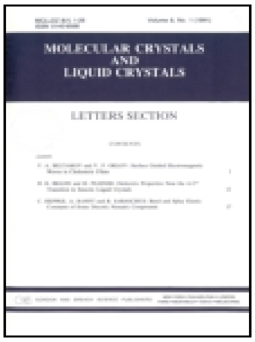

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Brownian diffusion in a triple-well potential

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ABSTRACT

In this work we present a general theory for diffusion mechanism of Brownian particle submitted to a symmetric periodic triple-well potential. The kinetics description is done by the Fokker-Planck equation, which is resolved numerically using the Matrix Continued Fraction Method, in order to calculate some important correlation functions. The half-width $\lambda(q)$ at half maximum of the quasi-elastic peak of dynamic structure factor $S(q,\omega)$ and the diffusion coefficient D are studied in the high friction regime and low temperature for different form of triple-well potential. Our numerical results of half-width $\lambda(q)$, show that the diffusion process in triple-well potential can be described by a superposition of both simples hopping and liquid-like motion when the ratio Δ of two potential barriers V_1 and V_2 is less than one $(\Delta < 1)$ and by the longs jumps when Δ tends towards one.

For some values of ratio of potential barriers, the diffusion coefficient results show that the intermediates potential barriers accelerate the diffusion process.

KEYWORDS
Fluctuation phenomena; random processes; noise and Brownian motion; Theory of diffusion; Ionic conduction in solids

I. Introduction

The diffusion of Brownian particles in a periodic potential is one of the interesting problems which has been studied in many different scientific areas of physics [1]. It represents a model that can be applied to numerous systems, ranging from super-ionic conductors [2] and intercalation compounds to sub-monolayer films adsorbed on surfaces of crystalline substrates. These systems are characterized by diffusion constants in the range of liquids, but the periodicity due to the crystalline substrate is not completely lost. If the diffusing particle is sufficiently massive, the diffusion problem can be treated within a classical approach. Moreover, the theoretical method to understand this important problem has been developed mainly in two directions: The first is numerical Molecular Dynamics or the Monte Carlo simulation method [3, 4] and the second method is an analytical study based on the Langevin equation [5] or the Fokker-Planck equation (also called a forward Kolmogorov equation) describing the Brownian motion in a periodic potential [6, 7]. The largest part of the results on the Fokker-Planck dynamics problem has been obtained for a simple cosine potential [8, 9], whereas the diffusion problem in symmetric and asymmetric double-well potentials has been recently investigated [10–14]. Here, we shall be mainly concerned with the Fokker-Planck dynamics in a periodic triple-well potential (Fig. 1) [15], which is very interesting because it presents an intermediate wells, that can accelerate the diffusion of particles [15–17]. This type of potential geometry

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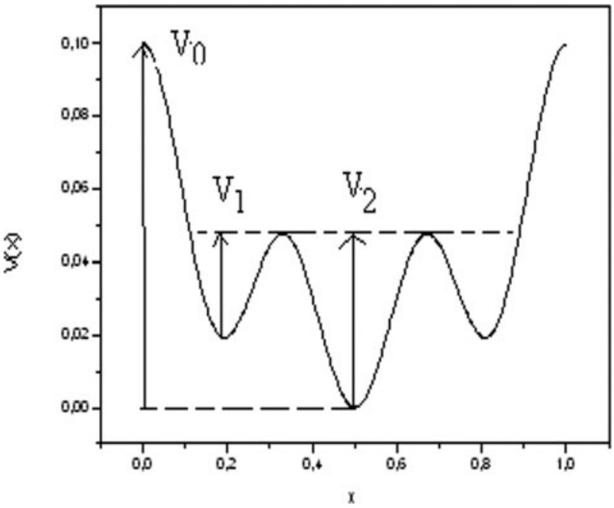

Figure 1. The schema of a cell of the periodic, symmetric triple-well potential: $V_0 = 0.1eV$, $\Delta_1 = V_1/V0$, $\Delta_2 = V_2/V0$ and $\Delta = V_1/V2$.

is observed in the cluster diffusion on reconstructed surface for the real systems such as the case of the system $Cu_3/Ag(110)$ given in reference [18]. So, our main purpose in the present paper is to illustrate the effect of intermediate barriers of triple-well potential on the diffusion process at low temperature and high friction regime. Starting from the Fokker-Planck equation and using the Matrix Continued Fraction Method as a numerical method to solve this equation. For different shapes of the triple-well potential, we have calculated the half-width $\lambda(q)$ at half maximum of the quasi-elastic peak of dynamic structure factor $S(q, \omega)$. However, the diffusion coefficient is also calculated, indicating that the diffusion process, in some limits, is accelerated.

This paper is organized as following: In Sec. II, we describe the model and treated the numerical method, our numerical results and discussion began In Sec. III and the last part of work, Sec. IV, contains the general conclusion.

II. Model and method of calculations: The matrix continued fraction method (MCFM)

The physical quantity carrying the most complete information on the correlation effects between the diffusing particles in space and time is contained in the dynamic structure factor $S(q, \omega)$ defined (In *1D* notation) as time Fourier transform of the characteristic function $F(q, t)$:

$$S(q, \omega) = \frac{1}{2\pi N} \int_{-\infty}^{+\infty} dt \, \exp(i\omega t) F(q, t), \tag{1}$$

with

$$F\left(q, t\right) = < \exp -iq\left(x(t) - x(0)\right) > \tag{2}$$

Where the angle brackets refer to the thermal average, $x(t)$ and $x(0)$ denote the position of same particle respectively at instant $\boldsymbol{t}$ and at the initial moment 0. The dynamic structure factor can be obtained from the characteristic function $F(q, t)$ after expanding the probability

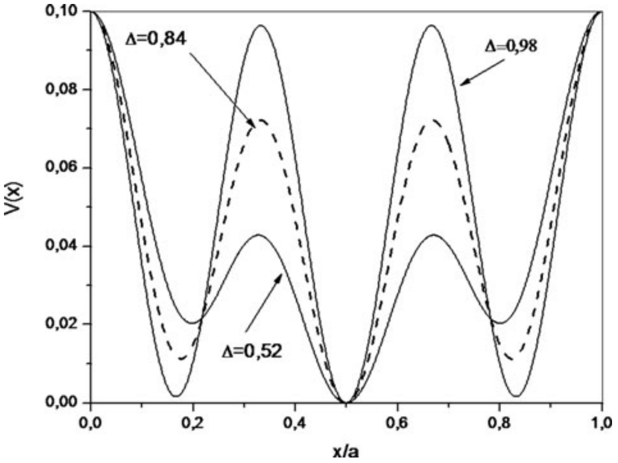

Figure 2. Structure of the symmetric triple-well potential V(x) presented for different values of the ratio Δof two potential barriers V_1 and V_2.

density into a basis set of plan waves for position variable and of hermit function for the velocity variable which from together a complete system, via the Green Kubo relation [19].

Let us illustrate how the average in equation (2) can be calculated, the starting point is the Fokker-Planck equation (*FPE*) Eq. (3), which describes the diffusion motion of a Brownian particle of mass ***m*** in a potential field with friction coefficient γ.

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

L_{FP} is the Fokker-Planck operator given by :

$$L_{FP} = -v\frac{\partial}{\partial x} + \frac{1}{m}\frac{\partial V(x)}{\partial x}\frac{\partial}{\partial v} + \gamma\frac{\partial}{\partial v}\left(v + \frac{K_B T}{m}\frac{\partial}{\partial v}\right) \tag{4}$$

$f(x, y, t)dxdv$ is the probability of finding the particle to the phase space element between (x, v) and $(x + dx, v + dv)$, $\boldsymbol{T}$ is the temperature, K_B is the Boltzmann's constant ($K_B T$ is the thermal energy) and $V(x)$ is the periodic potential. Under assumption of simple periodic potential many authors [20, 21] have calculated different correlation functions; and the problem is now well understood. In this work we present some results of diffusion particles in periodic triple-well potential (Fig. 1). Its analytical expression is given by:

$$V(x) = A_1 \cos(q_0 x) + A_2 \cos(2q_0 x) + A_3 \cos(3q_0 x) \tag{5}$$

where $q_0 = \frac{2\pi}{a}$ denotes the reciprocal lattice vector and $\boldsymbol{a}$ is the lattice constant.

Our study was performed using the potential given in Eq. (5) for various values of ratio $\Delta_1 = V_1/V_0$, $\Delta_2 = V_2/V_0$ and $\Delta = V_1/V_2$ of barriers potential V_0, V_1 and V_2. The choice of A_1, A_2 and A_3 determines the desired value of the ratio Δ, Δ_1 and Δ_2 (Fig. 2).

The Fokker-Planck equation cannot be solved analytically in every regime of friction and potential barrier. For that, the exact numerical results for diffusion in such type of potential can be obtained by solving the *FPE* in position and velocity variables (x, v) using the Matrix Continued Fraction Method (*MCFM*) in order to calculate the dynamical structure factor $S(q, \omega)$ and the half-width $\lambda(q)$ of the quasi-elastic peak of dynamic structure factors $S(q, \omega)$ to large values of $\boldsymbol{q}$ for different physical parameters such as temperature, friction and the ratio of the potential barrier heights.

This numerical method developed by Risken et al [6], have been already presented elsewhere [22]. Here we will recall only the final expression of the dynamic structure factor $S(q, \omega)$ in the first Brillouin zone:

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

where N is a normalized factor given by $N^{-1} = \int_{-\pi}^{\pi} dx \exp(-V(x))$, $q = q_0(k+r)$ with $-\frac{1}{2} < k \leq \frac{1}{2}$, $\boldsymbol{r}$ integer and M_r is the modified Bessel function defined by:

$$\mathrm{M_r} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \exp\left(-\frac{\mathrm{V(x)}}{2} + \mathrm{irx}\right) dx \tag{7}$$

Defining the following quantity: $\xi = \frac{a}{2\pi}\sqrt{\frac{m}{K_B T}}$ and $\Gamma = \frac{2\pi\gamma}{\omega_0}$ where $\omega_0 = \frac{2\pi}{a}\sqrt{\frac{V}{2m}}$ is the characteristic frequency for vibration at the bottom of the well when $\Delta = 0$.

The Green function $\tilde{G}_{0,0}$ can be expressed as a continuous fraction of some matrix depending on the potential and the friction:

$$\tilde{\mathrm{G}}_{0,0}\left(\mathrm{k, i}\omega\right) = \frac{\mathrm{I}}{\mathrm{i}\xi\omega\mathrm{I} + \mathrm{B}\frac{\mathrm{I}}{\xi\left(\mathrm{i}\omega+\gamma\right)+2\mathrm{B}\frac{\mathrm{I}}{\xi\left(\mathrm{i}\omega+2\gamma\right)\mathrm{I}+\ldots..}\tilde{B}}\tilde{B}} \tag{8}$$

In Eq. (8) $\boldsymbol{I}$ is the identity matrix and the matrix elements B and $\tilde{B}$ are given in the case of the triple-well potential $V(x) = A_1\cos(q_0 x) + A_2\cos(2q_0 x) + A_3\cos(3q_0 x)$ respectively by the following equations Eq. (9) and Eq. (10)

$$\begin{aligned} B^{p,q}(k) = (p+k)\delta^{p,q} - \Bigg[& \frac{G_1}{2}\left(\delta^{p+1,q} - \delta^{p-1,q}\right) + G_2\left(\delta^{p+2,q} - \delta^{p-2,q}\right) \\ & + \frac{3}{2}G_3\left(\delta^{p+3,q} - \delta^{p-3,q}\right)\Bigg] \end{aligned} \tag{9}$$

$$\begin{aligned} \tilde{B}^{p,q}(k) = (p+k)\delta^{p,q} + \Bigg[& \frac{G_1}{2}\left(\delta^{p+1,q} - \delta^{p-1,q}\right) + G_2\left(\delta^{p+2,q} - \delta^{r-2,p}\right) \\ & + \frac{3}{2}G_3\left(\delta^{p+3,q} - \delta^{p-3,q}\right)\Bigg] \end{aligned} \tag{10}$$

where $G_1 = \frac{q_0 A_1}{2}$, $G_2 = q_0 A_2$ and $G_3 = q_0 A_3$

Moreover, a significant quantity which describes the intrinsic properties of a system is the diffusion coefficient $\boldsymbol{D}$ which is defined by:

$$D = \underset{t\to+\infty}{Lim} \frac{1}{2Nt} \sum_{i=1}^{N} \left\langle |x_i(t) - x_i(0)|^2 \right\rangle \tag{11}$$

$\boldsymbol{N}$ is the total number of particles in the system, $x_i(t)$ indicates the position of *ith* particle at time $\boldsymbol{t}$ and $\langle \ldots \rangle$ is the thermal average. It has been shown that many correlation functions may be derived from the dynamical structure factor in a periodic system [23]. The diffusion coefficient may be also computed from $S(q, \omega)$ via Kubo relation [19]:

$$D = \frac{a}{4\pi}\sqrt{\frac{m}{K_B T}} \underset{q\to 0}{lim} \frac{\lambda(q)}{q^2} = D_0 \underset{q\to 0}{lim} \frac{\lambda(q)}{q^2} \tag{12}$$

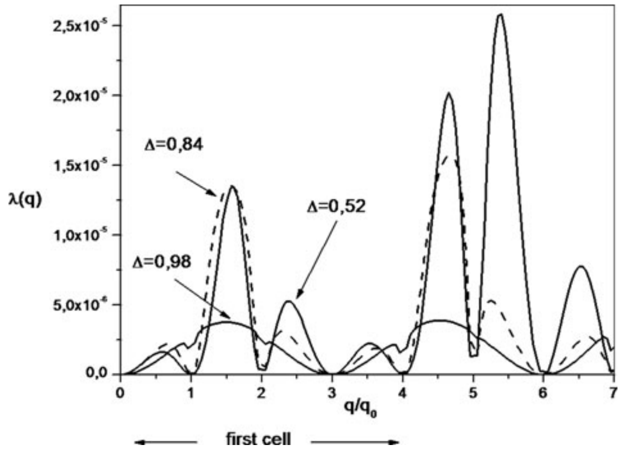

Figure 3. The q-dependence of the half-with of the quasi-elastic line λ(q) of dynamic structure factor S(q,w) associated with different shapes of the triple well potential. The parameters of this figure are $V_0 = 0.1\text{eV}$, $K_B T = V_0/6$ and $\Gamma = 10$ (strong damping friction).

$$D_0 = \frac{a}{4\pi}\sqrt{\frac{m}{K_B T}}$$

Where ***a*** is the lattice constant and $\lambda(q)$ is the half-width of the quasi-elastic peak of $S(q, \omega)$.

Eq. (12) means the behaviour of $\lambda(q)$ for the small value of $\boldsymbol{q}$, which is usually investigated in neutron and atom scattering experiments to investigate the diffusion coefficient. In this way, we will use this formula to compute the quantity D/D_0 which gives the most important information about the effect of the intermediate barriers of the potential on the diffusion processes.

III. Results and discussion

In the strong friction regime, the diffusion takes place by jump from one site to nearest neighbour one, independently of the structure of the periodic potential and the long jumps are less probable [15, 24–26]. So, the curves given in this article (Figs. 3,7) represent the behaviour of the particle inside the cells of length $a = 1$ (Fig. 2). When the ratio Δ of two potential barriers V_1 and V_2 $(\Delta = V_1/V_2)$ Δ tends towards 1, the potential tends towards a cosine function of period equal to $\frac{a}{3}$. So, the half-width $\lambda(q)$ (Fig. 3) presents the same behaviour for different values of the ratio Δ except for $\Delta \approx 1$ for which $\lambda(q)$ is a cosine function with a period equal to three period of the potential, in this case the diffusion process is described by longs jump. This found results are in perfect agreement with the results given in sinusoidal potentials [15, 24], bistable and metastable potential with the ratio of barriers is equal to 0 or 1 [15, 25]. In (Fig. 3) the first pick $(x = 0, 5)$ represents the jump through V_0, the second pick $(x = 1, 5)$ with big intensity represents the jump through V_1 whereas the third pick $(x = 2, 5)$ represents the jump through V_2. We remark that the intensity of $\lambda(\boldsymbol{q})$ decreases when Δ is very large, reflecting the difficulty to jump over the barrier of potential that increases with Δ. The presence of middle well reduces the rate from left to right, relative to the double well case [17]. So, instead of crossing V_0, the particle crossed at first V_1 then V_2 to pass in a nearly neighbour site. The diffusion process in this form of potential can be described by a superposition of both simples hopping and liquid-like motion. For $q/q_0 > 4$, one recovers the same

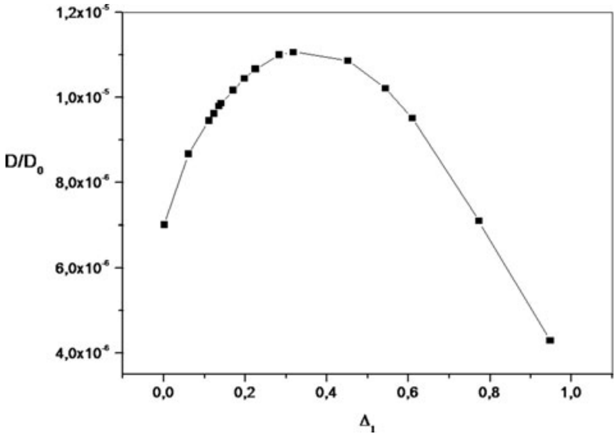

Figure 4. Diffusion coefficient D/D_0 of system in triple well-potential as function of $\Delta_1 = V_1/V0$. Effect of barrier V_1 on the diffusion process. The parameters of this figure are $V_0 = 0.1\text{eV}$, $K_BT = V_0/6$ and $\Gamma = 10$ (strong damping friction).

behaviour for $\lambda(q)$ as in the first cell $q/q_0 < 4$. But this time with a very great intensity that reflects the motion of the particle inside the cell in the hydrodynamic limit.

In the (Figs. 4, 6) we present the diffusion coefficient D/D_0 as function of the ratio, $\Delta_1 = V_1/V_0$, $\Delta_2 = V_2/V_0$ and $\Delta = V_1/V_2$, respectively. For low values of the ratio the diffusion coefficient is also low.In this case characterized by flat bottom the particles oscillate without being able to leave the cell. As these ratio increase, for $0,001 \leq \Delta_1 \leq 0,45$ (Fig. 4) and $0,18 \leq \Delta_2 \leq 0,60$ (Fig. 5), the diffusion coefficient increases reaches a maximum and decreases quickly. So, the intermediate barrier V_1 accelerates the diffusion when Δ_1 is lower than 0.45 (Fig. 4) and V_2 accelerates the diffusion when Δ_2 is lower than 0.60 (Fig. 5). But, when Δ_1 is higher than 0.45 the diffusion coefficient decreases, indicating that the barrier V_1 becomes difficult to cross. Also, the barrier V_2 becomes difficult to cross when Δ_2 is higher than 0.60. In figure 7 we plotted together the curves of corresponding to the ratio Δ_1, Δ_2 and Δ, we observe that the two barriers and have an effect equivalent to the effect of only one intermediate barrier characterized by ratio Δ. This barrier accelerates the diffusion when

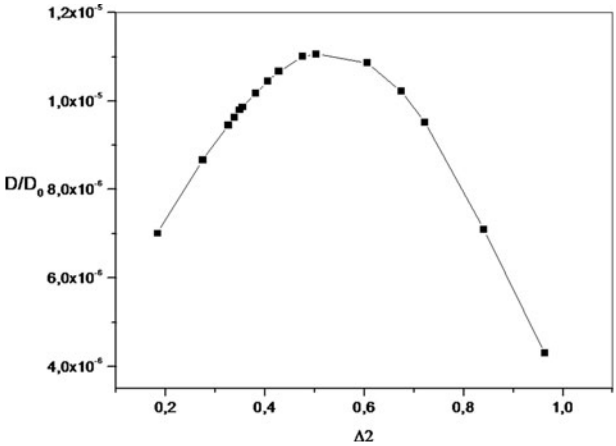

Figure 5. Coefficient of diffusion D/D_0 of system in triple well-potential as function of $\Delta_2 = V_2/V0$. Effect of barrier V_2 on the diffusion process. The parameters of this figure are $V_0 = 0.1\text{eV}$, $K_BT = V_0/6$ and $\Gamma = 10$ (strong damping friction).

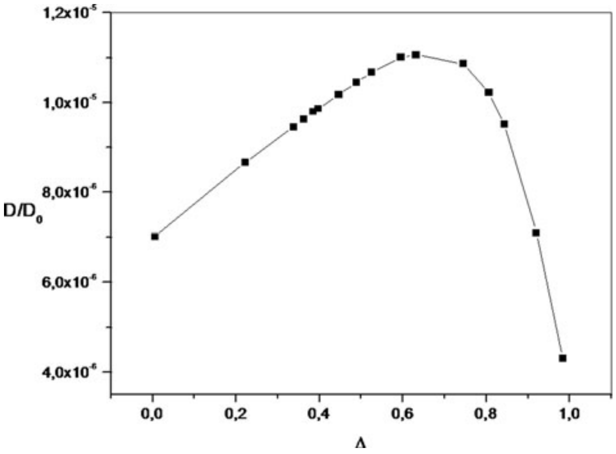

Figure 6. Coefficient of diffusion D/D_0 of system in triple well-potential as function of $\Delta = \Delta_1/\Delta_2 = V_1/V_2$. The parameters of this figure are $V_0 = 0.1\text{eV}$, $K_BT = V_0/6$ and $\Gamma = 10$ (strong damping friction).

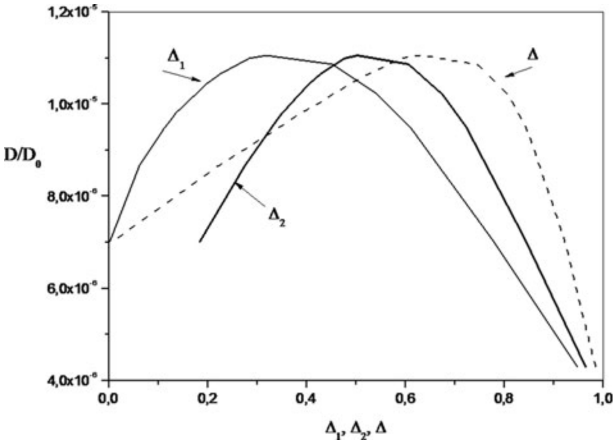

Figure 7. Curves of the coefficient of diffusion of system in triple well-potential D/D_0 plotted together as function of the ratios Δ_1, Δ_2 and Δ. The parameters of this figure are $V_0 = 0.1$ eV, $K_BT = V_0/6$ and $\Gamma = 10$ (strong damping friction)

$0, 006 \leq \Delta \leq 0, 75$. By taking into account of these points, we can conclude that the diffusion motion is easy in a triple-well potential than in potentials with simple or double wells.

V. Conclusion

Let us summarize and add some additional remarks on the results presented in this paper. We have investigated the diffusion process of a Brownian particle moving in triple-well potential. This movement is modelled by the Fokker-Planck equation which has been solved numerically by the Matrix Continued Fraction Method. At low temperature and high friction regime, we have calculated the half-width $\lambda(q)$ at half maximum of quasi elastic peak of dynamic structure factor $S(q, \omega)$ and the diffusion coefficient D/D_0. Taking into account the entire behaviour of $\lambda(q)$, we conclude that the diffusion process in triple-well potential can be described by a superposition of both simples hopping and liquid-like motion. Whereas, the behaviour of $\lambda(q)$ for the small value of q, which is usually investigated in neutron and atom scattering experiments, gives the diffusion coefficient. The presence of intermediate barriers of potential accelerates, in some cases, the diffusion process which becomes important than in potentials with simple or double well.

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