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Fokker-Planck dynamics in a bistable periodic potential

A. Asaklil, M. Mazroui, and Y. Boughaleb[a]

Laboratoire de Physique de la Matière Condensée, Faculté des Sciences Ben M'sik, Casablanca, BP 7955, Morocco

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Abstract. Dynamic properties of Brownian particles immersed in a periodic potential with two barriers V_1 and V_2 (symmetric bistable potential) are studied by using the Fokker-Planck equation which we solve numerically by the matrix continued fraction method. This study will therefore serve to demonstrate the influence of this form of potential, which is of great interest for superionic conductors and for many other solid systems, on the diffusion process. Thus, we have calculated the full width at half maximum (FWHM) $\lambda(q)$ of the quasi-elastic line of the dynamic structure factor, for a large range of values of the wave-vectors q. Our results show clearly that, by varying the ratio of the barriers $\Delta = V_2/V_1$ strictly between 0 and 1, the Fokker-Planck equation describes a diffusive process which has some characteristic of jump and liquid-like regimes. While in the limit cases, *i.e.* when Δ tends to 0 or 1, the diffusion process can be described only by a simple jump motion. However, the jump-lengths corresponding to each limit case are not equal. In general the change of the ratio is found to have a significant effect on the character of the diffusive motion. We have also performed Fokker-Planck dynamics calculations of the diffusion coefficient in a bistable potential. We have found a good agreement between numerical calculations and analytical approximation results obtained in the high friction limit.

PACS. 05.40.-a Fluctuation phenomena, random processes, noise, and Brownian motion – 82.20.Fd Stochastic and trajectory models, other theories and models – 05.60.-k Transport processes

1 Introduction

The Brownian motion of particles in a periodic potential is an important problem in several fields of physics, and has been the subject of intense investigations recently [1,2]. This model is of more general interest also, since dissipation and periodic potentials are frequently encountered phenomena in condensed-matter physics. In the special case of a cosine periodic potential, which is certainly an oversimplification, its one particle version has been studied in detail in connection with superionic conductors [3–6]. It applies also to weakly pinned charge-density-wave condensates [7], to submonolayer films adsorbed on crystalline substrate [8] and to Josephson junctions [9]. The common feature of these systems is that they consist of species of highly mobile particles, with diffusion coefficients comparable to those found in liquids. All the ions of one sublattice are in this highly mobile state. There is another species of ions which cannot diffuse. They form a framework which is usually called the rigid sublattice. The activation energy required for the mobile ions to diffuse is far lower than that found in ordinary ionic solids, *e.g.*, in α-AgI at 300 °C the diffusion coefficient for Ag^+ ions is close to 2×10^{-5} cm^2/s. The one of the I^- ions is negligible. These materials show high ionic conductivity and have given impetus to a new technology, termed Solid State Ionics, which contains devices based on the motion of ions in solids (fuel cells, solid state batteries, gas sensors, timers, *etc.*). In a number of these materials the conduction process is confined to lower dimensionality; examples include β-alumina ($d = 2$), potassium hollandite ($d = 1$), *etc.*

The main goal of the work reported here is to study dynamic properties of a Brownian particle in connection with superionic conductors in a symmetric bistable potential. The bistable potential may represent a large class of potentials of interest in physical problems. The dynamic properties can be investigated by calculating the dynamic structure factor $S(q, \omega)$, which contains the most complete information about the diffusing particle and reflects the collective motion of the mobile particles on a microscopic scale. This quantity is proportional to the quasi-elastic scattering intensity both in neutron [10,11] and in atom scattering experiments [12]. Its full width at half maximum $\lambda(q)$ of its quasi-elastic peak contains valuable information about the interaction of the mobile ions with the rigid framework and with each other. At small values of q, it is proportional to the diffusion constant, and larger q values turn out to give information on the diffusion process itself. We have also calculated the diffusion coefficient of Brownian particle from the FWHM $\lambda(q)$. This result will be compared to the one of an analytical expression. For this purpose, we start from the Fokker-Planck equation (FPE) which describes quite well the many-particle

[a] e-mail: cui@techno.net.ma

diffusion in a periodic medium, for all friction and barrier regimes. Generally, it is difficult to obtain solutions of this equation especially if no separation of variables is possible or if the number of variables is large. For that the FPE will be solved by the matrix-continued-fraction method [13] which seems to be a powerful tool to treat this problem. In this way, the Green function of the FPE and $S(q,\omega)$ can be obtained.

The present paper is organized as follows. In Section 2 we summarize the most relevant parts of the theory of Brownian particles, which can give a complete treatment of the diffusive process. The matrix continued fraction method is outlined for our potential $V(x)$ which we describe in detail in this work. Section 3 contains the results and discussions; in Subsection 3.1 we discuss the influence of the different shapes of potential on the diffusion process. Whereas Subsection 3.2 is concerned with the diffusion coefficient calculated analytically and numerically. We end by making some general remarks and by summarizing the main conclusions in Section 4.

2 Fokker-Planck equation

We assume that the ions of the rigid framework are fixed at their equilibrium positions and they generate a periodic potential in which the mobile species are assumed to perform Brownian motion. In a real system, the ions of the framework vibrate around their equilibrium positions, giving rise to two phenomenological forces: the dissipative and the random force, related to the friction via the fluctuation-dissipation theorem [14]. The dynamic of the particles is then governed by the Langevin equation [6]. For convenience, it is useful to work with the transition probability density $w(x,v,t/x',v')$ in the phase space (x,v) of all mobile particles. This function determines the probability that a particle initially prepared at position x' and velocity v' will be found at x and v after a time t, and obeys partial differential equation which is the Fokker-Planck equation [15].

$$\frac{\partial w\left(x,v,t/x',v'\right)}{\partial t} = L_{\mathrm{FP}} w\left(x,v,t/x',v'\right) \qquad (1)$$

with the Fokker Planck operator L_{FP}

$$L_{\mathrm{FP}} = -v\frac{\partial}{\partial x} + \frac{1}{m}\frac{\partial V\left(x\right)}{\partial x}\frac{\partial}{\partial v} + \gamma\frac{\partial}{\partial v}\left(v + \frac{k_{\mathrm{B}}T}{m}\frac{\partial}{\partial v}\right) \qquad (2)$$

where m, x and v represent respectively the mass, the position and the velocity of the particle. γ is the friction coefficient, k_{B} is the Boltzmann's constant and T is the temperature of the surrounding heat bath. The shape of the potential $V(x)$ which is of particular interest in this work, will be specified in the following subsection.

The operator L_{FP} describes the time evolution of the system. It is non-hermitian and therefore the eigenvalues are in general complex, containing oscillation and relaxation. The first two terms of the operator are identical with the Liouvillian of classical mechanics. The others are dissipative and linear in γ. The Fokker-Planck equation describes the Brownian motion in a periodic potential and is just an equation of motion for the distribution function of fluctuating macroscopic variables. For a deterministic treatment we neglect the fluctuations of the macroscopic variables. In this case (*i.e.* the free field case) the solution of the stationary solution of equation (1) (which is periodic in x) is the Boltzmann distribution.

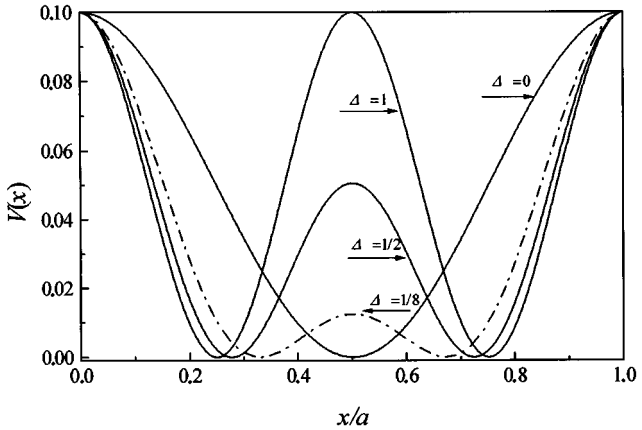

Fig. 1. Structure of the symmetric bistable potential $V(x)$ for different values of the ratio of the two potential barriers $\Delta(\Delta = V_2/V_1)$. The shape of this potential is similar to the one for interacting Brownian particles.

2.1 Bistable potential model

Let us consider a form of the potential $V(x)$ by taking the first two terms of the Fourier expansion of the periodic potential, we can then write

$$V(x) = A_1\cos(q_{\mathrm{o}}x) + A_2\cos(2q_{\mathrm{o}}x) \qquad (3)$$

where $q_{\mathrm{o}} = 2\pi/a$ denotes the reciprocal lattice vector and a is the lattice constant. The bistable potential depends on two parameters, A_1 and A_2, which determine the amplitudes of both potential barriers (V_1 and V_2). Our investigations were performed using the potential (3) for various values of Δ which we define as the ratio of the two different barriers of potential $V(x)$: $\Delta = V_2/V_1$. In order to take different values of Δ, we vary only the second barrier V_2. The first one is chosen to be constant and equal to 0.1 eV (see Fig. 1). The bistable potential may represent a large class of potentials of interest in physical problems. In a previous paper [16], we have shown that for strongly interacting Brownian particles in two-dimensional periodic potential, the effective potential computed along the direction where the system is incommensurate presents the same shape as the one chosen in this work (Fig. 1). Note that the effective potential experienced by an ion of the mobile species is essentially the sum of the periodic static framework potential due to interactions with the ions of the rigid sublattice and the potential of interactions with other mobile ions. Indeed, in the low temperature regime, the effective potential exhibits a complicated structure characterized by the appearance of new equilibrium sites. Most ions are displaced away from the lattice sites. Such structure was

observed by means of X-ray diffraction along the tunnel axis deduced by Weber and Schultz [17].

The concept of the effective potential has been deduced experimentally for a number of materials and previous theoretical studies have discussed their role in controlling the diffusion process. It greatly simplifies the many-body problem so that a broader range of superionic conductors may be studied and ionic transport more fully understood on the basis of this simple concept. In fact, the barrier height of the effective potential can be very useful in interpreting the transport properties of the system. In particular, in the high damping limit, it can be interpreted as an activation energy. Also, the experiment performed on $RbAg_4I_5$ has shown effectively that the potential felt by a silver ion located at a tetrahedral site has two different barriers [18]. For all these reasons, we choose the form of potential presented in Figure 1 in order to describe a real situation of the systems in connection with superionic conductors.

2.2 The Matrix Continued-Fraction Method (MCFM)

Various methods for solving the Fokker-Planck equation have been used, such as the simulation method and eigenfunction expansion [13]. 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 [13], and which can hardly be solved by any other method. In several papers Ferrando *et al.* [1,2] have applied the MCFM, in order to study the dynamic of a classical Brownian particle in simple potential. This method 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.* [19] is based on the expansion of the solution into a basis set of plane waves 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 $-\infty < v < \infty$. For further considerations it is convenient to introduce the annihilation and creation operators (b and b^+) [13,19]

$$b = \frac{\partial}{\partial v} + \frac{1}{2}v; \quad b^+ = -\frac{\partial}{\partial v} + \frac{1}{2}v \tag{4}$$

whose commutator is equal to one ($bb^+ - b^+b = 1$). We introduce also the following differential operators

$$D = \frac{\partial}{\partial x} + \frac{1}{2}\frac{\partial V(x)}{\partial x}; \quad \tilde{D} = \frac{\partial}{\partial x} - \frac{1}{2}\frac{\partial V(x)}{\partial x}\cdot \tag{5}$$

For numerical calculations it is convenient to use the Fokker-Planck equation in normalized form. Thus, by introducing the following variables and parameters

$$x_n = \frac{2\pi}{a}x; \quad t_n = \frac{2\pi}{a}\sqrt{\frac{k_{\mathrm{B}}T}{m}}t; \quad \gamma_n = \frac{a}{2\pi}\sqrt{\frac{m}{k_{\mathrm{B}}T}}\gamma$$
$$V_n(x) = \frac{V(x)}{k_{\mathrm{B}}T} \tag{6}$$

and with the aid of the definitions of operators $(b, b^+, D, \tilde{D})$, the Fokker-Planck operator can be rewritten as (for simplicity, we omit the normalisation index n)

$$L_{\mathrm{FP}} = -\Psi_0(v)\exp\left(-\frac{V(x)}{2}\right)\left(\gamma b^+ b + bD + b^+\tilde{D}\right) \times \exp\left(\frac{V(x)}{2}\right)(\Psi_0(v)) \tag{7}$$

where

$$\Psi_0(v) = \frac{1}{(2\pi)^{1/4}}\exp\left(-\frac{v^2}{4}\right)\cdot$$

By solving the Fokker-Planck equation one obtains distribution functions from which averages of macroscopic variables are obtained by integration. Since the application of the FPE is not restricted to systems near thermal equilibrium, we may as well apply it to systems far from thermal equilibrium. The solution of this equation depends on the following parameters: the friction γ, the temperature T and the ratio of two potential barriers Δ defined above.

From both a theoretical and an experimental point of view, the quantity carrying the most important information on the correlation effects between the diffusing ions in space and time is the coherent dynamic structure factor $S(q,\omega)$. It determines the cross section for inelastic neutron scattering and reflects both essential dynamical features: the collective excitations of the particles show up in its high frequency spectrum while its low energy part give us information about the diffusion process. $S(q,\omega)$ is defined in terms of the dynamical correlation function for density fluctuations.

$$S(q,\omega) = \frac{1}{2\pi}\int \mathrm{e}^{i\omega t}F(q,t)\,\mathrm{d}t \tag{8}$$

with

$$F(q,t) = \left\langle \mathrm{e}^{-iq(x(t)-x(0))}\right\rangle .$$

The brackets $\langle ... \rangle$ represent a statistical average, and $x(t)$ and $x(0)$ refer to the same diffusing particle. Generally, $S(q,\omega)$ consists of the quasi-elastic line and of oscillatory side peaks associated with phonon modes of the mobile sublattice. The oscillatory side peaks in addition to the conventional diffusive peak are found for small q, low friction and low temperature. As T increases, the side peaks disappear and merge into a broad background [20]. The dynamic structure factor can be obtained experimentally by neutron scattering which is the most powerful technique to study microscopic properties like diffusion mechanisms. The computed spectra $S(q,\omega)$ shows qualitatively some of the essential features which have been observed on AgI [21] in neutron scattering experiments.

In this paper we applied the MCFM for calculating the characteristic function and consequently the dynamic structure factor $S(q,\omega)$, the expression of which can then

$$\tilde{G}_{0,0}(k,i\omega)=\cfrac{I}{i\frac{a}{2\pi}\sqrt{\frac{m}{k_{\rm B}T}}\omega I+D\cfrac{I}{\frac{a}{2\pi}\sqrt{\frac{m}{k_{\rm B}T}}(i\omega+\gamma)I+2D\cfrac{I}{\frac{a}{2\pi}\sqrt{\frac{m}{k_{\rm B}T}}(i\omega+2\gamma)I+...}\tilde{D}}\tilde{D}} \tag{12}$$

be calculated by

$$F(q,t)=\int_{-\infty}^{\infty}{\rm d}x\int_{-\infty}^{\infty}{\rm d}v\int_{-\infty}^{\infty}{\rm d}x'\int_{-\infty}^{\infty}{\rm d}v'{\rm e}^{-iq(x-x')}\times P(x,v,t/x',v',0))w_{\rm st}(x',v') \tag{9}$$

$w_{\rm st}(x,v)$ is the Maxwell-Boltzmann distribution normalized to one particle per cell.

$$w_{\rm st}(x,v)=N\Psi_0^2(v){\rm e}^{-V(x)}$$

where

$$N^{-1}=\int_{-\pi}^{\pi}{\rm d}x\ {\rm e}^{-V(x)}.$$

The conditional probability $P(x,v,t/x',v',0)$ of having the particle in x,v at time t, if it was in x',v' at time 0, is the Green function of the probability density $w(x,v,t)$ and is then obtained by solving Fokker-Planck equation with initial δ-condition in the position and velocity variables. We finally obtain the following expression

$$F\left(q,t\right)=2\pi N\sum_{p,q=-\infty}^{\infty}G_{0,0}^{p,q}\left(k,t\right)M_{p-l}M_{q-l}^{*} \tag{10}$$

where M_r is the modified Bessel function depending on the potential $M_r=\frac{1}{2\pi}\int_{-\pi}^{\pi}{\rm e}^{-\frac{V(x)}{2}+irx}{\rm d}x$, $q=2\pi/a(k+l)$ with $|k|\leq 1/2$ (k restricted to the first Brillouin zone), l integer and N is a normalization factor. The dynamic structure factor can then be written as:

$$S\left(q,\omega\right)=N{\rm Re}\left\{\sum_{p,q=-\infty}^{\infty}\tilde{G}_{0,0}^{p,q}\left(k,i\omega\right)M_{p-l}M_{q-l}^{*}\right\} \tag{11}$$

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

See equation (12) above

where I is the identity matrix. The normalization factors have been introduced in the equation (12). The problem of calculating the dynamic structure factor is essentially reduced to the evaluation of the matrix continued fraction (Eq. (12)) which can even be estimated for small friction constant so that the connection to the zero friction limit can be made [19]. In the case of bistable potential, the matrix elements of D and $\tilde{D}$ are given by the following equations

$$\begin{aligned}D^{p,q}(k)&=(p+q)\delta^{p,q}+\frac{A_1}{4k_{\rm B}T}\left(\delta^{p,q-1}-\delta^{p,q+1}\right)\\&\quad+\frac{A_2}{2k_{\rm B}T}\left(\delta^{p,q-2}-\delta^{p,q+2}\right)\\\tilde{D}^{p,q}(k)&=(p+q)\delta^{p,q}-\frac{A_1}{4k_{\rm B}T}\left(\delta^{p,q-1}-\delta^{p,q+1}\right)\\&\quad-\frac{A_2}{2k_{\rm B}T}\left(\delta^{p,q-2}-\delta^{p,q+2}\right).\end{aligned}$$

The dimension of the matrix employed and the number of iterations in the continued fraction must be chosen in order to ensure a good convergence of the results. The speed of convergence depends also on the range of friction. For small friction the number of iterations may be very large whereas for large friction only a few terms need to be taken into account. However, the MCFM seems to converge even for a very small friction constant. For this last case one may use energy as a variable [13]. In the very low temperature limit ($k_{\rm B}T/V_1\ll 1$) the dimension of the matrices, which have to be inverted, becomes too large and then the method ceases to be tractable.

3 Results and discussions

3.1 The different diffusion mechanisms

We focus on the quasi-elastic peak of $S(q,\omega)$ whose half-width contains valuable information on the diffusion mechanism. At sufficiently small values of q, the width $\lambda(q)$ gives the diffusion coefficient D:

$$\lambda(q)=Dq^2.$$

This equation is valid for all diffusion models, since information on the microscopic details of the diffusion is lost at sufficiently small q values. While at larger q the behaviour of $\lambda(q)$ depends on the diffusion mechanism.

We make clear that all our numerical calculations which we will present in the following are done for the high friction limit, *i.e.* for $\Gamma=2\pi\gamma/\omega_{\rm o}\gg 1$ where $\omega_{\rm o}=(2\pi/a)(V_1/2m)^{1/2}$ is the characteristic frequency for vibration at the bottom of the well when $\Delta=0$.

We now turn to the presentation of the results obtained from our calculations. In Figure 2 we show the half-width at half maximum $\lambda(q)$ of the quasielastic peak as a function of the scattering wave-vector q, for different values of Δ and at low temperature ($k_{\rm B}T/V_1\ll 1$). Thus, for $\Delta=0$ the full-width $\lambda(q)$ is found to be approximately periodic in q with a period equal to $2\pi/a$. In determining the full-width we have subtracted the inelastic part. For reciprocal lattice vectors $q/q_{\rm o}=1,2,3...$, the half-width vanishes and

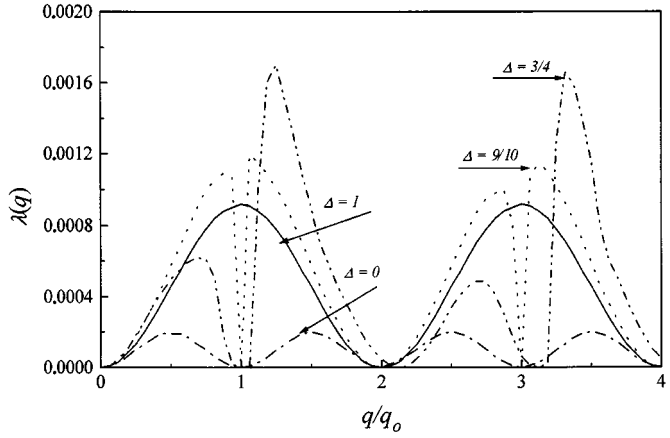

Fig. 2. The q-dependence of the half-width of the quasi-elastic line $\lambda(q)$ of dynamic structure factor $S(q,\omega)$ associated with different shapes of the bistable potential. Different diffusion processes are displayed. The parameters for this figure are $V_1 = 0.1$ eV, $k_{\rm B}T = V_1/6$, $\Gamma = 36$ (strong damping).

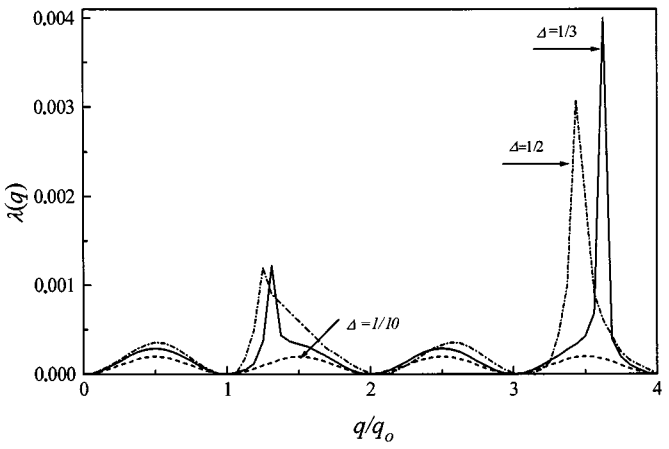

Fig. 3. The q-dependence of $\lambda(q)$ associated with different low values of Δ. The parameters are the same as for Figure 2.

it reaches its maxima at $q/q_{\rm o} = 1/2, 3/2, ...$ *etc.* We rejoin the calculations performed by Ferrando *et al.* [22] in the case of a simple potential. The system is described by a jump diffusion process and the jump length is close to the lattice constant a. This behaviour can be derived exactly from the hopping model where the only jumps considered are those connecting nearest-neighbour sites. Within this simple model the half-width takes the following form:

$$\lambda(q) = \tau^{-1}(1 - \cos(qa)) \qquad (13)$$

τ is the residence time of the diffusing particles at the bottom of the periodic potential and a is the lattice constant. This latter expression can also be obtained from the Smoluchowski equation which assumes strong damping of the dynamical behaviour of the particles (their mean free path is smaller than the lattice constant a). While in some cases of low friction ($\Gamma \ll 1$) the half-width of the quasi-elastic peak differs strongly from (13), and a more general form for $\lambda(q)$ has been calculated from a model which takes into account the possibility of jumps to more distant sites than to the nearest-neighbour ones [23]. It remains generally true that the half-width vanishes and the intensity of the quasi-elastic line sharpens for reciprocal vectors $q = nq_{\rm o}$, in agreement with expression (13).

Let us analyse now the behaviour of $\lambda(q)$ for $\Delta = 3/4$ and $9/10$. For $\Delta = 3/4$, we see that $\lambda(q)$ presents a complicated structure which is far from being simply a periodic function of q; indicating that the dynamic of mobile ions cannot be described by a simple jump model. Furthermore by increasing still more the value of Δ ($\Delta = 9/10$) we note clearly that the width of the minima at $q_{\rm o}$ and $3q_{\rm o}$ become narrower; this implies that the jumps of length a are practically forbidden. Consequently, the jump-length probabilities are not equivalent for all values of Δ. However, the diffusion mechanism is dominated by jumps of length $a/2$, inside and between the unit cells. While for $\Delta = 1 (V_1 = V_2)$, the periodic potential becomes simple with one barrier and with a spatial period equal to $a/2$. The half-width $\lambda(q)$ recovers then its cosine shape. The diffusion mechanism is entirely represented by instantaneous jumps from an equilibrium site to another one with jump length $a/2$. In this case, $\lambda(q)$ describes a thermally activated jump diffusion. In fact, in this situation the diffusion coefficient shows the usual Arrhenius behaviour and the diffusing particle spends most of its time around the bottom of the potential well, jumps being rare events. Qualitatively, its behaviour with q remains the same as represented for $\Delta = 0$ except for the jump length which becomes equal to $a/2$.

However for low values of Δ ($1/10 < \Delta < 1/2$), the behaviour of the half width of the quasi-elastic peak $\lambda(q)$ differs from the one seen in Figure 2. In fact, for $\Delta = 1/10$, as can be seen in Figure 3 the shape of $\lambda(q)$ is very close to a simple cosine as it is in the case for $\Delta = 0$. But by increasing slightly the value of the ratio of two potential barriers Δ, we notice the appearance of the pointed peaks which move toward the left *i.e.* toward the low value of the scattering wave-vector q. So, the change of the ratio (shape of potential) is found to have a significant effect on the character of the diffusion motion.

Let us analyse now the influence of the temperature on the diffusion process in bistable potential. In Figure 4, the full-width $\lambda(q)$ is reported as a function of q at high temperature ($k_{\rm B}T = V_1/2$), for $\Delta = 0, 9/10$ and 1. By comparing the two Figures 2 and 4, we observe that the $\lambda(q)$ is no longer more periodic, reflecting that the motion is more liquid-like as we increase the temperature independently of the value of Δ. If the temperature is much higher than the potential barrier, the particle diffuses almost freely. The same conclusion can be drawn from comparison between Figures 3 and 5 which are reported for two different temperatures.

3.2 Diffusion coefficient

The diffusion coefficient D of Brownian particles moving in a periodic potential is an important quantity since it can describe the intrinsic properties of the system. Let us recall briefly some of these fundamental relationships. The time integrals of auto-correlation functions

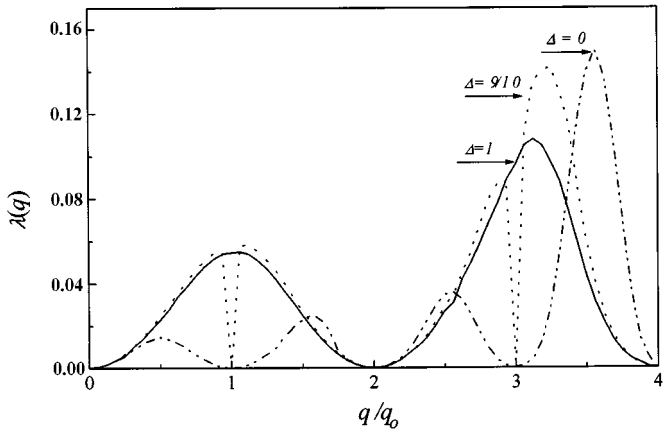

Fig. 4. Same as in Figure 2 but for high temperature $k_{\mathrm{B}}T = V_1/2$.

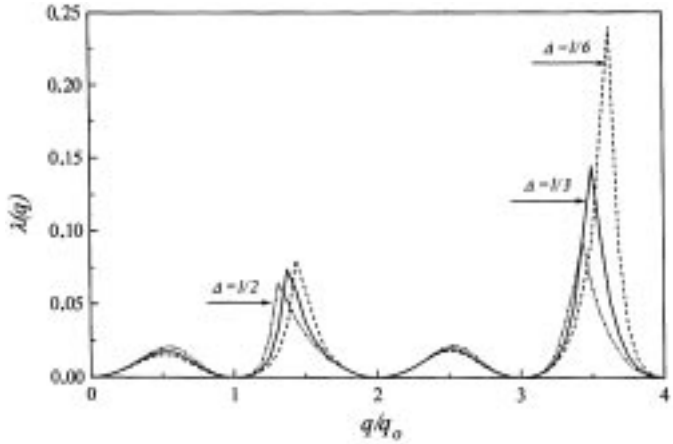

Fig. 5. Same as in Figure 3 but for high temperature $k_{\mathrm{B}}T = V_1/2$.

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are the well known Green-Kubo (GK) relation [24], which connect the equilibrium fluctuations of the system to the relevant transport coefficients. In the case of self-diffusion

$$D = \lim_{t\longrightarrow\infty} \int_0^t \frac{\mathrm{d}t'}{3} \langle v(0)v(t')\rangle \tag{14}$$

where $v(t)$ is the particle velocity. In this case the angle brackets $\langle ...\rangle$ mean averages over particles and time origins. There is another expression for calculating D which was derived in this form first by Einstein [24]. It is straightforward to show that the Green-Kubo and the Einstein expressions are equivalent [25,26]

$$\begin{aligned} D &= \lim_{t\longrightarrow\infty} \int_0^t \frac{\mathrm{d}t'}{3} \langle v(0)v\left(t'\right)\rangle = \lim_{t\longrightarrow\infty} \int_0^t \frac{\mathrm{d}t'}{3} \langle v(t)v\left(t'\right)\rangle \\ &= \lim_{t\longrightarrow\infty} \frac{1}{3} \langle v(t)\Delta\mathbf{r}(t)\rangle = \lim_{t\longrightarrow\infty} \frac{1}{6}\frac{\mathrm{d}}{\mathrm{d}t} \langle \Delta\mathbf{r}\left(t\right)\rangle \end{aligned} \tag{15}$$

where the displacement vector $\Delta\mathbf{r}(t)$ is defined by

$$\Delta\mathbf{r}\left(t\right) = \mathbf{r}\left(t\right) - \mathbf{r}\left(0\right) = \int_0^t \mathrm{d}t' v\left(t'\right)$$

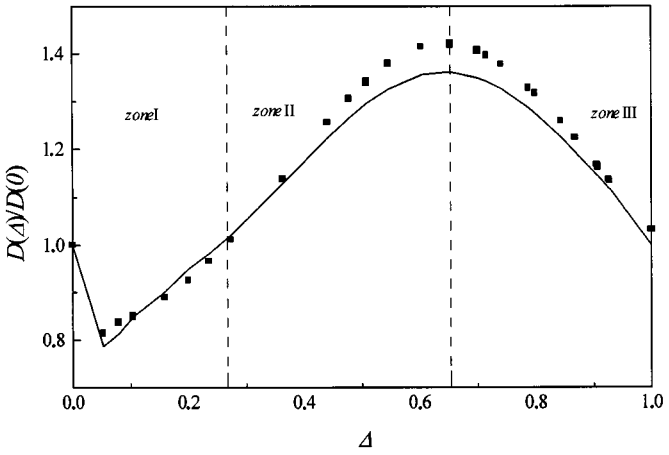

Fig. 6. We present the diffusion coefficient D normalized by the diffusion constant, calculated in the case of simple potential ($\Delta = 0$), as a function of the ratio Δ. The black squares correspond to the exact MCFM results and the solid lines to the analytic results (Eq. (17)). Three different zones are distinguished pointing out to different diffusion mechanisms going from a jump diffusion process to a superposition of hopping and liquid-like motion. The parameters are the same as for Figure 2.

if the mean square displacement is linear in time

$$D = \frac{1}{6} \lim_{t\longrightarrow\infty} \frac{\left\langle \Delta r\left(t\right)^2 \right\rangle}{t} \cdot \tag{16}$$

Every transport coefficient can be expressed in the form of an Einstein relationship. Detailed analytical studies have been completed in some limiting cases such as high temperature and strong damping on the basis of the Smoluckowski equation [27,28]. In the high friction limit, the diffusion coefficient can be expressed as a functional of $D_{\mathrm{o}} = k_{\mathrm{B}}T/m\gamma$ and $V(x)$. In the one-dimensional case the functional takes the simple form [9]

$$D = D_{\mathrm{o}} \left[\frac{1}{a} \int_0^a \exp\left(\frac{V(x)}{k_{\mathrm{B}}T}\right) \mathrm{d}x \frac{1}{a} \int_0^a \exp\left(-\frac{V(x)}{k_{\mathrm{B}}T}\right) \mathrm{d}x \right]^{-1} . \tag{17}$$

The results for the diffusion coefficient will be presented and discussed separately in the different damping regimes. This quantity will be calculated analytically from equation (17) and numerically by a direct solution of the FPE in terms of a matrix continued fraction expansion as:

$$D = \frac{a}{4\pi} \sqrt{\frac{m}{k_{\mathrm{B}}T}} \lim_{q\longrightarrow 0} \frac{\lambda(q)}{q^2} \cdot \tag{18}$$

In Figure 6, D is plotted as a function of the ratio $\Delta = V_2/V_1$. The figure shows the results of the analytical approximation (Eq. (17)) and numerical calculations (black squares), which are in quantitative good agreement for all values of Δ. In this figure, three regions can be

clearly distinguished pointing out to three different diffusion processes. In fact, in zone I, the system can be described by a jump diffusion process with jump length close to the lattice constant. In zone II, the diffusion process consists of a superposition of both liquid-like and hopping motions. For this zone, we can find different jump lengths with different probabilities of jump (in addition to jump length a we can find $a/3$ and $a/2$). While the diffusion process in zone III is described only by the hopping motions like zone I except that for this case the jump length is equal to $a/2$.

The important feature of the curves in Figure 6, is the fastest decay of D from its initial value $D(0)$ within a short interval ($0 < \Delta < 1/8$). This is due essentially to the form of potential which seems to be rectangular (the width of its well increases; see Figure 1 for $\Delta = 1/8$ for example). Geisel [29] has studied this effect, by using different periodic potentials with equal barrier heights but different curvatures (or harmonic frequencies). In his work, he found that the highest mobility is found for the narrowest potential but the lowest mobility is found for an almost rectangular potential. After this rather rapid initial decay, D increases normally and essentially in zone II in which it attains its maximum. The aspect of correlated motions contributes significantly to the diffusion coefficient, which explains its increase with D in this zone.

4 Conclusion

In this work, we have investigated the dynamics described by the Fokker-Planck equation in symmetric bistable potential. The equation is solved numerically by the matrix continued fraction method which proves turns to be quite effective. The continuous theory here presented, based on a Brownian model in the framework of the Fokker-Planck equation can furnish complete information on the diffusion process. The character of the diffusion process is quite clearly revealed through the q dependence of the full-width of the quasi-elastic peak of $S(q, \omega)$. In general two different cases have been considered differing only by the form of periodic potential: cosine and symmetric bistable forms. In the former case the diffusion process is very well described by a jump diffusion model. The diffusion process is more complicated in the second case and this is due to the important liquid-like motion inside the unit cell which is added to the hopping motion. This aspect of these correlated motions contributes significantly to the diffusion coefficient which we have calculated numerically (from the full-width at half maximum $\lambda(q)$) and analytically. A comparison of the two results shows that the agreement is excellent.

Finally, we conclude that we have solved the FPE, which is of general interest for Brownian systems and is the only good first approximation to the description of their dynamics, by the MCFM extended to potential shapes different from the cosine, which is certainly an oversimplification. The results obtained for symmetric bistable potential can give clear indications for discussion of the analogous problem in symmetric metastable potential [30].

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