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Substrate effects on the diffusion process

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ABSTRACT

In this paper, we investigated the dynamic proprieties of one-dimensional system of a classical Brownian particle immersed in a symmetric periodic Remoissenet-Peyrard potential using the Fokker Planck equation. This equation is solved by the Continued fraction expansion method (CFEM). Our results presented for different physical situations, indicated that the dynamical properties are very sensitive to the structure of the Remoissenet-Peyrard potential. Further, we have shown how translational and oscillator motion show up in the dynamic conductivity. Possible applications of this model lie in the field of solid electrolytes and molecular crystals.

KEYWORDS

Brownian motion; Fokker –Planck equation; transport process; deformable substrate

1. Introduction

Surface science is one of some concerns of all researchers in condensed matter subject. This can be viewed through crystal growth, adsorption phenomena …etc. In this context, several experimental techniques have been employed for the measurement of the diffusion coefficients such as, Scanning Tunneling Microscopy experiment (STM), Field Imission electronic field (FIM) etc. 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. The Remoissenet and Peyrard (RP) [3] potential is obtained in a controlled manner by an adequate choice of parameters. This potential was firstly introduced in the context of soliton theories [4]. The parameter of deformability S can be obtained directly from the measured values of the activation energy for the diffusion of an isolated adatom and the frequency of adatom oscillations parallel to the surface [5–6], however, it has been also used in many different domains such as deformable spin model Hamiltonian [7], discrete lattice systems [8–9], diffusion mechanism [10–11], thermodynamical properties of kink-antikink at low temperatures. Previously in the same context, we studied the dynamic proprieties of one-dimensional system of Brownian particle immersed in bistable and metastable periodic potential; in other words, in periodic potentials with two wells. The calculation is developed by using the Fokker-Planck equation which is solved numerically by the continued fraction expansion method (CFEM), in order to calculate the frequency-dependent conductivity for different barriers and temperatures T

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[12]. Now, we introduce another form of the potential called Remoissenet-Peyrard deformable substrate potential that describes realistic and more general situations.

The present paper is organized as follows. In the second section, we summarize the most relevant parts of Brownian particles which can give a complete treatment of the diffusive process. The third section is devoted to results and discussions. The concluding results will be given in the last section.

2. Theoretical model and method of calculation

2.1 Langevin equation

As said in the in introduction, a variety of phenomena in physics and other fields can be modeled as Brownian motion in an external periodic potential. The study of diffusion of particles in periodic medium is interesting and can be described by means of some form of the Langevin equation [13–14]. In the simplest Langevin equation

$$m\frac{d^2x_i}{dt^2} = -m\gamma v_i + k_i(x_i) + \xi_i(t) \tag{1}$$

Where m, x_i and v_i are respectively the mass, the position and the velocity of the particle i. In this equation, the energy exchanged between the diffusing particles and the substrate is modeled by a viscous frictional force with the coefficient γ and by the stochastically fluctuating force $\zeta_i(t)$ which corresponds to Gaussian white noise with zero average and autocorrelations [15–16]:

$$\begin{cases} < \xi_i(t) > = 0 \\ \\ < \xi_i(t)\xi_j(t') > = 2m\gamma k_B T\delta_{ij}\delta(t-t') \end{cases} \tag{2}$$

With k_B and T are respectively the Boltzmann's constant and the temperature

2.2 Fokker-Planck equation

In our case, the dynamic of the particle is governed by the Fokker Planck equation [17–20]. For convenience, it is useful to use the transition probability density $f(x', v', t/x, v)$ in the phase space *(x,v)* of all mobile particles. This function determines the probability that a particle initially prepared at positions x' and velocity v' will be found at x and v after time t, and obeys to the partial differential equation which is the Fokker-Plank equation.

$$\frac{\partial f\,(x', v', t/x, v)}{\partial t} = L_{FP} f\left(x', v', t/x, v\right). \tag{3}$$

With the Fokker –Planck operator is expressed:

$$L_{PF} = -v_i'\frac{\partial}{\partial x_i'} - \frac{K_i\,(x')}{m}\frac{\partial}{\partial v_i'} + \gamma\left(1 + v_i'\frac{\partial}{\partial v_i'} + \frac{k_B T}{m}\frac{\partial^2}{\partial v_i'^2}\right). \tag{4}$$

Where m, x and v represent respectively the mass, the position, the velocity of the particle and γ is the friction coefficient. The operator L_{FP} that describes temporal evolution of the system is not hermitic. Then, the eigen-values are in general complex containing oscillation and relaxation terms. The two first operator's terms are identical with those of Liouville in classical mechanics; the others are dissipative and linear in the friction γ. Here, we applied the Fokker-Plank equation to describe the Brownian motion in a periodic potential.

2.3 Continued fraction expansion method (CFEM) for frequency–dependent conductivity

Various methods for solving the Fokker-Plank equation have been used in literature, such as simulation method and eigen-function expansion [14]. In this work, we use the continued fraction expansion method (CFEM) introduced by Zwanzing and Mori to solve such evolution equation [19–20]. The dynamical conductivity can be formally represented by a continued fraction:

$$\sigma\ (\omega) = \frac{\beta Q^2}{L} \cfrac{a_0}{-i\omega+b_1+\cfrac{a_1}{-i\omega+b_2+\cfrac{a_2}{-i\omega+b_3+\ddots}}} + \cfrac{a_{p-1}}{-i\omega+R_p(\omega)} \tag{5}$$

Where L is the length of chain, Q is the particle's charge of system and the quantities $\mathbf{a_p}$ and $\mathbf{b_p}$ are static correlation functions. The physical quantity $k(x) = -\partial U_{RP}/\partial x$ $\mathrm{k\ (x)} = -\frac{\partial \mathrm{V}}{\partial \mathrm{x}}$ is the force acting on the particle derived from the potential $U_{RP}(x)$. We shall come back to this potential in some of our considerations is section III. Several methods have been proposed for an approximate calculation of $R_p(\omega)$. The most interesting one, which has frequently been used in the literature, consists of replacing the function $R_p(\omega)$ by a constant $R_p(\omega) = R_p(0)$ which can be determined from static conductivity known by other means.

The appropriate dynamical variable A_0 for the conductivity is the current defined as

$$A_0 = \sum_j v_j. \tag{6}$$

Let $A_0(t)$ be a generic classical dynamic variable and let $A_0(t) = A_0(t = 0)$. By assuming that the evolution of the dynamic variable is governed by the following equation:

$$A\ (t) = e^{\widetilde{L}\,t} A_0. \tag{7}$$

We can generate the functions

$$A_{p+1} = Q_p\, \widetilde{L}\, A_p \tag{8}$$

Where $\widetilde{L}$ is the Kolmogorov operator and Q_p is a projection operator by:

$$Q_p X = X - \sum_{k=0}^{p} \frac{\langle A_k^* X\rangle}{\langle A_k^* A_k\rangle} A_k. \tag{9}$$

The coefficients a_p and b_p are given by:

$$a_0 = \langle A_0^* A_0\rangle \qquad ; \qquad a_{p+1} = \frac{\langle A_{p+1}^* A_{p+1}\rangle}{\langle A_p^* A_p\rangle} \tag{10}$$

$$b_{p+1} = -\frac{\left\langle A_p^*\, \widetilde{L}\, A_p\right\rangle}{\left\langle A_p^* A_p\right\rangle}. \tag{11}$$

The continued fraction method expansion is a powerful method to study dynamic properties for wide range of parameters of the system. According to the algorithm technique developed by Zwanzig-Mori [20–21], the first few coefficients of the conductivity are given by :

$$a_0 = \frac{k_B T}{m}. \tag{12}$$

$$a_1 = \left(\frac{-1}{mk_B T}\right)\left\langle k(x)^2\right\rangle_0. \tag{13}$$

$$a_2 = \frac{1}{m^2 a_1}\left[\left\langle k'(x)^2\right\rangle - \left\langle k'(x)\right\rangle^2\right]. \tag{14}$$

The coefficients b_p are damping terms, which vanish in the Hamiltonian case $(\gamma = 0)$ $(\gamma = 0)$

$$b_1 = \gamma;\ b_2 = 0;\ b_3 = \gamma; \tag{15}$$

In order to calculate the dynamical conductivity by applying CFEM, one has to answer to two principal questions. The first consists of finding a suitable approximation of the remainder of the infinite continued fraction. In the large friction limit, it is obtained by $R_p = \gamma$. The second problem appears in the evaluation of the static correlation functions.

3. Results and discussion

Considering a form of the potential $U_{RP}(x, S)$ non sinusoidal Remoissenet-Peyrard potential, which we can write as:

$$U_{RP}(x, S) = \frac{V_0}{2}(1+S)^2\frac{\left(1-\cos\left(q_0 x\right)\right)}{\left(1+S^2-2S\cos\left(q_0 x\right)\right)} \quad , \quad |S| < 1 \tag{16}$$

Where V_0 constant which measures amplitudes of the potential, and x is the displacement field. The shape of the potential is determined by the parameter of deformability S . The parameter S describes different shapes of the on-site potential. Negative values of S lead to a shape with sharp wells separated by flat wide barriers, while positive values give flat bottom separated by thin barriers, as shown in Figure 1. When S tends to 1, this profile appears as a periodic distribution of the Dirac function. We give for some parameter values deformability s forms of this potential.

As mentioned above, the continued fraction method expansion is a powerful method to study dynamic properties for wide range of parameters of system. The principal problems arise only at extremely low friction. In this limit, the computational efforts are different: higher order continued fractions are necessary and no analytical solutions are then available. But, in many cases, at high temperatures or in high and intermediate friction regimes a few poles are sufficient to describe qualitatively, the dynamic proprieties. In our case, a continued fraction expansion up to order 4 ($\beta = \frac{1}{k_B T}$) is used:

$$\sigma(\omega) = \frac{\beta Q^2}{L}\frac{a_0}{-i\omega + b_1 + \frac{a_1}{-i\omega + b_2 + \frac{a_2}{-i\omega + R_3(\omega)}}}. \tag{17}$$

Within our model potential given by Eq.(10), the static correlation functions are expressed as:

$$a_0 = \frac{k_B T}{m}, \tag{18}$$

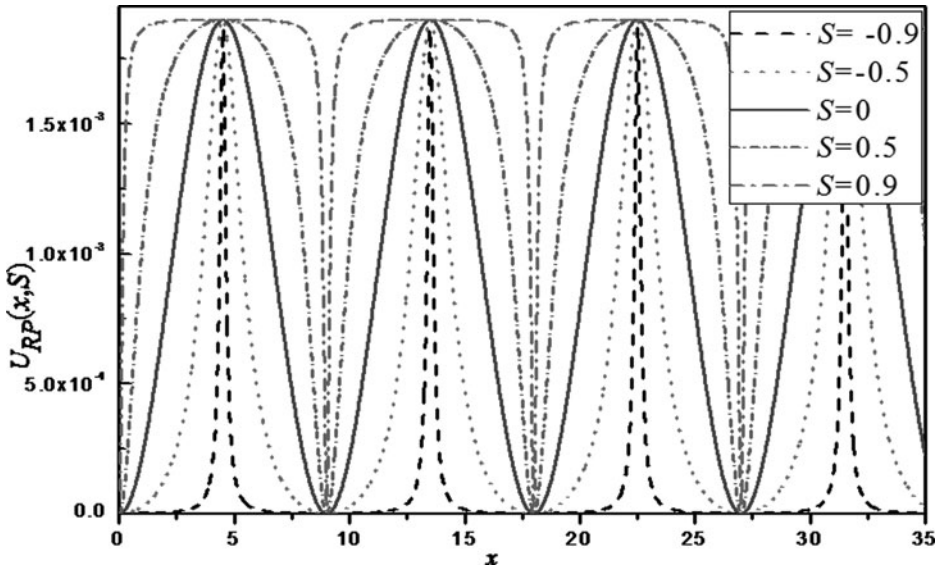

Figure 1. Representation of the potential for some parameter values deformability S. For $S = -0.9$, $S = -0.5$, $S = 0$, $S = 0.5$, $S = 0.9$

$$a_1 = \left(\frac{V_0 q_0 \left(1 - S^2\right)^2}{2mk_B T}\right) \left\langle \left(\frac{\sin\left(q_0 x\right)}{\left(1 + S^2 - 2S\cos\left(q_0 x\right)\right)^2} \right)^2 \right\rangle_0, \tag{19}$$

$$a_2 = \left(\frac{V_0 q_0^2 \left(1 - S^2\right)^2}{2m^2 a_1}\right) \left[\left\langle \left(\frac{\cos\left(q_0 x\right)\left(1 + S^2 - 2S\cos\left(q_0 x\right)\right) - 4S\sin\left(q_0 x\right)^2}{\left(1 + S^2 - 2S\cos\left(q_0 x\right)\right)^3} \right)^2 \right\rangle_0 \right.$$
$$\left. - \left\langle \left(\frac{\cos\left(q_0 x\right)\left(1 + S^2 - 2S\cos\left(q_0 x\right)\right) - 4S\sin\left(q_0 x\right)^2}{\left(1 + S^2 - 2S\cos\left(q_0 x\right)\right)^3} \right) \right\rangle_0^2 \right]. \tag{20}$$

The ensemble averaging ($< \ldots >$) is calculated from the equilibrium distribution of Boltzmann by using the continued fraction expansion method. Then, we can easily calculate the dynamic conductivity $\sigma(\omega)$ as a function of oscillation frequency ω. In the following, we present and discuss qualitatively the motion of particles for large friction, i.e., for $\Gamma = 2\pi\gamma/\omega_0 >> 1$, where $\omega_0 = q_0(1 + S/1 - S)\sqrt{V_0/2m}$ is the characteristic frequency for vibration at the bottom.

Figure 2 shows the variation of dynamic conductivity as a function of the frequency for different positive values of S in the limit of high friction limit. For the parameter of deformability $S = 0$ the specter of $\sigma(\omega)$ is dominated by an oscillator peak situated at frequency around $\omega = 1, 2\omega_o$. In this situation, the particle spends the most part of the time by making small-amplitudes oscillations around the well bottoms, and sometimes is activated and makes a jump from a well to another [12]. For the other values of S, the conductivity $\sigma(\omega)$ behaves differently, as was seen on the figure 2. Indeed, for $S = 0.5$, the peak around $\omega = 1, 2\omega_o$ becomes less pronounced and is shifted towards higher frequencies. While for $S = 0.9$, the oscillatory peak is completely suppressed and the conductivity is enhanced for frequencies between 0 and $\omega = 1, 2\omega_o$, indicating that for this structure of periodic potential the motion is essentially diffusive.

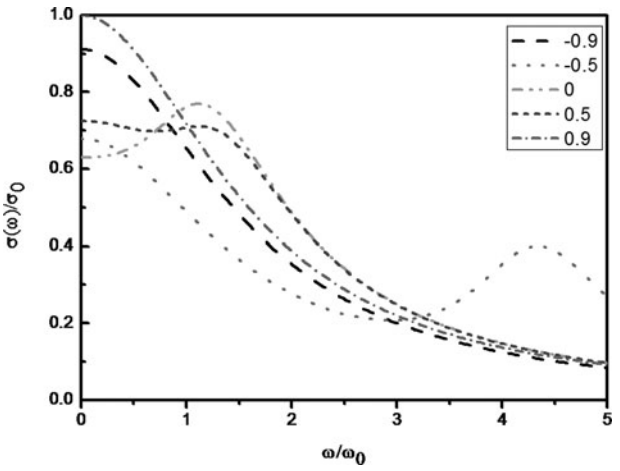

Figure 2. Dependence of dynamic conductivity $\sigma(\omega)$ .with the frequency ω for different values of the parameter of deformability S. The other parameters are $\Gamma = 7$, T = 300 K.

In figure 3, we have reported the variation of dynamic conductivity as a function of the frequency for different negative values of S. Thus, for $S = -0.5$, the position of the oscillatory peak is shifted to higher frequencies. It is situated at frequency around $\omega = 4, 5\omega_o$. Further, the central peak $(\omega = 0)$ is relatively intense, indicating that the displacement of the mobile particle is assured by oscillations and diffusive motions. While for $S = -0{,}9$, the spectrum of the dynamic conductivity is dominated by the central peak, reflecting that the motion is essentially diffusive inside the unit cell (cf. Figure 1).

In order to compare the behavior of the dynamic conductivity for the negative and positive values of S, (in particular for $S = 0.5$ and $S = -0.5$) the corresponding results have been reported in figure 4. From this figure, we can deduce that the dynamic conductivity exhibits two opposite behaviors. Indeed, at low frequency, the diffusive regime corresponding to the positive value of $S = 0.5$, seems more important than the one of negative value of $S = -0.5$. This behavior was reversed in the case of high frequency.

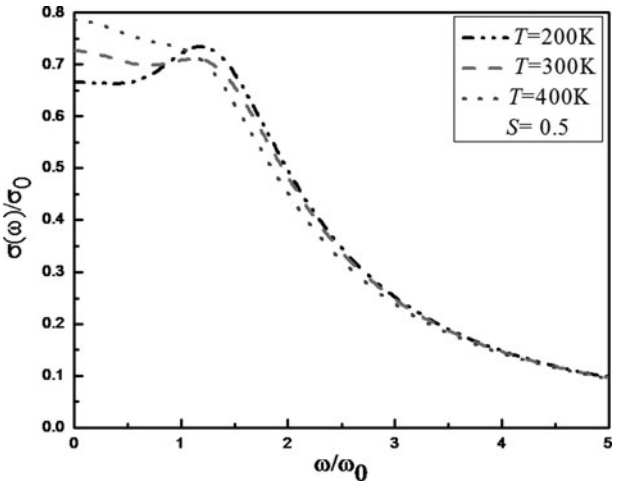

Figure 3. Dependence of dynamic conductivity $\sigma(\omega)$ with the frequency ω for different values of *T*. The other parameters are $\Gamma = 7$ and the parameter of deformability $S = 0.5$.

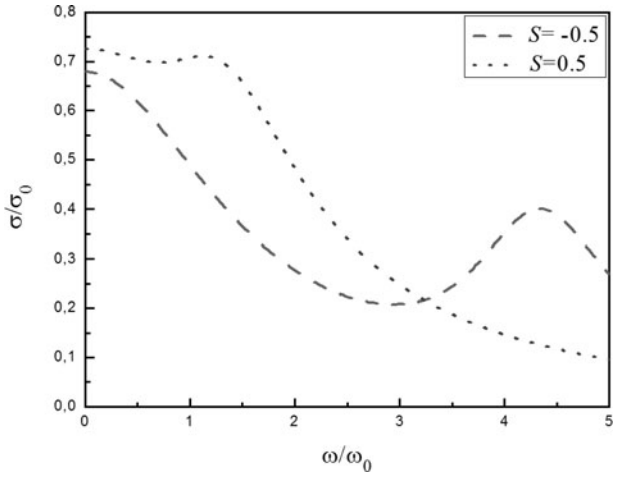

Figure 4. Dependence of dynamic conductivity with the frequency for different values of the parameter of deformability. The other parameters are $\Gamma = 7$, T = 300 K.

Finally, in figure 5 we studied the behavior of $\sigma(\omega)$ as a function of frequency for different values of the temperature and for selected value of S ($S = 0.5$). The transition from the oscillatory to the diffusive regime is clearly observed, as the temperature increased. Indeed, at low temperature $T = 200$ K a relatively important peak appears approximately at the frequency $\omega = 1, 2\omega_o$. While, at high temperature $T = 400$ K, the spectrum is dominated by a central peak, reflecting the diffusive motion of the particle over the potential barrier.

4. Conclusion

This work describes the Fokker-Planck dynamics of a Brownian particle subject to a non sinusoidal Remoissenet-Peyrard potential (RPP). The Fokker-Planck equation is solved numerically by using the continued fraction expansion method. On the one hand, we studied the

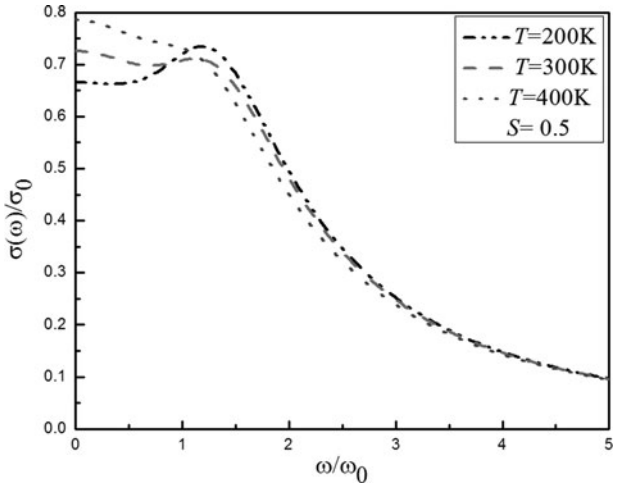

Figure 5. Dependence of dynamic conductivity with the frequency for different values of T. The other parameters are $\Gamma = 7$ and the parameter of deformability.

behavior of dynamic conductivity as a function of frequency for various shapes of the periodic potential. The obtained results shown that the diffusion process is more important for the positive values of *S*. This property was weakened in the case of negative values of *S*. On the other hand, we treated the temperature effect on dynamic conductivity behavior. The results show that by increasing the temperature, a transition from oscillatory regime to the diffusive regime can be observed in this model of Remoissenet-Peyrard potential.

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