Diffusion in Inhomogeneous Systems: Self-Consistent Random Phase Approximation

L. EL arroum, M. Chhib, M. Mazroui and Y. Boughaleb*
Laboratoire de Physique de la Matière Condensée. Faculté des sciences
Ben M'sik, BP 7955,Casablanca, Morocco

The classical diffusion of particles in an inhomogeneous periodic system is studied employing the Fokker-Planck equation. The full width at half-maximum (fwhm) of the quasielastic peak in the dynamic structure factor S(**q**,ω) is calculated numerically by the matrix continued fraction method up to large values of the momentum transfer covering several Brillouin zones. It is shown that fwhm exhibits strong oscillations with the scattering wave-vector **q** as it has been observed in β-Ag_2S by the mean of neutron scattering.

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I. INTRODUCTION

The diffusion problem in a periodic medium has been extensively studied in connection with surface kinetic phenomena and transport processes in microelectronic devices [1,2]. If the particles are sufficiently massive the problem can be treated within a classical approach. From this point of view the analytical method consists in the solution of some kind of Fokker-Planck equation with an external field [3,4]. The stochastic theory based on the Fokker-Planck equation is able to describe different diffusion mechanisms. Quasi-continuous diffusion and hopping mechanism (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 times scales. The most statistical information about the diffusing particles is contained in the dynamic structure factor $S(\boldsymbol{q},\omega)$, which is proportional to the quasi-elastic scattering intensity both in neutron and in atom scattering experiments [5,6]. It is defined as Fourier transform of density-density correlation function:

$$\boldsymbol{S}(\boldsymbol{q},\omega)=\frac{1}{2\pi \boldsymbol{N}}\int_{-\infty}^{+\infty}\boldsymbol{dt}\exp(\boldsymbol{i}\omega\boldsymbol{t})\langle\rho_{-\boldsymbol{q}}(0)\rho_{\boldsymbol{q}}(\boldsymbol{t})\rangle \qquad (1)$$

Where

$$\rho_{\boldsymbol{q}}(\boldsymbol{t})=\int \boldsymbol{d}^3\boldsymbol{r}\exp(\boldsymbol{iqr})\sum_i \delta(\boldsymbol{r}-\boldsymbol{r}_i(\boldsymbol{t})) \qquad (2)$$

The half width at half maximum (hwhm) of the quasi-elastic peak of $S(\boldsymbol{q},\omega)$, at small momentum transfer $\hbar\boldsymbol{q}$ is proportional to the diffusion constant, while its behaviour at larger $\hbar\boldsymbol{q}$ depends on the diffusion mechanism. Much work has been devoted to the calculation of the diffusion coefficient in the presence of a periodic potential. The purpose of this work is to study diffusion processes of interacting Brownian particles in relation with superionic conductors. These materials can be modelled [3,4], in first approximation, as a distribution of particles evolving in a periodic potential, either through a host lattice or on a substrate. These studies will be treated by using the generalized Fokker-Planck equation.

II. FOKKER-PLANCK APPROACH

In the theory of Brownian motion , the particles are subject to three forces: two deterministic forces, derived from the potential $V(\boldsymbol{r})$, a friction force (γ is the friction coefficient) and a white noise, related to the friction via the fluctuation dissipation theorem. In these conditions, the phase-space probability density satisfies a Fokker-Planck equation given by[7]:

$$\frac{\partial \boldsymbol{f}}{\partial \boldsymbol{t}}=\sum_i[-\boldsymbol{v}_i\frac{\partial}{\partial \boldsymbol{r}_i}-\frac{\boldsymbol{F}_i(\boldsymbol{r})}{m}\frac{\partial}{\partial \boldsymbol{v}_i}+\gamma\frac{\partial}{\partial \boldsymbol{v}_i}(\boldsymbol{v}_i+\frac{k_BT}{m}\frac{\partial}{\partial \boldsymbol{v}_i})]\boldsymbol{f} \qquad (3)$$

where $f(\boldsymbol{r},\boldsymbol{v},t)d\boldsymbol{r}d\boldsymbol{v}$ is the probability of finding the particle in the phase space element between $(\boldsymbol{r},\boldsymbol{v})$ and $(\boldsymbol{r}+\boldsymbol{dr}, \boldsymbol{v}+d\boldsymbol{v})$, T is the temperature and k_B is the Boltzman's constant. The total force acting on particle i is derived from the potential $V(\boldsymbol{r})$:

$$F(\boldsymbol{r})=-\frac{\partial V(\boldsymbol{r})}{\partial r_i}$$

where

$$V(\boldsymbol{r})=\sum_i V^1(\boldsymbol{r}_i)+\frac{1}{2}\sum_{I\#J}V^2(\boldsymbol{r}_i-\boldsymbol{r}_j) \qquad (4)$$

$V(\boldsymbol{r})$ contains the lattice constant V^1 originating from the host ions and the pair interactions V^2. The Fokker-Planck equation is applicable to a general situation of many-particle diffusion in a periodic medium. Two cases of Eq.(3) deserve special attention. The first is for vanishing pair interaction one obtains a single Fokker-Planck equation including an external potential. This problem is treated by the matrix continuated fraction method [7]. The second is the homogeneous Brownian fluid obtained by setting $V^1=0$ which is particularly important for understanding the dynamic properties of macromolecular solutions.

III. METHOD OF CALCULATION

A. SELF-CONSISTENT RANDOM PHASE APPROXIMATION (SCRPA)

In inhomogeneous systems, contrary to the homogeneous ones, the translation symmetry of the

* Yboughaleb@yahoo.fr

problem is lost and the transition probability is invariant only under discrete lattice translations. In Fourier space, the two-particle correlation functions depend on two momentum variables and their equations of motion are matrix equations with respect to summations over reciprocal lattice vectors $\boldsymbol{k}$. In this paper we confine ourselves to the self-consistent random phase approximation (SCRPA) [8], which neglects memory effects. Within this approximation, one shows [9] that the dynamic susceptibility $\chi(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}')$ obeys the equation (5)

$$\chi(\boldsymbol{q}+\boldsymbol{k}1,\boldsymbol{q}+\boldsymbol{k}',\omega)=\sum_{k_1}\left[\delta(\boldsymbol{k}-\boldsymbol{k}1)+\sum_{k_2}\chi_{eff}(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}2,\omega)\bar{V}2(\boldsymbol{q}+\boldsymbol{k}2,\boldsymbol{q}+\boldsymbol{k}1)\right]\chi_{eff}(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}',\omega) \quad (5)$$

Whose solution can be written in matrix notation as

$$\chi=\left[I+\chi_{eff}\bar{V}2\right]^{-1}\chi_{eff} \quad (6)$$

It is important to note that the interaction enters in two ways. First, one has to solve for the dynamic susceptibility χ_{eff} of a one-particle problem. Second, one obtains a mean field, which is determined by the effective pair interaction

$$\bar{V}2(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}')=-\boldsymbol{k}_B T c(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}') \quad (7)$$

where $c(\boldsymbol{q}+\boldsymbol{k},\ \boldsymbol{q}+\boldsymbol{k}')$ are the Fourier components of the direct correlation function $c(\boldsymbol{r},\boldsymbol{r}')$. Since detailed information on the static quantities is lacking even for model systems, we have to confine discussion in the low temperatures regime, where $k_B T$ is much smaller than the barrier height V_o. According to this assumption we retain only the lowest band characterised by the index $_{\text{o}}$, in the representation of the susceptibility χ_{eff} in terms of eigenfunctions and eigenvalues for the effective single-particle problem:

$$\chi_{eff}(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}',\omega)= \boldsymbol{M}_o(\boldsymbol{q}+\boldsymbol{k})\boldsymbol{M}_o^*(\boldsymbol{q}+\boldsymbol{k}')\frac{\lambda_{eff}(\boldsymbol{q})}{-i\omega+\lambda_{eff}(\boldsymbol{q})} \quad (8)$$

with $M_o(\boldsymbol{q}+\boldsymbol{k})=\langle \boldsymbol{q},0/\exp[i(\boldsymbol{q}+\boldsymbol{k})\boldsymbol{r}]/0,0\rangle$

The matrix inversion in equation (6) is now immediately performed to give

$$\chi(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}',\omega)= \boldsymbol{M}_o(\boldsymbol{q}+\boldsymbol{k})\boldsymbol{M}_o^*(\boldsymbol{q}+\boldsymbol{k}')\rho\beta\frac{\lambda_{eff}(\boldsymbol{q})}{-i\omega+\lambda_{eff(q)}(1+\rho\beta\omega(\boldsymbol{q}))} \quad (9)$$

with

$$\omega(\boldsymbol{q})=-k_B T\sum_{k,k'}\boldsymbol{M}_o^*(\boldsymbol{q}+\boldsymbol{k})c(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}')\boldsymbol{M}_o(\boldsymbol{q}+\boldsymbol{k}')$$

In addition we put $\boldsymbol{M}_o(\boldsymbol{q}+\boldsymbol{k})=1$. This means that due to the strong localisation of the particles the Wannier functions are simply replaced by δ-functions. Then the susceptibility becomes independent of k and k'. Thus we define $\chi(\boldsymbol{q}+\boldsymbol{k},\boldsymbol{q}+\boldsymbol{k}',\omega)=\chi(\boldsymbol{q},\omega)$, which is found to be fitted by the poten

$$\chi(\boldsymbol{q},\omega)=\rho\beta\frac{\lambda_{eff}(\boldsymbol{q})}{-\boldsymbol{i}\omega+\dfrac{\lambda_{eff}(\boldsymbol{q})}{\boldsymbol{S}(\boldsymbol{q})}} \quad (10)$$

where $S(\boldsymbol{q})$ is the static structure factor of inhomogeneous system. We recall that the dynamic structure factor S($\boldsymbol{q}$,ω) is given by:

$$S(\boldsymbol{q},\omega)=\frac{k_B T}{\rho\pi\omega}\mathrm{Im}\chi(\boldsymbol{q},\omega)=\frac{1}{\pi}\frac{\lambda_{eff}(\boldsymbol{q})}{\omega^2+\left[\dfrac{\lambda_{eff}(\boldsymbol{q})}{S(\boldsymbol{q})}\right]^2} \quad (11)$$

Where the quantity

$$\lambda(\boldsymbol{q})=\frac{\lambda_{eff}(\boldsymbol{q})}{S(\boldsymbol{q})} \quad (12)$$

is the full width at half-maximum of the quasi-elastic line of $S(\boldsymbol{q},\omega)$. It contains valuable information about the interaction and can provide a good indication of the dynamical correlation effects in the system, therefore, it characterises the diffusion process. The computation of this quantity requires the knowledge of effective potential from which it may be obtained. Here, by using the Langevin dynamic simulation for a one dimensional system, we have calculated the effective potential of a system of strongly interacting Brownian particles through a Fenkel-kontorova potential [10,11]. This potential can tail function:

$$V_{eff}(x)=E_1\cos(q_o x)+E_2\cos(2q_o x) \quad (13)$$

The potential depends on two parameters E_1 and E_2. The numerical values of E_1 and E_2, which give the best fit with numerical data, are (see figure 1):
$E_1=43{,}44\times10^{-6}$ and $E_2=54{,}51\times10^{-6}$.

B. MATRIX CONTINUED FRACTION METHOD

The Fokker-Planck equation cannot be analytically solved in every regime, i.e at every friction and at every value of the potential barrier. A numerical method of solution, the matrix continued fraction method, has been developed by Risken [7]; the method, extended to the very general case of a position-dependent friction, has been already explained elsewhere [12-14] with much detail; the procedure is rather heavy and tedious, so here only the final results are recalled. The result of the dynamic structure factor corresponding to $\lambda_{eff}(q)$ can be expressed in terms of a matrix continued fraction:

$$S_{eff}(q,\omega)=N\,\mathrm{Re}\left[\sum_{p,r=-\infty}^{\infty}\tilde{G}_{pr}(k,i\Omega)I_{p-l}(g)I_{r-l}(g)\right] \quad (14)$$

where N is a normalisation factor, I_r a modified Bessel function, $q=2\pi a^{-1}(k+l)$, $|k|<1/2$ and l is an integer.

Defining the following dimensionless quantity $\Omega=(2\pi)^{-1}a\omega\,(m/k_BT)^{1/2}$,the Green function G is given by: in the case of the potential (Eq.13), are given by:

$$\tilde{G}(k,i\Omega)=$$
$$[i\Omega I+B_+[(i\Omega+\gamma)I+2B_+[(i\Omega+2\gamma)I+....]B_-]B_-]^{-1}$$

where I is the identity matrix and the matrices $B^{\pm}$ in the case of the potential (Eq.13), are given by:

$$B^{+}_{pr}(k)=(p+k)\delta^{p,r}+g_1\left(\delta^{p,r-1}-\delta^{p,r+1}\right)+ g_2\left(\delta^{p,r-2}-\delta^{p,r+2}\right)$$

$$B^{-}_{pr}(k)=(p+k)\delta^{p,r}-g_1\left(\delta^{p,r-1}-\delta^{p,r+1}\right)- g_2\left(\delta^{p,r-2}-\delta^{p,r+2}\right) \quad (15)$$

where
$g_1=E_1/4k_BT$; $g_2=E_2/2k_BT$

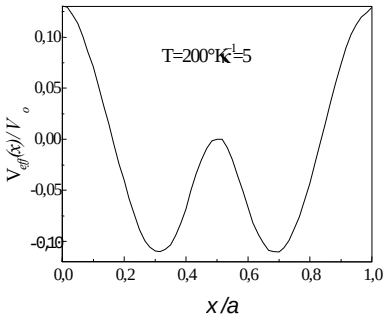

FIG.1: The normalized effective potential assumed In the text for qualitative considerations

Eq.(14) 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. Problems in the computing time needed to get a good convergence can arise only at really extreme values of the parameters involved. The solution given here, being valid for every periodic potential shape and friction, is quite general.

IV. CONCLUDING REMARKS

The effective half-width $\lambda_{eff}(q)$ at half maximum of the quasi-elastic peak of $S(q,\omega)$, presented in figure 2 as a function of the wave-vector q of the non interacting systems, is clearly not periodic. This indicates that the dynamics cannot be described even approximately any discredited jump model. In Figure 3, we report the variation of $\lambda(q)$ as a function of q of inhomogeneous systems (eq.9). The interesting features of this result with respect to the one presented in fig.2 are the strong oscillations of $\lambda(q)$ with q. The function $\lambda(q)$ presents some relative minima at $q's$ which coincide with the maxima of the static structure factor of the inhomogeneous system especially at $q_1=2q_o/3$ and at the modulation peak [15]. This behaviour is similar to De Gennes narrowing.

The physical base for such phenomena is that peaks in $S(q)$ occur at wave-vectors which correspond to the most probable arrangements of the ions resulting from high correlation. These arrangements are long lived because of the cooperative motions necessary for the ions to break them up and to establish other configurations with different interionic spacing. In spite of this structure, the diffusion process is far from being simply liquid-like.
In effect, the (hwhm) exhibits also minima at Bragg peaks q_o and $2q_o$ and relative maxima at $q_o/2$ and $3q_o/2$.

This behaviour reflects strongly the correlated account of the entire behaviour of $\lambda(q)$, we conclude that the most probable diffusion process consists of a superposition of both liquid-like and correlated hopping motions.

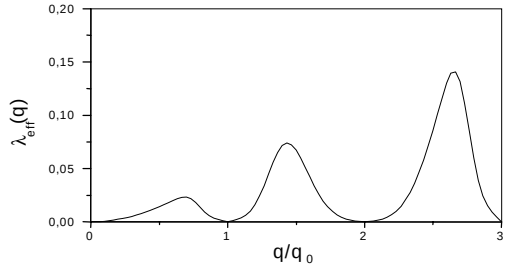

FIG 2:The effective half-width at half-maximum of the quasielastic peak of $S(q,\omega)$ as a function q/q_0 for non interacting systems. Parameters are $Vo=0.1\ eV$, $T=200°K$.

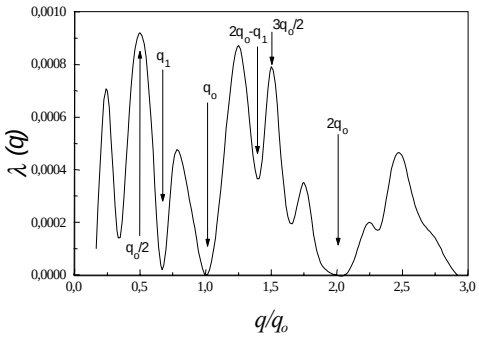

FIG.3: The same as figure 2, but here for an inhomogeneous system. The function $\lambda(q)$ shows a complicated structure with respect to the one corresponding to non - interacting systems.

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