

CORRELATION EFFECTS ON IONIC MOTION IN FRAMEWORK SOLID ELECTROLYTES

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We investigate the static and dynamic properties of a one-dimensional system composed of Brownian particles subject to a periodic potential by using Langevin dynamics simulation. In addition to different types of interaction between the mobile particles, we study the effect of the coupling of the diffusing particle with the crystalline cage. For each kind of interaction potential, we also discuss how the bulk frequency-dependent conductivity is affected by the correlated motion of the particles.

1. INTRODUCTION

Framework solid electrolytes can be thought of as a mobile sublattice of one type of ions diffusing through a rigid framework. The activation energy required for the mobile ions to diffuse is far lower than that found in ordinary ionic solids. Therefore, the probability for finding an ion between preferred lattice sites becomes significant. Beyeler [1] has shown from analysis of the X-ray scattering in K-hollandite that some ions are displaced from the minima of the single particle potential as the result of interionic repulsion. This clearly affects the transport properties, and therefore a fully dynamic calculation is required to examine the mechanistic details of the ionic motion, since hopping models do not permit ions to be present except at lattice sites [2]. Most analytical investigations of dynamical, as opposed to hopping models have been performed in the high friction limit, which is unrealistic for most real framework electrolytes, in which the finite width of vibrational lines shows that the damping is relatively weak [3]. In this paper, we use Langevin dynamics simulation to investigate

dynamical behavior and the diffusion mechanics for a one-dimensional model of framework electrolytes for different interaction potentials. We focus on the frequency-dependent conductivity, which reflects the dynamical collective behavior of the ions for different stoichiometries.

2. MODEL AND GENERALITIES

(a) The model

We assume that the mobile ions perform a Brownian motion in a periodic potential provided by the rigid framework. The interaction of a mobile ion with the static lattice can be represented by a periodic potential:

$$V_1(x_i) = -(A/2)\cos(2\pi x_i/a) \quad (1)$$

where A is the barrier height and a is the lattice spacing. In a real system, the ions of the framework vibrate around their equilibrium positions, giving rise to two phenomenological forces: the dissipative force $-m\dot{x}$ and the random force $R(t)$. The continuous motion of the diffusing ion i is described by the Langevin equation:

$$m_i \ddot{x}_i = -m_i \gamma \dot{x}_i - \nabla_i V_{TOT}(\{x_i\}) + R_i(t) \quad (2)$$

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where m_i , x_i , v_i are respectively the mass, the position, and the velocity of the ion i ; γ represents the friction coefficient. The random force is assumed to have a white noise spectrum:

$$\langle R_i(t) \rangle = 0 \quad (3a)$$

$$\langle R_i(t)R_j(0) \rangle = 2m\gamma k_B T \delta_{ij} \delta(t) \quad (3b)$$

In what follows we use also the dimensionless quantity

$$\Gamma = \frac{2\pi\gamma}{\omega_0} \quad (3c)$$

where

$$\omega_0 = \frac{2\pi}{a} \left(\frac{A}{2m} \right)^{1/2} \quad (4)$$

is the vibration frequency of a single particle at the bottom of the well. Assuming pair interactions, the total potential energy may be written as:

$$V_{TOT}(\{x\}) = \sum_{i=1}^N V_1(x_i) + \sum_{i,j>1} V_2(x_i - x_j) \quad (5)$$

where $\{x\}$ denotes the configuration of the system in real space $\{x\} = \{x_1, x_2, \dots, x_N\}$, and $V_2(x_i - x_j)$ represents the pair potential. The pair potential V_2 consists of several contributions. Since the mobile particles are charged, coulomb interaction potentials seem most appropriate. But in such mixed conductors as α -Ag₂S [4a] or α -Ag₂Se the long range interaction cannot occur because of the electronic screening (a screening radius for α -Ag₂Se has been calculated on the basis of Debye-Hückel theory, and found to be of the order of the silver-silver nearest-neighbor distance [4b]).

Detailed analytical studies [2,5] have been completed in the high friction limit $\gamma \gg \omega_0$ using the Smoluchowski equation. More generally the dynamical properties of the system have been derived using a continued fraction truncated at a certain order. However, the accuracy of this approximation

drops with decreasing friction. In the low friction limit, a higher order fraction is necessary and no analytical solutions are then available in the presence of V_2 . By solving numerically N -coupled Langevin equations (eq. 2), one can [6] follow the trajectories of the particles (position vs time) in order to obtain qualitative information about the diffusion mechanism, and quantitative results for frequency-dependent transport properties.

(b) Conductivity

The physical quantities which characterize the dynamics of the mobile sublattice and those of a tagged particle, can be expressed in terms of correlation functions [7]. For example, frequency-dependent conductivity (for unit cross-sectional area) $\sigma(\omega)$ is given by the Fourier transform of the velocity-velocity correlation function:

$$\sigma(\omega) = \frac{Q^2}{k_B T L} \int e^{i\omega t} \sum_{i,j} \langle v_i(t)v_j(0) \rangle_0 dt \quad (6)$$

where L is the chain length and Q the ion charge; $\langle \dots \rangle$ represents the average with respect to the equilibrium distribution and $k_B T$ the thermal energy.

(c) Static quantities

The static properties of the system are drastically affected by interactions among the diffusing ions. Experiments performed on one-dimensional ionic conductors β -eucryptite [8] and potassium hollandite [1] showed pronounced structures in the liquid structure function $S(q)$ due to short-range correlation between the conducting ions. If the interaction is very strong, it creates an almost regular arrangement of the ions of the mobile sublattice: such situation affects significantly the transport properties, which can then become liquidlike [6c].

The static quantities of greatest interest are the one particle density $\rho(x)$ and the two-particle density $\rho^{(2)}(x,x')$ defined as follows:

$$\rho(x) = \sum_i \langle \delta(x-x_i) \rangle \quad (7)$$

$$\rho^{(2)}(x,x') = \sum_{i \neq j} \langle \delta(x-x_i) \delta(x'-x_j) \rangle .$$

We also define the pair correlation function $g(x,x')$ which is related to $\rho^{(2)}(x,x')$ by:

$$\rho^{(2)}(x,x') = \rho(x)g(x,x')\rho(x') \quad (8)$$

The pair correlation function $g(x,x')$ reflects the static correlations between the mobile ions due to V_2 . In inhomogeneous systems such as ours, the explicit dependence of $g(x,x')$ on both x and x' has to be considered: this makes it a very difficult quantity to derive analytically [9]. The mutual repulsion of the diffusing ions induces an effective single-particle potential which can have a completely different shape from the bare framework potential V_1 (Eq. 1). At equilibrium the one-particle density probability can be represented as ($\beta = 1/k_B T$):

$$\rho(x) = \text{const} \exp \{-\beta[V_1(x) + \int dx' V_2(x,x') \rho(x') g(x,x')]\} \quad (9)$$

In formal analogy to non-interacting particles, Eq. (9) can be written in the form [10,11]

$$\rho(x) = \text{const} \exp [-\beta V_{\text{eff}}(x)] \quad (10)$$

where $V_{\text{eff}}(x)$ is the effective single particle potential given by

$$V_{\text{eff}}(x) = V_1(x) + \int dx' V_2(x-x') \rho(x') g(x,x') \quad (11)$$

The barrier height of the effective potential can be very useful in interpreting the transport properties of the system. In particular, in the high-friction limit of the one-dimensional case, it can be interpreted as an activation energy.

3. NUMERICAL RESULTS AND DISCUSSION

In this section we focus on the effects of the interionic interaction in both static and

dynamic properties, using numerical simulations based on the solution of N -coupled Langevin equations (eq. 2) with periodic boundary conditions.

It has been demonstrated previously that the ion-ion interaction alters significantly the transport properties. Depending on the strength of the interaction V_2 compared to the barrier height A , its range, the density of the mobile ions and the coupling of the diffusing ions with the framework represented by the friction coefficient γ , different diffusion mechanisms are to be expected. To compare our result with the analytical one already available, we consider first a short range interaction potential between the mobile ions.

(a) Hard-Core Potential

Many investigations of the effect of the interionic interaction have been done using short range interaction in both continuous and lattice gas models [12,13]. One then assumes that the pair potential has the following form:

$$V_2(x) = B(b/x)^n \quad (12)$$

where $n \geq 2$, b is the interaction diameter, B and A are taken of the same order, so that the effect of V_2 is relatively weak unless the particles occupy the same lattice site. For heavily damped particles, solution of the Langevin equation yields good agreement with the analytical results of [12,13]. In particular the conductivity is seen to be a nonmonotonic function of the interaction diameter b .

To extend this study to the realistic cases of intermediate and low friction, the Langevin equation (2) must be solved. It is known both for continuous dynamics [14a] and for lattice gas models [14b] that in the underdamped regime, the diffusion of a single particle subject to a periodic potential is faster than that predicted by classical rate theory. This results from the fact that the mean free path

can be larger than the lattice spacing a if the relation

$$\frac{\pi \gamma A}{\omega_0 k_B T} \ll 1 \quad (13)$$

is satisfied. In this limit, the thermalization of the particle requires a time far exceeding one oscillation period, so diffusive jumps exceeding a in length can be observed, and mobile ions can exhibit both oscillatory and quasifree behavior [15,16].

When the interaction potential (Eq. 12) is switched on, the barrier height of the effective potential decreases and goes through a minimum (exact equality is obtained for large n) at $b \sim a/4$. This arises from a double occupancy effect: when one particle enters an occupied site (which is possible because of the short range of V_2), it pushes the occupying particle toward the top of the well: the activation energy required by either particle to perform a jump is then smaller than A .

Figure 1 shows the bulk conductivity $\sigma(\omega)$ with and without the interaction V_2 for small

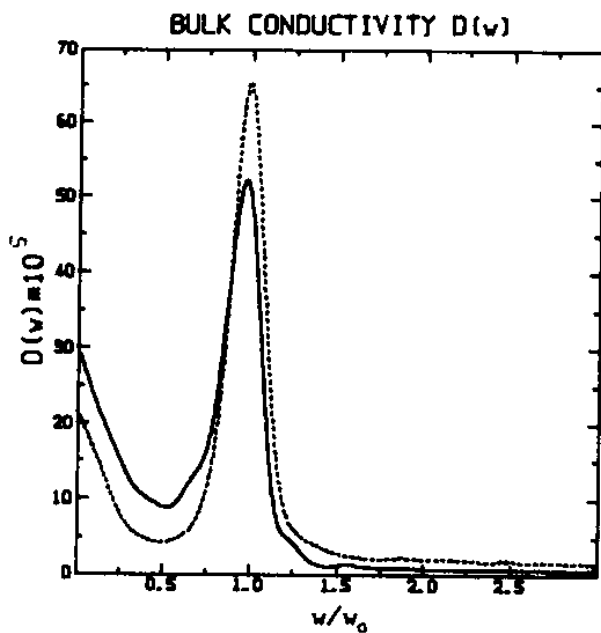


FIGURE 1

Bulk frequency dependent conductivity $\sigma(\omega)$, for short-range repulsion. (—) with the interaction V_2 ($b=1/4$ and $n=7$) (···) without V_2 . $T=400K$, $\Gamma = 0.3$ (low friction regime), $A=1eV$.

friction $\Gamma = 0.3$ and $(A/k_B T) = 3$. The change of the shape of $\sigma(\omega)$ compared to the non-interacting particle system indicates that the forward scattering between the ions dominates the bounce-back effect. The computed d-c conductivity is enhanced by 50% with respect to the independent particle case, because, in part, of the important collective motion (e.g., the caterpillar mechanism [17] of the diffusing ions).

(b) Frenkel-Kontorova Potential

The Frenkel-Kontorova (FK) model has been used extensively in important work by Geisel [18] to investigate the static and dynamic features of certain one-dimensional conductors such as potassium hollandite.

When the interaction between the ions is strong enough, it tends to keep them separated by a distance $b = a/C$, where C is the concentration (ions/site). The expansion of the pair potential up to harmonic terms around the average interparticle distance then leads to the FK expression

$$V_2 = (\alpha/2) \sum_{i=1}^N (x_{i+1} - x_i - b)^2 \quad (14)$$

The model consists then of a harmonic chain, subject to a periodic potential $V_1(x)$ of equation 1. The force constant α is given by [18]:

$$\alpha = \frac{2\pi^2 \kappa^{-1} k_B T}{b^2} \quad (15)$$

where κ^{-1} is a correlation length (in units of b) which measures interaction strength. Within this model, Geisel has computed the frequency dependent conductivity from the Fokker-Planck equation by using a continued fraction expansion truncated at the third order. The many-body averages have been performed with the help of the transfer-integral technique. His results overestimate the effect of the friction on $\sigma(\omega)$. Geisel reported results for two high friction values: $\Gamma = 5$ and $\Gamma = 10$ (all the other parameters were kept unchanged). He

finds that the oscillatory peak is shifted to frequency larger than ω_0 and that this shift is strongly dependent on Γ . He also finds that the initial slope of the low frequency conductivity ($\omega \rightarrow 0$) associated with the commensurate case becomes negative. This modification of the frequency dependence of $\sigma(\omega)$ persists even for very small correlation length ($\kappa^{-1} = .1$). Our simulation studies are in disagreement with these results as detailed below.

To study commensurability effects in the dynamical behavior of the conducting ions, we have computed the bulk and the tracer frequency dependent conductivity for different friction regimes and several interaction strengths. As expected [6,18,19], our results show that the diffusive behavior is enhanced for incommensurate density ($C = .75$) and reduced for commensurate case ($C = .5$) compared to the case of non-interacting particles.

Figure 2 shows that the tagged particle

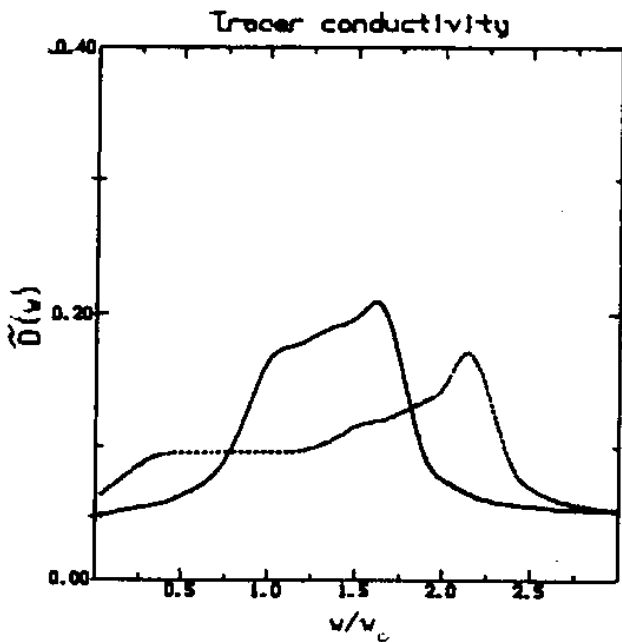


FIGURE 2

Tracer conductivity, $\tilde{D}(\omega) = D(\omega) / \langle v(0)^2 \rangle$ resulting from the FK interaction ($\kappa^{-1} = 3$), $\Gamma = 1$, $T = 600K$, $A = 1eV$. (—) commensurate case $C = .5$. (···) incommensurate case $C = .75$.

oscillates at some frequency ω which exceeds

ω_0 for large interaction between nearest-neighbor ions. This behavior holds for both commensurate and incommensurate densities. In contrast, the bulk conductivity shown in figure 3 presents an oscillatory peak near ω_0 for the commensurate case. (The small red shift is obtained at finite temperature because of the anharmonicity of the potential $V_1(x)$.) The position of this resonance structure does not depend on Γ , contrary to the results obtained by Geisel. Also Figure 3 shows that the ini-

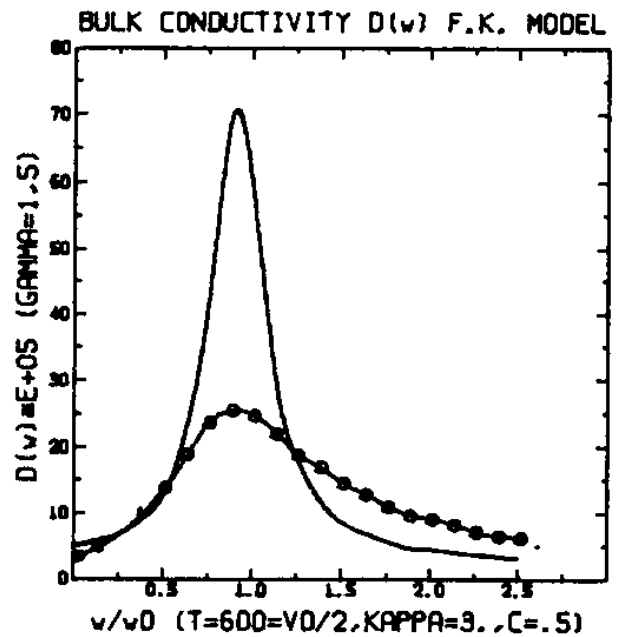


FIGURE 3

Frequency dependent conductivity for two regimes of friction: (—); $\Gamma = 1$ (low friction) and curve (o-o) for $\Gamma = 5$. $T = 600K$, $C = .5$, FK interaction $\kappa^{-1} = 3$. FK model.

tial slope in $\sigma(\omega)$ is positive, again in contradiction to Geisel's finding. The value of the friction affects the magnitude of the diffusion (conductivity) and the width (but not the position) of the oscillatory peak [20].

(c) Coulomb Potential

Due to its simplicity the FK model has been used extensively for the study of commensurate-to-incommensurate transition and for soliton-type motion when the particles interact strongly [20]. Although the FK model does

illustrate the essential features resulting from the interaction between the conducting ions in some high density solid electrolytes it is not obvious that the true coulomb type interaction between the ions of the mobile sublattice can be reproduced by an effective short range interaction.

Finally we consider a long range interaction model, taking the pair interaction potential to be

$$V_2(x_i - x_j) = (Q)^2/|x_i - x_j| \quad (16)$$

where the effective charge Q is expected to be less than the formal ionic charge because of screening effects [16].

The static properties have been evaluated to obtain information about the correlated motion of the ions in the presence of inter-ionic coulomb forces. We first consider commensurate stoichiometries ($C^{-1} = \text{integer}$), where the backward correlation dominates in the sense that when a particle at the equilibrium position tries to jump to the next site, the periodic potential and the coulomb interaction collaborate to restore the particle to its initial position [6a]. This results in a reduction of the d-c conductivity compared to the non-interacting particle system, and an activation energy exceeding A .

Figure 4 shows the tracer frequency dependent conductivity (the diagonal terms in eq.(6)) for a commensurate density $C = 0.5$ at low friction $\Gamma = 1$. A pronounced oscillatory peak appears at frequency larger than ω_0 . The position of the peak is shifted to higher frequencies when the effective charge of the carriers increases inducing an ordered configuration where occupied sites are separated by a vacancy. The pair correlation function $g(0,x)$ exhibits maxima at distances which are multiples of $2a$ (see [21]) indicating the strong order established by the mutual

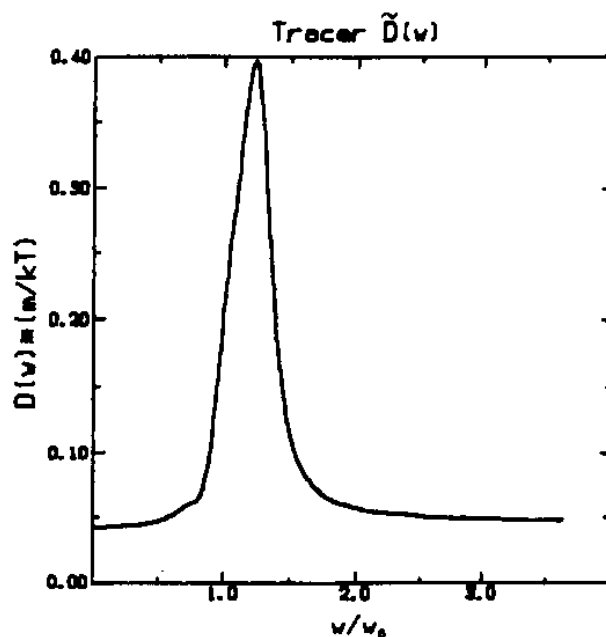


FIGURE 4

Tracer $\tilde{D}(\omega)$ with coulomb interaction. $C=0.5$, $Q=0.6$, $kT=0.1A$, $\Gamma=1$, $A=0.1eV$.

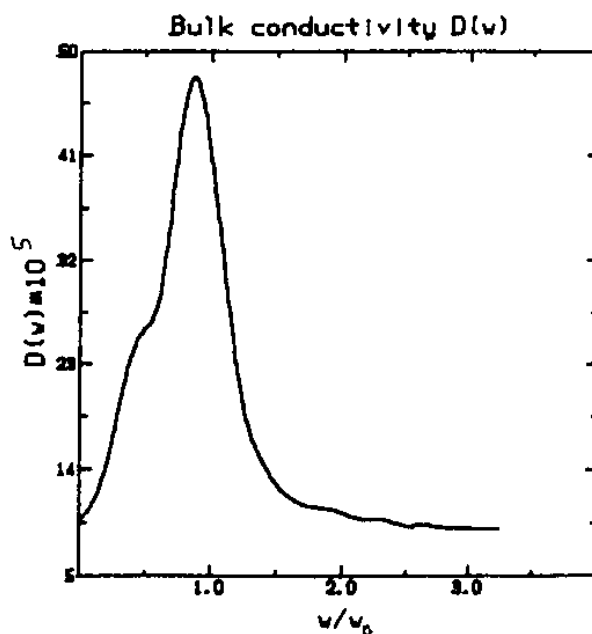


FIGURE 5

Bulk $D(\omega)$. $Q=0.6$, $C=0.5$, $T=500K$, $A=0.1eV$, $\Gamma=1$, D is related to $\sigma(\omega)$ by Einstein relation.

repulsion of the ions. The effective potential obtained directly from the density via eq. (10) shows a greater barrier height than A , expressing reduced diffusion of the ions in the

commensurate situation with respect to a non-interacting particle system. We have also computed the bulk frequency dependent conductivity from which one can extract information about the correlated motion of the ions (see Figure 5). Contrary to what one might expect, but as in the FK model discussed above, the oscillatory peak is found around ω_0 , and does not shift to higher frequencies when the effective charge of the ions is increased. This is because a strongly correlated motion of N particles of mass m in a field with force constant k may be viewed as motion of a particle of mass Nm with force constant Nk . Figure 6 shows the

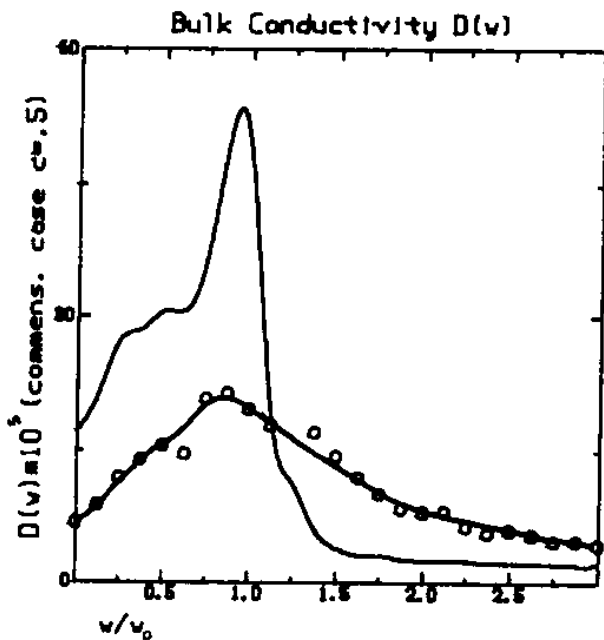


FIGURE 6

Bulk conductivity $C=0.5$. $Q=0.6$, $T=600K$, $A=1eV$. (—) low friction limit $\Gamma=0.3$, (o-o) is for the high friction $\Gamma=5$.

bulk conductivity $\sigma(\omega)$ for low and high friction. As in the FK case the position of the oscillatory peak is unchanged but it is sharper for the small damping coefficient. If temperature is substantially increased, the anharmonic regions become important, and the frequency peak drops slightly below ω_0 .

Turning now to incommensurate densities, $C = 0.75$, the coulomb interaction between the diffusing ions and the periodic potential compete for their own preferred spacing. As a consequence of this competition some ions are located near the top of the periodic potential in the ground state [6,22]. To determine the arrangement of the mobile ions, we computed the pair correlation function $g(x,x')$ which in this inhomogeneous case should depend explicitly on x and x' [1,6e,9]. It shows a formation of a group of ions (3 ions for the density $C = 0.75$) separated by a vacancy: the effective interaction between the vacancies tends to order them almost regularly. Beyeler et al. [23] have calculated the probability of having n ions between successive vacancies in potassium hollandite ($C = 0.77$); they found that $n = 2,3,4$ are highly probable. In Figure 7, we plot the

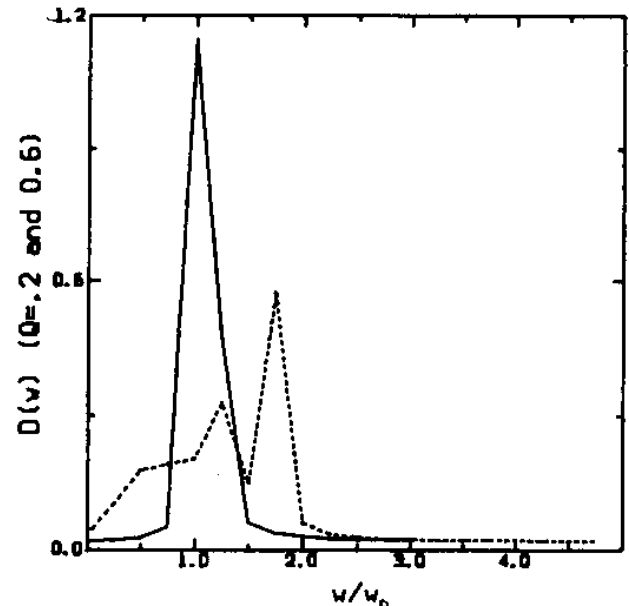


FIGURE 7

Tracer $D(\omega)$. $C=0.75$, $T=120K$, $A=1eV$, and low friction $\Gamma=0.3$. (—): $Q=0.2$ and (---): $Q=0.6$.

tracer conductivity for $C = 0.75$ and different effective charges; it shows two oscillatory peaks [6a] which reflect the possibility of finding the tagged particle in two completely different environments. The first peak

indicates the oscillatory motion of the ion near a vacancy and the second one is associated with the vibration of the ion at the bottom of the well surrounded by two ions shifted from the minima of the periodic potential. Like the commensurate case, the tagged particle oscillates at higher frequencies when the interaction between the ions increase. One should keep in mind that for this strongly interacting one-dimensional system, the ions are strongly correlated, which means that the contribution of the tracer diffusion to the bulk one is insignificant: the bulk conductivity comes almost entirely from the collective motion of the ions.

IV Comments

As has been observed elsewhere, for incommensurate coulomb systems, increasing the strength of the repulsion V_2 decreases the effective activation energy for ion hopping and therefore raises the ionic conductivity, which occurs by a liquid-like motion [3,6,18,19,21]. This can be seen from the bulk conductivity of Figure 8, which shows the shift in oscillator

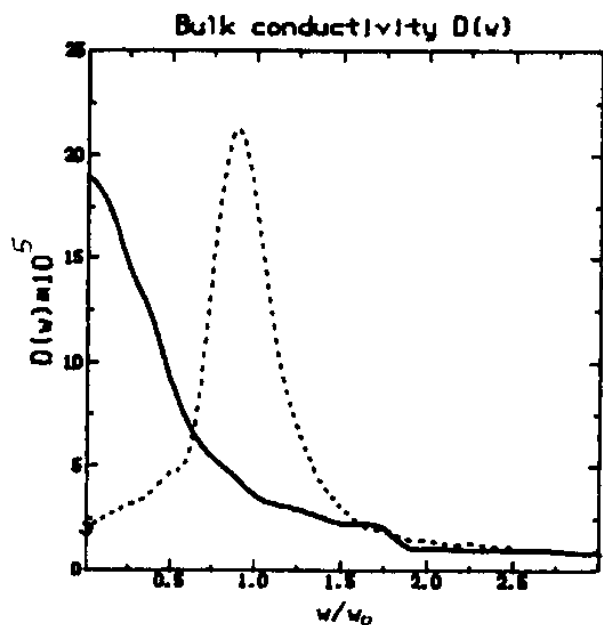


FIGURE 8

Bulk $D(\omega)$ for 2 strengths of interaction and low friction value $\Gamma=1$. $T=200K$, $A=.1eV$, $C=.75$. Curve (---): $Q=.3$ and curve (—) is for $Q=.6$.

strength from high to low frequency as V_2 increases. At high densities, where the ions interact strongly, the two basic motion aspects (diffusion and oscillation) have to be thought of as collective motion because of the overcorrelation existing in one-dimensional systems. The Haven ratio, which reflects the contribution of the individual particle to the overall properties, goes to zero as time goes to infinity: this situation is typical of one-dimensional systems.

ACKNOWLEDGMENTS

We are grateful to the NSF-MRL program and to AFOSR for partial support of this research (the former under grant #DMR-82-16972, through the Northwestern MRC)

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