantaneous jump from an equilibrium site to another one with jump length $a/2$. Qualitatively, its behaviour with q remains the same as represented for $\Delta = 0$ except for the jump length which becomes equal to $a/2$.

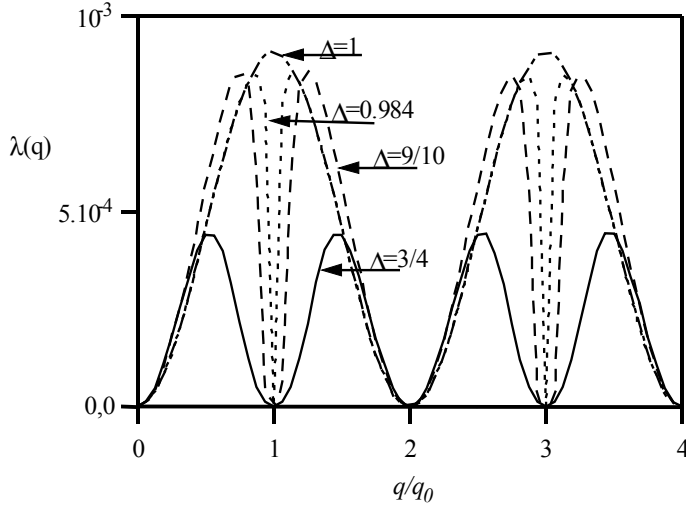


Fig. 3 : The q -dependence of the half-width of the quasi-elastic line $\lambda(q)$ of dynamic structure factor $S(q, \omega)$ associated with different shapes of the metastable potential. Different diffusion process are displayed. The parameters for this figure are $V_1 = 0.1 \text{ eV}$, $k_B T = V_1/6$, $\Gamma \gg 1$

At high temperature ($T = V_1/2$), we observe that the behaviour of $\lambda(q)$ differs strongly from that presented for low temperature. In effect, for $0 \leq \Delta \leq 1$, the shape of $\lambda(q)$ is no more periodic reflecting that the migration process is far from simply jump diffusion; but consists of a superposition of both liquid-like and hopping motion Fig(4).

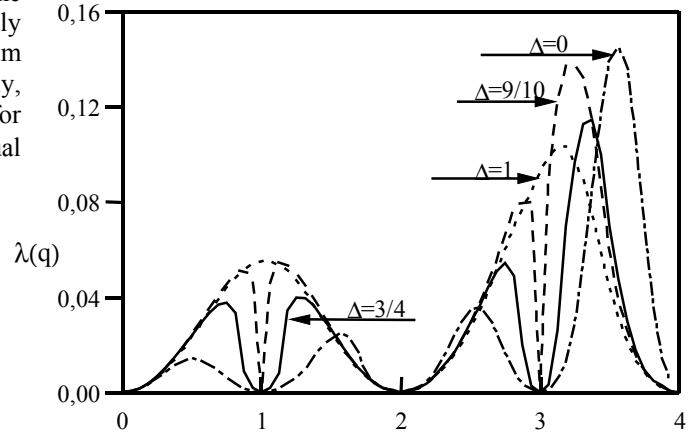


Fig. 4 : The same as in Fig.3, but here for a higher temperature $k_B T = V_0/2$.

IV. CONCLUSION

This paper describes Fokker-Planck dynamics of a Brownian particle subject to a metastable periodic potential. The Fokker-Planck equation is solved numerically by using the matrix continued fraction method. The character of the diffusion process is quite clearly revealed through the q dependence of width of the quasi-elastic peak of $S(q, \omega)$. Taking into account the entire behaviour of $\lambda(q)$, we conclude that the most probable diffusion process in the real system such as superionic conductors consists of three different diffusion processes. In fact, for $0 \leq \Delta \leq 1/2$, the system can be described by jump diffusion process with jump length close to lattice constant. For $3/4 \leq \Delta \leq 1/2$, the diffusion process can be described by two types of jumps (jump of length a and jump of length $a/2$), while the diffusion for $\Delta=1$ is also described by the hopping motion like $0 \leq \Delta \leq 1/2$ except that for these case the jump length is equal $a/2$.

A direct comparison between the results of the present studies and those presented in Ref.[8] is in course of preparation [10].

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