

A stochastic Langevin dynamics study of correlated ionic motion in one dimensional solid electrolytes

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(Received 19 October 1979; accepted 30 November 1979)

The motion of mobile ions in one dimensional ionic conductors is described by stochastic Langevin dynamics. The interactions of the mobile ions with the framework lattice are approximated by a sum of periodic and random potentials, yielding a set of coupled Langevin equations, which are then solved numerically. The parameters in these phenomenological equations of motion include the potential in which the ion moves and the lattice temperature. Correlated motion is considered by including long range (Coulombic) and short range potentials among the mobile ions. Inclusion of these potentials in calculations describing systems with an integral ratio of total sites to mobile ions (commensurate stoichiometry) shifts the frequency dependent conductivity (increase of maximum frequency, decrease of dc conductivity) in a manner indicating that the mobile ions are driven towards their equilibrium positions. The conductivity then decreases with increasing effective charge. However, when the carrier/site ratio is not integral (incommensurate stoichiometry, e.g., potassium hollandite) the long range ion-ion interaction drives the mobile ions into arrays which are distorted near the vacancies. This lowers the effective potential barrier, and therefore is responsible for increasing the calculated diffusion coefficient and conductivity. As the strength of the ion-ion interactions is increased this cooperative behavior is enhanced. The results for potassium hollandite are in good agreement with x-ray scattering data.

I. INTRODUCTION

The ionic species in most solids are not mobile; however, in the so-called ionic conductors or solid electrolytes, the ionic mobility is several orders of magnitude greater than that detected in typical solids, and the ionic conductivity may exceed $10^{-3} (\Omega \text{ cm})^{-1}$. Since the ionic conductivity in these solids is often as great as the conductivity of electrolytic solutions, it is possible to build galvanic cells using these solid electrolytes. Thus, ionic conductors are useful for the construction of batteries and energy storage devices.¹ Interest in these energy related applications has stimulated research pertaining to solid electrolytes. Both macroscopic properties such as the power density and microscopic properties such as the fundamental nature of the ionic diffusion process need to be elucidated. This paper will deal with the latter.

One of the first models for diffusion of ions through a solid assumes that the mobile ions form a liquidlike sublattice.² The basis for this model is that the diffusion coefficient for the mobile ion is approximately that of a liquid. This oversimplified model neglects any relationship between the particular solid and the observed properties and is therefore not quantitatively useful. A more realistic picture postulates the existence

of several available equivalent sites (potential wells) with a sufficiently low potential energy barrier (i.e., $\approx k_B T$) to allow migration from site to site, i.e., the mobile ions diffuse in a periodic potential provided by the vibrating counterion sublattice. Many ionic conductors, such as the antimonates, β -gallates, and β -aluminas for which the immobile sublattice is strongly covalent, can be thought of as "framework conductors." Several workers^{3,4,5} have considered analytical solutions for the motion of independent carriers in these lattices. However, experiments measuring tracer diffusion and dc conductivity⁵ in β -alumina are not in agreement with random walk theory, demonstrating that coupling between mobile ions is an important factor in ionic conductivity. A simple Ising-like model for correlated motion of carriers has been provided by Sato and Kikuchi.⁶ Wang and co-workers^{7,8} have calculated the activation energy based on the differences between lowest and highest potential energy configurations. Both these calculations indicate that correlated mobile-ion motion has smaller activation energy than individual jumps, both for β -alumina and for RbAg_4I_5 . Moreover, the calculations of Wang indicate that long range Coulombic interactions are quite important for the dynamics of ionic motion.

Diffusion of interacting particles is a many body problem which is hard to solve analytically. A numerical approach would allow one to study ionic motion in solids more readily. We first note that the mass of the diffusing ions is usually large and that the relevant temperatures are high so the dynamics of the ionic motion can be treated classically. Molecular dynamics, which

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numerically solves Newton's equations of motion for several hundred interacting particles, has been successfully applied to some ionic conductors.^{9,10} For framework conductors, however, there is probably no need to include equations of motion for the lattice ions explicitly. The interaction between the mobile ions and the framework lattice can be represented by a sum of phenomenological forces: the equilibrium framework gives rise to a static periodic potential while the thermal motion of the lattice atoms may be represented by stochastic force and damping terms in the equations of motion of the mobile ions. These equations thus have the form

$$m\ddot{x}_i = f_{\text{lat}} + f_{\text{damp}} + f_{\text{int}} + R(t), \quad (1)$$

where f_{lat} , f_{damp} , f_{int} , and R denote the periodic force, the viscous damping force, the ion-ion interaction, and the thermal random noise, respectively.

In the stochastic dynamics approach¹¹ Eq. (1) is solved directly, yielding stochastic trajectories which are used to calculate desired observables. In comparison with the full molecular dynamics approach this method has both advantages and disadvantages. The advantages are as follows: (a) fewer interacting particles are included in the computation since the framework atoms are represented by the phenomenological forces; (b) high frequency lattice vibrations are not included in the calculation, and therefore the numerical integration of the equations of motion is easier; and (c) tests of approximate analytical solutions of models based on Eq. (1) may be easily completed. The main disadvantage lies in the phenomenological nature of Eq. (1), which for tractable choices of R and f_{damp} does not allow for polarization of the host lattice by the moving ions. When this effect is important the dynamics of the host lattice must be represented in greater detail. Either the full molecular dynamics approach or a Langevin dynamics approach incorporating dynamic coupling to lattice modes may be required. In framework systems this effect is small and stochastic dynamics provides a powerful tool for investigating diffusion and conductivity in such systems.

In this paper we present a Langevin-dynamic analysis of ionic conductivity in one dimensional model systems of framework type. In Sec. II we introduce the Langevin equation and discuss the single carrier limit. Interactions between carriers are included in Sec. III, where we present results of numerical studies for transport and structural properties in systems characterized by different stoichiometries. Some concluding remarks are presented in Sec. IV.

II. THE LANGEVIN EQUATION AND FRAMEWORK IONIC CONDUCTORS

It is useful to discuss ionic motion by comparison of the calculated frequency dependent conductivity with the result of two limiting forms of the Langevin equation of motion [Eq. (1)]. The first limit assumes that the mobile ion is purely diffusive; the ion-ion interaction potential and the periodic lattice potential are both zero. Equation (2) then describes simple Brownian motion¹²

$$m\ddot{x} = -m\Gamma\dot{x} + R(t). \quad (2)$$

Here m is the mass of the carrier, Γ is the damping coefficient, and $R(t)$ is the random force which is assumed to be a δ -correlated Gaussian random variable. The time correlation function of R and the damping coefficient Γ are related to each other by the fluctuation dissipation theorem¹³

$$\langle R(0)R(t) \rangle = \delta(t) 2m\Gamma k_B T.$$

Equation (2) is solved by letting $\dot{x} = v(t)$, multiplying each term by $v(0)$, and taking the ensemble average. We obtain

$$\frac{dg(t)}{dt} = -\Gamma g(t), \quad (3)$$

where

$$g(t) = \langle v(0)v(t) \rangle = \langle v(s)v(t+s) \rangle,$$

and where we have used the identities

$$\langle R(t)v(0) \rangle = \langle R(t) \rangle = 0.$$

The (frequency dependent) conductivity $\sigma(\omega)$ is related to the real part of the Laplace-Fourier transform of $g(t)$:

$$\sigma(\omega) = \frac{N(eZ)^2}{k_B T} \text{Re} \left[\int_0^\infty e^{-i\omega t} g(t) dt \right].$$

For the simple Brownian motion described by Eq. (2) we obtain

$$\sigma_D(\omega) = \frac{N(eZ)^2}{m} \text{Re} \left(\frac{1}{-i\omega + \Gamma} \right), \quad (4)$$

where N is the number density of the mobile ions and eZ is the charge of a single carrier.

In the second limit the lattice potential V_{lat} is replaced by a single harmonic well resulting in the following Langevin equations:

$$m\ddot{x} = -m\Gamma\dot{x} - m\omega_0^2 x + R(t), \quad (5)$$

where ω_0 is the frequency associated with the underlying harmonic motion. Equation (5) may be solved by taking its Laplace transform, yielding

$$\sigma_H(\omega) = \frac{N(eZ)^2}{m} \text{Re} \left(\frac{1}{-i\omega + \Gamma + \frac{\omega_0^2}{-i\omega}} \right). \quad (6)$$

The ω dependence of σ_D and σ_H is displayed in Fig. 1. In general, $\sigma(\omega)$ attains a maximum at a characteristic frequency ω_{max} . In the pure diffusive limit $\omega_{\text{max}}^D = 0$. In the harmonic limit $\omega_{\text{max}}^H = \omega_0$ and $\sigma_H(\omega) \rightarrow 0$ as $\omega \rightarrow 0$. Any model for the ionic motion must yield the correct harmonic and diffusive limits. The motion will be said to be more harmonic if $\sigma(\omega)$ approaches $\sigma_H(\omega)$ [i. e., $\sigma(0)$ is small and $\omega_{\text{max}} \rightarrow \omega_0$] and more diffusive if $\sigma(\omega) \sim \sigma_D(\omega)$ (i. e., $\omega_{\text{max}} \rightarrow 0$).

In actual cases the ionic motion is characterized by some intermediate behavior. The harmonic and diffusive limits are obtained at the high and low frequency limits, respectively. Indeed, quasielastic neutron scattering results for α -AgI obtained by Funke¹⁴ indicate that at high frequencies particle motion may be described by a damped harmonic oscillator (i. e., the ion

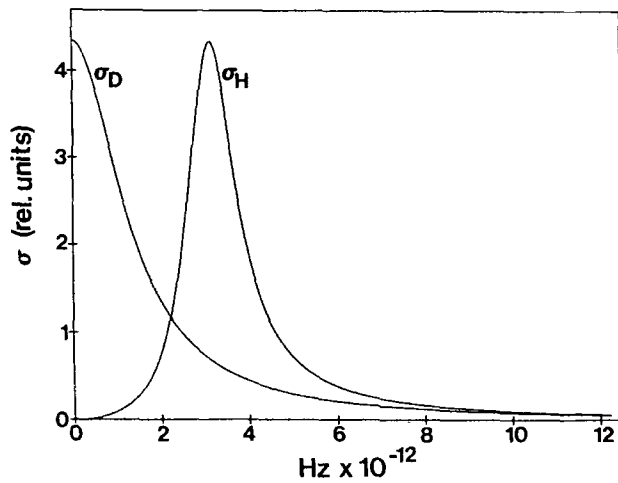


FIG. 1. Comparison of frequency dependent conductivity of a diffusive ion σ_D and an ion subject to a harmonic lattice potential σ_H . $\Gamma = 1.35 \times 10^{12} \text{ sec}^{-1}$, $\omega_0 = 4.30 \times 10^{12} \text{ sec}^{-1}$.

is localized in a potential well), while at low frequencies the system is described by diffusive motion from one site to another (i. e., Drude-like free ion motion). It is intuitively clear that this behavior characterizes the Brownian motion of a particle in a periodic potential. In the calculations reported in the present paper we have chosen a simple cosine potential to represent V_{lattice} :

$$V_{\text{lat}}(x) = -m\omega_0^2 \left(\frac{a}{2\pi}\right)^2 \cos \frac{2\pi x}{a}, \quad (7a)$$

where a is the lattice constant. Equation (1) thus takes the form

$$m\ddot{x} = -m\Gamma\dot{x} - m\omega_0^2 \frac{a}{2\pi} \sin \frac{2\pi}{a} x + f_{\text{int}} + R(t). \quad (7b)$$

Note that the parameter ω_0 determines both the local frequency at the potential minima and the potential barrier height A :

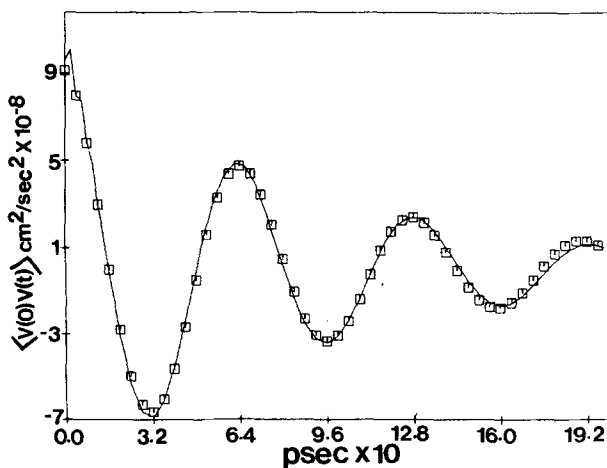


FIG. 2. Velocity auto correlation function for noninteracting particles; parameters used are from the second column of Table I (\square), and the inverse Laplace-Fourier transform of Eq. 9 (—). $\omega_{\text{eff}} = 9.5 \times 10^{12} \text{ sec}^{-1}$, $t_c^{-1} = 0.6 \times 10^{12} \text{ sec}^{-1}$, $\omega_0 = 1.1 \times 10^{13} \text{ sec}^{-1}$ [values calculated from data of Table I following Eq. (6) of Ref. 15].

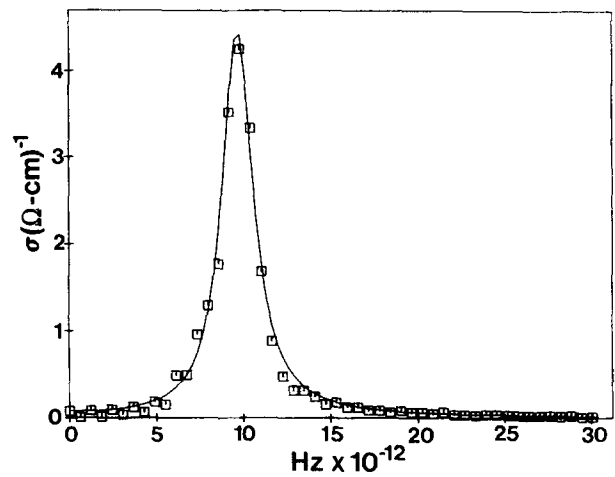


FIG. 3. Frequency dependent conductivity for system with the same parameter as Fig. 2.

$$A = 2m\omega_0^2 \left(\frac{a}{2\pi}\right)^2.$$

Approximate solutions for the single carrier model represented by Eq. (7) without the ion-ion interaction f_{int} have been recently presented by several workers.^{3,4,15} An elegant phenomenological model was suggested by Bruesch *et al.*,³ who represented the effect of the lattice potential by a memory function chosen such as to provide the appropriate oscillatory and diffusive limits in the short and long time regimes, respectively. They make the substitution

$$f_{\text{int}}(x) \rightarrow M\omega_{\text{eff}}^2 \int_0^t M(t-t') \dot{x}(t') dt', \quad (8a)$$

$$M(t-t') = \exp[-(t-t')/t_c], \quad (8b)$$

where $\omega_{\text{eff}}^2 < \omega_0^2$ and is related to height of the periodic potential. This leads to

$$\sigma(\omega) = \frac{N(eZ)^2}{m} \text{Re} \left(\frac{1}{-i\omega + \Gamma + \frac{\omega_{\text{eff}}^2}{-i\omega + 1/t_c}} \right), \quad (9)$$

which is characterized by the correct low and high frequency limits. The justification for the application of Eq. (8) is provided by an approximate solution of the independent carrier version of Eq. (7). Fulde *et al.*¹⁵ showed that the simple exponential memory term of Eq. (8) reproduced the continued-fraction expansion for $\sigma(\omega)$ to very high accuracy. To characterize the accuracy of stochastic trajectory procedure, we have compared our numerical results for the single-carrier case to the analytic result (9). Figures 2 and 3 show these comparisons in both frequency and time spaces for typical parameter values; it is clear that the simulations are sufficiently accurate for characterizing the dominant features of $\sigma(\omega)$.

In the following sections we present the results of computer simulations based on Eq. (7b). These calculations employed the data in the first column of Table I, following Bruesch *et al.*³ These data were actually obtained to model AgI; however, we have varied several of the parameters to investigate features of particular

TABLE I. List of parameters used in stochastic dynamics studies.

Parameter	α -AgI ^a	Hollandite ^b
Temperature	453 °K	453 °K
Barrier height (A)	0.1 eV	0.38
Damping coefficient (Γ)	$1.35 \times 10^{12} \text{ sec}^{-1}$	$1.35 \times 10^{12} \text{ sec}^{-1}$
Distance between sites (a)	3.1 Å	2.9 Å
Mass	$1.776 \times 10^{-22} \text{ g}$	$6.492 \times 10^{-23} \text{ g}$
ω_0	$4.30 \times 10^{12} \text{ sec}^{-1}$	$1.48 \times 10^{13} \text{ sec}^{-1}$
Effective charge (q)	0.6 ^c	1.0
Ratio of mobile ions to total sites (ρ)	1/2	3/4
Short range repulsive potential strength (C)	$0.56 \times 10^{17} \text{ cm Å}^8/\text{sec}^2$	$0.56 \times 10^{17} \text{ cm Å}^8/\text{sec}^2$

^aReference 3.^bReferences 16 and 17.^cReference 10.

interest, and to examine the hollandite system. We use the computed stochastic trajectories to discuss the effect on the frequency dependent conductivity due to systematic variation of (a) the barrier height of the crystal framework potential, (b) the nature of the ion-ion interaction potential, (c) the density of mobile ions, and (d) the temperature. Moreover, we establish the importance of cooperative motion in the diffusion of ions through a model framework ionic conductor. The present studies are limited to one dimensional systems; however, extensions to two dimensions are in progress.

III. EFFECTS OF ION-ION INTERACTIONS

Correlated motion was investigated by considering two types of interactions; a long range Coulombic term with an effective charge, and a short range $1/r^7$ repulsive interaction. Periodic boundary conditions simulating an infinite system were imposed. Two periodic images of a box containing N particles were created by adding and subtracting the length of the box to the coordinate of each particle in the "real" box. The range of the potential was cut off at half the length of the box so that the effect of each particle was counted only once. If a particle left the box through the right boundary, a new particle simultaneously entered the box from the left, conserving the density. Thus, the interionic forces are

$$f_{\text{int}} = \sum_{ij} f_{ij} \quad (10a)$$

and

$$f_{ij} = \frac{7C}{r_{ij}^8} + \frac{(qe)^2}{r_{ij}^2}, \quad (10b)$$

where q is the effective charge, and C is based on Pauling atomic radii.¹⁰

The Haven ratio H_r , defined as the ratio of the tracer diffusion coefficient to that of the bulk, is a transport property related to correlated behavior:

$$H_r = D_{\text{Tr}}/D_0. \quad (11)$$

Here D_{Tr} and D_0 are the experimentally observed tracer

and bulk diffusion coefficients, respectively. Consider now the vacancy mechanism in which an ion jumps from one lattice site to a neighboring vacant site. If the concentration of particles is high, this will effect neighboring ions, which will tend to move together in the same direction, making D_0 greater than D_{Tr} . However, if the system is infinitely dilute, each ion moves independently, so $D_0 = D_{\text{Tr}}$. Thus, we expect that $H_r = 1$ for uncorrelated motion while $0 \leq H_r < 1$ when correlations are present.

The Haven ratio is conveniently calculated by stochastic molecular dynamics. The diffusion coefficients are

$$D_{\text{Tr}} = \frac{1}{N} \int_0^\infty \sum_{i=1}^N \langle v_i(0) v_i(t) \rangle dt \quad (12)$$

and

$$D_0 = \frac{1}{N} \int_0^\infty \sum_{i,j} \langle v_i(0) v_j(t) \rangle dt, \quad (13)$$

where N is the number of particles. For noninteracting Brownian particles $D_0 = D_{\text{Tr}}$ since the velocity of any given particle will in no way depend on the other particles and the off diagonal terms ($i \neq j$) in the expression for D_0 vanish. Therefore, for noninteracting species $H_r = 1$. On the other hand, for ions with Coulombic interactions our calculated value of H_r was two orders of magnitude less than unity, indicating that Coulombic forces cause ionic motion to be highly correlated, as is expected for a one dimensional channel.

The results obtained from a systematic study of the stochastic trajectories of one dimensional motion of interacting ions in a periodic potential are presented in Tables II-IV and in Figs. 4-9. Figures 4-6 display the effect of short range r^{-7} and long (Coulombic) range interaction potentials on the frequency dependent conductivity (Figs. 4 and 5) and the velocity autocorrelation function (Fig. 6) of tracer atoms. These effects are summarized in Table II, where we present the results for $\sigma(0)$ and for ω_{max} in a system of noninteracting ions as well as in the presence of repulsive short and long range interaction potentials. Variations in the strength

TABLE II. Comparison of long and short range interaction potentials at two temperatures: $A = 0.1$ eV, $a = 3.1$ Å, $q = 0.6$, $\Gamma = 1.35 \times 10^{12}$ sec $^{-1}$, $\rho = 0.5$, $m = 1.776 \times 10^{-22}$ g.

Form of V_{int}	Temp. (°K)	$\sigma(0)$ (Ω cm) $^{-1} \times 10^1$	$\omega_{\text{max}} \times 10^{-13}$ (sec $^{-1}$)
No interaction	453	17.1	0.368
	800	37.6	0.0
$1/r^7$	453	11.7	0.368
	800	30.7	0.199
Coulombic	453	0.1	0.476
	800	0.6	0.420

of the long range forces, expressed in terms of the effective charge of the mobile ions, have a strong effect on the transport properties, as seen from the results presented in Table III. The important role played by interionic forces implies that the mobile ion concentration will also affect the transport properties. This is seen in Table IV, which shows the effect of varying site occupation on the frequency dependent conductivity. Observation of the detailed ionic motion reveals that the source of the effect on the transport properties is the correlated nature of the ionic motion in the presence of interionic interaction. Figure 7 shows neighboring ions which jump together in a highly correlated way.

These results lead to the following conclusions concerning the effects of interionic interaction on ionic transport in commensurate conductors:

(a) For a system characterized by a short range (r^{-7}) interaction potential between the mobile ions $\sigma(\omega)$ is slightly "more harmonic" than that calculated for the same system in the absence of ion-ion interaction. This is expressed by the fact that $\sigma(0)$ slightly decreases when V_{int} is switched on (Fig. 4, Table II). It is interesting to note that the presence of the short range repulsive potential gives rise to some structure in $\sigma(\omega)$ at low frequency.

(b) The ratio of the number of transits per second (defined by $\langle v^2 \rangle^{1/2}/a$) to the effective number of hard sphere collisions (defined by the number of times per second that two particles come within an effective hard-sphere radius of 0.63 Å) 10 was 6/1 for the parameters of Table I, column 1. Since the $1/r^7$ potential is short range, its dominant influence is to augment the periodic crystal lattice potential. At higher temperatures, the ratio decreases, as the average excursion of each particle from its equilibrium point increases. Then the short-range repulsion effects become more important, as the thermally averaged kinetic energy becomes comparable to A , and the particles are no longer effectively separated by the periodic lattice potential. Therefore,

TABLE III. Variation of the effective charge: $A = 0$, $a = 2.5$ Å, $T = 453$ K, $\rho = 0.5$, $m = 1.776 \times 10^{-22}$ g.

q	$\sigma(0)$ (Ω cm) $^{-1}$	$\omega_{\text{max}} \times 10^{-13}$ (sec $^{-1}$)
0.6	1.50	0.460
0.4	2.14	0.352
0.3	2.48	0.276
0.2	3.15	0.230

TABLE IV. Variation of the mobile ion density: $A = 0.1$ eV, $q = 0.6$, $a = 3.1$ Å, $T = 453$ K, $m = 1.776 \times 10^{-22}$ g.

ρ	$\sigma(0)$ (Ω cm) $^{-1} \times 1/N \times 10^{24}$	$\omega_{\text{max}} \times 10^{-13}$ (sec $^{-1}$)
1/2	0.02	0.476
1/3	0.17	0.399
1/4	1.16	0.387

the effect of short-range repulsion on ω_{max} increases as $k_B T/2$ becomes of the order of A (Table II).

(c) For our present range of parameter values, which seem reasonable for such systems as AgI or potassium hollandite, long range Coulombic interaction affects the transport properties of the system much more strongly than the short range repulsive interaction. The repulsive forces hold the ions more strongly in their equilibrium positions relative to the case where V_{int} is absent, thus making $\sigma(\omega)$ more harmonic. Quantitatively (Table II, Fig. 5) the presence of long range forces causes a dramatic change in $\sigma(\omega)$: ω_{max} becomes appreciably higher and $\sigma(0)$ becomes more than an order of magnitude smaller relative to the values of the noninteracting particle model. Note that Fig. 5 displays $\sigma(\omega)$ in the presence of both Coulombic and short range interionic forces. The results for a system with Coulombic interactions only were identical, indicating that the long range repulsive potential keeps the mobile ion separated so that the r^{-7} part of the potential does not contribute. The effect of the strength of the coulombic interaction determined by the effective charge of the ions is seen from Table III. As q increases $\sigma(\omega)$ behaves more harmonically.

(d) The microscopic effect of interionic forces, as seen from Fig. 7, is to generate the correlated motion of ionic clusters at low frequencies. Between jumps the positions of the ions oscillate with random amplitudes about the equilibrium sites, but when one particle gets enough thermal energy and moves to an adjacent site, other particles follow. In the trajectory displayed in

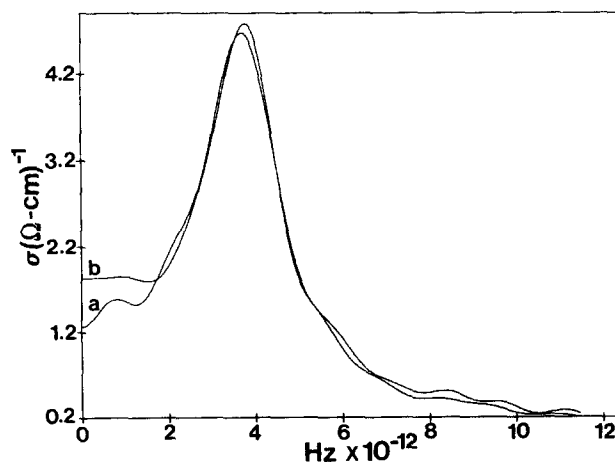


FIG. 4. Frequency dependent conductivity of a tracer ion subject to a $1/r^7$ potential (curve (a)), and with $V_{\text{int}} = 0$ [curve (b)]. Parameters of first column of Table I with $q = 0$.

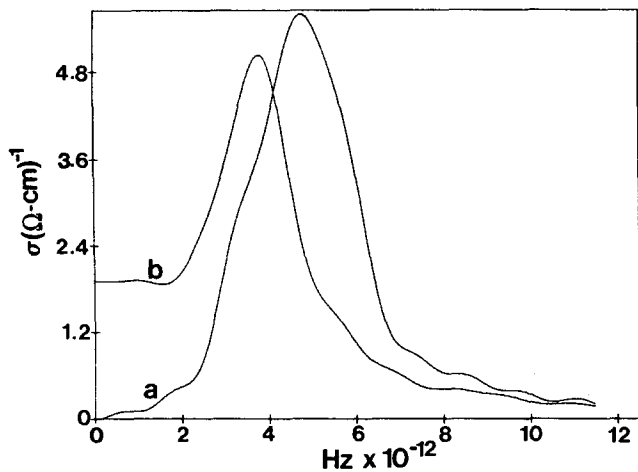


FIG. 5. Frequency dependent conductivity for a system with a Coulombic and short range interaction potential [curve (a)], and for a system with no interaction [curve (b)]. The parameters are listed in Table I, column 1.

Fig. 7, the three particles move within a period of 4 psec.

(e) In general, raising the temperature increases the diffusive behavior of the mobile ions; however, the degree of this change depends on the nature of the interaction potential (Table II). A noninteracting mobile ion displays complete diffusive behavior [$\sigma(0) = \sigma_{\max}$] when the temperature is increased from 453 to 800 °K, while for ions with a Coulombic ion-ion interaction, the frequency dependent conductivity at 800 °K is only slightly shifted from that at 453 °K, even though the strength of the Coulombic potential at the mobile ion equilibrium position (q^2/a) is approximately $k_B T$. This behavior can be attributed to the fact that as the temperature is raised the average displacement of the ion from its equilibrium site is increased, decreasing the average distance between charge carriers. Thus, contributions from Coulombic forces are greater at higher temperatures. The temperature dependence for a system with a short range interaction potential has been discussed in (b).

(f) In the absence of the "external" periodic potential,

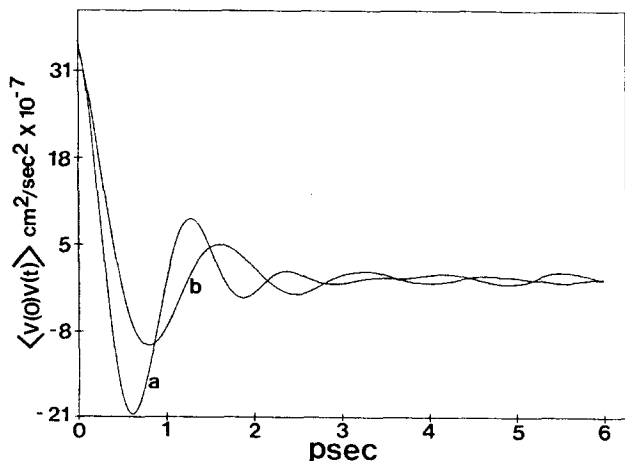


FIG. 6. Velocity autocorrelation functions for systems corresponding to Fig. 5.

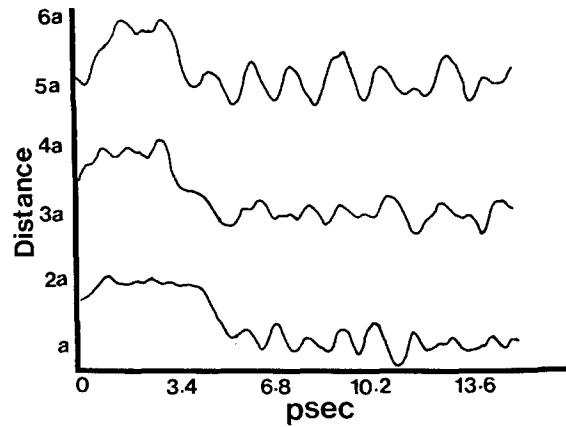


FIG. 7. Position as a function time of three mobile ions (parameters of the first column of Table I), showing correlated jumps.

but with Coulombic interionic forces present, the nature of the motion is qualitatively similar to that seen in the presence of only the lattice periodic potential. The repulsive interactions hold the ions near the corresponding equilibrium sites and the frequency dependent conductivity peaks at a frequency which characterizes the oscillations about these sites.

(g) Increasing the mobile ion concentration (expressed by the site occupation fraction ρ) affects the ionic motion so as to increase its harmonic nature (Table IV).

The data in Table IV are for values of ρ whose reciprocals are integral; however, for incommensurate systems (i.e., whose reciprocals are not integral) very different results are obtained. Potassium hollandite $K_{2x}Mg_xTi_{8-x}O_{16}$ ($0.75 \leq x \leq 1$) is such a system. In this material parallel channels with nearly square cross section are formed by a framework consisting of edge and corner sharing TiO_6 and MgO_6 octahedra.¹⁶ X-ray data suggests that the mobile ions diffuse through these one dimensional channels.¹⁶ Thus, one dimensional stochastic dynamics should be a reasonable approximation to the dynamics of this system.

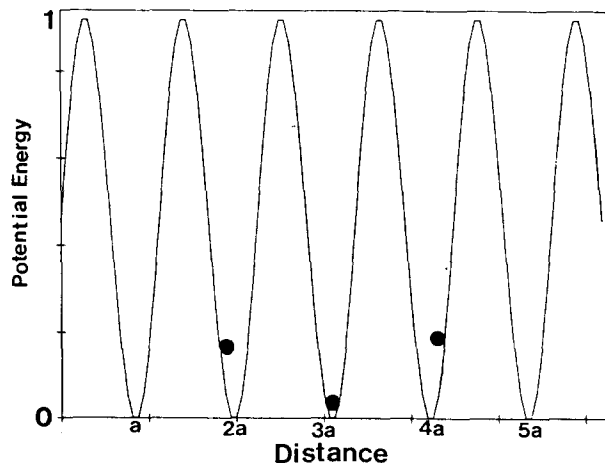


FIG. 8. Three mobile ions in a periodic lattice potential where $\rho = 0.75$.

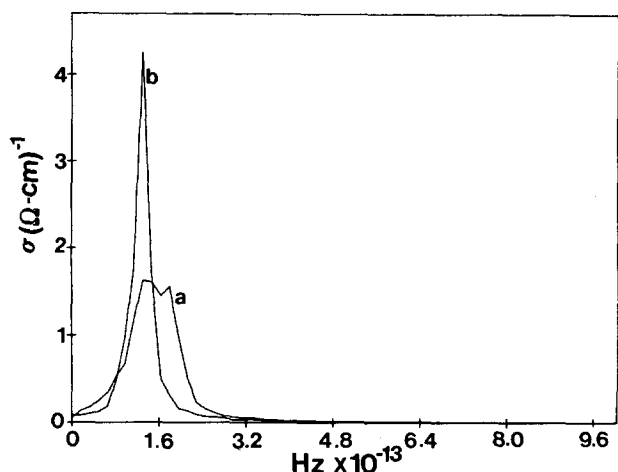


FIG. 9. Frequency dependent conductivity of tracer ions with the parameters of K-hollandite (Table I) for a system with [curve (a)] and without [curve (b)] a Coulombic V_{int} .

The ratio of mobile ions to available sites in the hollandite system is about 0.75. Thus, if the mobile ions occupy the positions where the crystal framework potential is minimum, the mobile ions will be grouped into arrays (linear clusters). From static considerations the expected array length is three; however, for dynamic systems there is a distribution of array lengths. We have defined the array length as the number of mobile ions between vacancies. This distribution was determined by the stochastic molecular dynamics method using parameters corresponding to potassium hollandite (Table I). The most probable array length was found to contain three particles: $P_3 = 0.48$. Arrays containing two or four particles were less probable: $P_2 = 0.27$ and $P_4 = 0.14$. The probability of all other array lengths was negligible ($P < 0.03$). This distribution is qualitatively in agreement with the model used to explain x-ray scattering data.¹⁶

The repulsive mobile ion-ion interaction potential imposes a distortion on ions neighboring a vacancy; the mobile ions move toward the vacancy. The magnitude of the distortion (i.e., the distance the ion is displaced from the equilibrium site relative to the lattice constants) was calculated to be 21%, compared to an experimental value of 24%.¹⁶ The density of mobile ions in the experimental crystal was 77%, slightly higher than the density used in this model. Hence, the calculated value might be expected to be slightly lower than the experimental value. Figure 8 represents three mobile ions in the periodic lattice potential. There are two environments which the mobile ions reside: (1) neighboring a vacancy, and (2) surrounded by mobile ions. The ion in the center of the array is driven to its equilibrium position, much the same as the ions in the calculation where $1/\rho$ was integral; however, the ions near the vacancies are able to jump to them. Thus, the frequency dependent conductivity (Fig. 9) shows two peaks due to these two environments. The higher frequency peak is due to the ions in the center of the array and the lower frequency peaks are from the ions near the vacancies. This suggests that for high-purity hol-

landite crystals the vibrational spectrum should show a split peak near 2×10^{13} cps.¹⁷

These distortions near vacancies have a considerable effect on the value of the bulk diffusion coefficients. The value of D_0 for a system with no long range interactions was calculated to 0.39×10^{-5} cm² sec⁻¹, compared to a value of 3.97×10^{-5} cm² sec⁻¹, which was calculated for a system with Coulombic interactions; the latter corresponds to $\sigma(0) = 4.20 \times 10^{-1}$ (Ω cm)⁻¹. The highest reported experimental measurement¹⁸ is 1.7×10^{-2} (Ω cm)⁻¹; the experimental scatter (10^{-4} – 10^{-2} for different crystals)^{18,19} strongly suggests that the measured $\sigma(0)$ is limited by imperfections or other extrinsic effects, and as such is lower than the true bulk $\sigma(0)$ with which the calculation should be compared. The Coulombic repulsions push ions neighboring vacancies up the crystal framework potential well, effectively lowering the potential barrier. The increase in the diffusion coefficient can be attributed to this cooperative behavior.²⁰ As the strength of the ion-ion interaction potential is increased (i.e., the effective charge is increased) the cooperative behavior is enhanced.

IV. DISCUSSION

A stochastic molecular dynamics simulation for ionic conductors with a rigid lattice framework is reasonable for describing the motion of the mobile ion. The interaction of the mobile ion with the fixed lattice is represented by periodic, damping, and random forces which yield a coupled set of Langevin equations. These equations, which are phenomenological in nature, are then solved numerically. The values of the parameters of the phenomenological equations of motion, such as the height of the periodic potential barrier, can be related to the degree of anharmonicity with which the ion moves.

Correlated motion was modeled by including a long range Coulombic and short range $1/r^7$ potentials. Inclusion of this interaction potential in a calculation with parameters corresponding to α -AgI shifted the frequency dependent conductivity in a manner indicating that the mobile ions are held close to their equilibrium positions, i.e., the motion was more harmonic. The magnitude of this shift was large, and hence a phenomenological study should include correlation effects. Moreover, the ion-ion interactions are long range, and thus an Ising-type model will not accurately represent the dynamics of ionic motion.

The results of the potassium hollandite calculations are in good agreement with experimental x-ray scattering. The x-ray comparison with the calculated results suggests that the periodic potential barrier is about the same order of magnitude as the ion-ion interaction. Further, the preliminary results for the hollandite system show the existence of arrays with distortions near the vacancies. The cooperative effects increase the value of the diffusion coefficient, suggesting that the ionic conductivity can be increased by ion-ion interactions in crystals for which the ratio of total sites to the number of mobile ions is nonintegral.

ACKNOWLEDGMENTS

We would like to thank D. Whitmore, G. Schatz, and D. Shriver for their useful discussions, and D. Ellis, G. Schatz, and D. Shriver for use of their computers. MR is grateful to R. D. Levine for his hospitality at the Advanced Study Institute. AN gratefully acknowledges the hospitality of the Department of Chemistry at Northwestern University during the spring of 1978 when this work was initiated, and the support of the Binational Science Foundation, Jerusalem, Israel. This work was partially supported by the Northwestern University Materials Research Center via a grant from the Materials Research Center Program of the National Science Foundation (Grant #DMR7680847).

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