

# Motion mechanisms in framework solid electrolytes: Correlated hopping and liquidlike diffusion

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Motion mechanisms for ions in framework solid electrolytes are investigated. The results are obtained from numerical studies on a one-dimensional model system, utilizing the method of stochastic Langevin dynamics. We find that, for commensurate systems (for which one mobile ion occurs exactly every  $l$  lattice sites), the mechanism always involves correlated hops, and the ion-ion repulsion decreases (always) the total conductivity. For incommensurate systems, the conductivity changes from hopping to liquidlike as the interaction forces are increased to dominate the potential due to the framework lattice. Different assumed ion-ion potentials produce different correlations, both local and overall; the nearest-neighbor harmonic forces, such as are assumed in the Frenkel-Kontorova model, will generally produce substantially different correlation effects from the Coulomb repulsion. The frequency-dependent conductivity at low frequency is shown to be proportional to the square of the frequency; the proportionality coefficient is positive for correlated hopping mechanisms. A double-peaked structure in the frequency-dependent conductivity, due to local oscillation and to long-time, long-range diffusive behavior, is observed when particle-particle interactions are absent and damping is weak.

## I. INTRODUCTION

A number of solid-state materials are known in which diffusion of atoms, ions, or molecules occurs in effective dimensionality of one or two. Examples include diffusion of intercalates in layered materials such as graphite, transition-metal dichalcogenides or montmorillonite clays, and ionic motion in framework superionic conductors of layered ( $\beta$  aluminas and gallates) or tunnel (sodium antimonate, potassium hollandite,  $\beta$  eucryptite, NASICON)<sup>1</sup> structure. In addition, diffusion of physisorbed or weakly chemisorbed atoms or molecules on metal or semiconductor surfaces at submonolayer coverage should show two-dimensional diffusion. In all of these materials, the diffusing species feels a one-particle generalized lattice potential, which is periodic, with the period determined by the host lattice in which or on which diffusion occurs. Because of the periodic potential, there will exist stable sites, at which the diffusing particle would be localized at very low temperatures and in the absence of interparticle interactions among the diffusers. In the limit of a dilute system, then, the diffusion motion should consist of thermally activated hops among the stable sites. This hopping model is a very attractive and simple one, and most analyses of diffusion in frameworks are couched in terms of hopping.

There are several phenomena which occur in these materials which can seriously modify the hopping behavior. The most obvious are the interactions among particles, both direct and via lattice polarization effects (the latter can be nonlocal both in space and in time). Several types of experimental and theoretical data on solid electrolytes suggest that the simple hopping, or

even correlated hopping, models require elaboration.<sup>2,3</sup> These include

- (1) The diffusion coefficients can be as large as those in liquid electrolytes ( $D \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ).
- (2) For heavy-metal electrolytes such as AgI, diffuse scattering experiments reveal both substantial disorder and a structure function more characteristic of liquids than of solids. Beyeler<sup>4</sup> has remarked that "all models which treat ion-ion interactions in terms of occupational short-range order are incomplete, and it is necessary to include strong deviations of the equilibrium positions from the lattice sites".
- (3) The vibrational spectra of AgI materials exhibit no strong change when the crystals are melted.<sup>5</sup>
- (4) While hopping models must<sup>6</sup> show a conductivity  $\sigma(\omega)$  increasing with increasing frequency for  $\omega \rightarrow 0$ , experimental data on AgI show<sup>7</sup> an initial drop in  $\sigma(\omega)$ .
- (5) Continuum (Brownian) diffusion models in a background potential are capable of reproducing many experimental data (commensurability behavior, temperature and density dependence of  $\sigma$ , vibrational spectra) for framework electrolytes.<sup>8-16</sup>

Partly on the basis of points (1) and (3), Geisel has suggested that the conduction mechanism in solid electrolytes of the AgI class might be thought of as liquidlike.<sup>17</sup> Although, as Flygare and Huggins<sup>18</sup> showed in a pioneering mechanistic model, the mobile Ag ions follow well-defined motion paths in the crystal, and stable sites occur among which hopping might be imagined, nevertheless the motion appears more liquidlike. This is doubtless partly because the anion motion timescale is not terribly different from that of the mobile ion (in the  $\beta$ , or nonconductive, phase of the silver halide conductors, the ionic "attempt frequency"

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is roughly  $10\text{--}20\text{ cm}^{-1}$ , while the totally symmetric anion stretch frequencies are of order  $100\text{--}150\text{ cm}^{-1}$ <sup>19</sup>) partly due to strong anharmonic and coupling effects among the modes, and partly due to strong residual cation-cation repulsion.

In framework solid electrolytes, as opposed to the softer, heavy-metal ones, the diffusion is nearly always considered to be by a hopping mechanism.<sup>8,20</sup> The timescales of cation "attempt frequencies" ( $\sim 60\text{ cm}^{-1}$ ) and oxide lattice vibrations ( $> 1000\text{ cm}^{-1}$ ) are widely separated, no effects of strong coupling between ions and lattice have been remarked upon widely, and  $\sigma(\omega)$  increases with  $\omega$  at low frequencies. Nevertheless, continuum-type Brownian motion studies can reproduce the behavior of these materials rather well,<sup>12-16</sup> and thus it is tempting to speculate on possible liquidlike conduction in these substances. Ordinarily, the distinction between hopping and liquidlike conductivity is couched in terms of two timescales.<sup>7</sup> The residence time  $\tau_0$ , or time between flights, is the time a typical particle spends in the neighborhood of a minimum in the one-particle lattice potential  $V_1(x)$  before moving to the next minimum, while the time of flight  $\tau_1$  is the time spent in the (higher potential) region between the minima of  $V_1(x)$ . For hopping,  $\tau_0 \gg \tau_1$ , while for liquidlike diffusion  $\tau_0 \sim \tau_1$ , and the minima in  $V_1(x)$  assume no special importance. Microscopically, this must mean that in the liquidlike regime the other interactions, ion-ion repulsion and lattice polarization, must produce an effective one-particle potential  $V_{\text{eff}}(x)$ , which is far flatter than  $V_1(x)$  so that the minima in the latter no longer dominate the diffusion. The possible occurrence of liquidlike, very strongly correlated diffusion in framework electrolytes is not merely an interesting theoretical issue: at incommensurate stoichiometries, if the correlations become strong enough they can lead to a sort of rigid-chain (in one dimension) or rigid sheet (in two dimensions) conduction, similar in some ways to the Fröhlich sliding charge-density wave in electronic conductors,<sup>21</sup> which can permit very substantial conduction even in the presence of traps such as those introduced by charge-compensating counterions.<sup>12</sup>

In the present paper, preliminary parts of which have already appeared,<sup>15</sup> we study the mechanism of ionic conduction in correlated one-dimensional models for solid electrolytes. The method is based on the stochastic Langevin dynamics introduced by Adelman and Doll<sup>22</sup> to study surface properties. By varying the strength of the ion-ion repulsion for fixed framework potential  $V_1(x)$ , we calculate both  $\sigma(\omega)$  and relevant correlation factors. We study the effects of the range of the potential and the effective range of the correlations. Our most striking finding for incommensurate stoichiometry is a fairly sudden change from correlated hopping behavior when repulsions are weak to liquidlike, very strongly correlated motions for higher repulsion.<sup>15</sup> This is manifested in the flight times, in the correlation factors, and most vividly in the actual behavior of the ion trajectories.

Bill Flygare made several important contributions to

the study of ionic conductivity, which at the end of his life was one of the many subjects on which he was actively working.<sup>23</sup> His efforts in this field, as in so many others, were marked by insight, experimental creativity, and a highly unusual, idiosyncratic and enormously fruitful approach to the problem. We hope he would have been interested in the present manuscript, which is dedicated to his memory.

## II. ION DYNAMICS IN FRAMEWORK SOLID ELECTROLYTES: APPLICATION OF STOCHASTIC LANGEVIN DYNAMICS

We wish to study the correlated motion of mobile ions in a framework lattice. The physical systems of interest are covalent, refractive ionic conductors of reduced effective dimensionality (hollandites,  $\beta$  aluminas, NASICON, eucryptites, antimonates, silicates, etc.)<sup>1</sup> The method used will be reduced molecular dynamics, or stochastic Langevin dynamics; i. e., we calculate the correlated motions of the ions by solving their classical equations of motion in the stochastic field of the framework.<sup>22</sup>

The justification for and the details of the calculation of the frequency-dependent conductivity  $\sigma(\omega)$  for framework solid electrolytes have been given previously.<sup>12-15</sup> Essentially the reasoning is based on a timescale difference between (slow) diffusion times characterizing the motion of the ionic mobile ions and (fast) vibration times characterizing the covalent framework lattice. Then the motions of the framework are uncorrelated on the ion's timescale, and can be treated as the source of random forces and of thermalizing damping. The framework atoms in their equilibrium positions provide a static potential. For a one-dimensional model the static potential is assumed sinusoidal, and the ion-ion potential Coulombic. Then we have

$$V_{\text{TOT}} = \sum_i V_1(x_i) + \sum_{i < j} V_2(x_i - x_j), \quad (1)$$

$$V_1(x_i) = \frac{A}{2} \cos(2\pi x_i/a), \quad (2)$$

$$V_2^c(x_i - x_j) = q^2/|x_i - x_j|. \quad (3)$$

Here  $x_i$  is the position of the  $i$ th mobile ion, moving in a one-dimensional periodic lattice of lattice constant  $a$ . Ions have an effective charge of  $q$ . The bare-lattice barrier is  $A$ ; note that  $A$  should correspond to the measured activation energy for conductivity only in the limit of very dilute samples for which  $V_2$  is unimportant; for higher mobile-ion concentrations, the activation energy will exceed  $A$  for commensurate densities, but fall below  $A$  for incommensurate ones.

The equation of motion for  $x_i$  is then

$$m\ddot{x}_i = -m\Gamma\dot{x}_i - \nabla_i\{V_{\text{TOT}}\} + R_i(t), \quad (4)$$

where the random force  $R_i(t)$  is related to the damping  $\Gamma_i$  (since both arise from stochastic lattice motions) by

$$\langle R_i(t)R_j(t+\tau) \rangle = 2\delta(\tau)\delta_{ij}mk_B T \Gamma. \quad (5)$$

The problem is a many-body one because of  $V_2$ . To solve it we use cyclic boundary conditions and simply

integrate the coupled stochastic equations for a system of several (in this case 30) particles.

### III. RESULTS: LOCAL AND OVERALL CORRELATIONS AND EFFECTS OF POTENTIAL RANGE

It has been demonstrated previously that ion-ion interactions have significant effects on the transport properties; this is most vividly shown by the Haven ratio,<sup>24</sup> but the vibrational spectrum and  $\sigma(\omega)$  for low frequencies are also significantly altered by ionic repulsion.<sup>2,8-15</sup> Our aims here are to characterize the correlation effects quantitatively, to study their dependence on the range of the potential, and to see how they affect the qualitative transport mechanism.

To characterize the correlations quantitatively, it is convenient to introduce a finite-time correlation factor  $F$ , which is the analog of the Haven ratio (which is itself rigorously zero in one dimension). Thus, we write

$$F = \langle x^2(t) \rangle_{\text{tracer}} / \langle x^2(t) \rangle_{\text{bulk}}, \quad (6)$$

where  $t$  is some fixed time (here 512 ps), and  $\langle x^2 \rangle$  is the mean square displacement. As the correlations become more important,  $F$  decreases.

The Haven ratio and the correlation factors provide a quantitative measure of the overall correlations. These can be further characterized by a local correlation function, which measures the correlation between particle 1 and particle  $n$ :

$$C_n(t) = \langle v_1(0)v_n(t) \rangle. \quad (7)$$

If the particles are uncorrelated,  $C_{n \neq 1} = 0$ . A relationship exists between  $F$  and  $C_n$ . Defining

$$I_n(t') = \int_0^{t'} C_n(t) dt; \quad (8a)$$

then the DC diffusion coefficient is simply

$$D_0(t') = \sum_{n=1}^N I_n(t'), \quad (8b)$$

and the correlation function becomes

$$F = \int_0^{t'} C_1(t) dt / D_0(t'). \quad (8c)$$

Examination of both  $I_n(t)$  and  $C_n(t)$  for systems with long range and nearest neighbor forces demonstrates the importance and differences between local and overall correlations.

#### A. Comparison of nearest neighbor and long range ion-ion interactions

The dynamics of charge carriers in framework solid electrolytes strongly depends on the interionic forces. Results are obtained from stochastic Langevin dynamics for systems with:

- (a) nearest neighbor harmonic potentials (NNH);

$$V_2^{\text{NNH}}(x_i - x_j) = K(x_i - x_j)^2 \cdot (\delta_{i,j+1} + \delta_{i,j-1}), \quad (9a)$$

- (b) nearest neighbor Coulombic (NNC);

TABLE I. Comparison of nearest neighbor and long range forces  $m = 1.776 \times 10^{-22}$  g,  $\Gamma = 1.35 \times 10^{12}$  Hz,  $A = 0.1$  eV.

$\rho$	$\phi_{\text{int}}$	$F \times 100$	$\sigma_B/\rho$
0.75	NNH, $K = 6.547 \times 10^{24}$ s <sup>-2</sup>	13.8	12.45
0.75	C	7.9	18.45
0.75	NNC	14.1	14.5
0.50	NNH, $K = 1.94 \times 10^{24}$ s <sup>-2</sup>	41.8	4.34
0.50	C	60.3	0.605
0.50	NNC	68.0	1.53
0.5	O	...	5.50

$$V_2^{\text{NNC}}(x_i - x_j) = (q^2/x_i - x_j) \cdot (\delta_{i,j+1} + \delta_{i,j-1}), \quad (9b)$$

and (c) long range Coulomb potentials as in Eq. (3). Values of  $F$  at 512 ps and  $\sigma$  for commensurate and incommensurate systems are given in Table I. The harmonic force constant was chosen so that the magnitude of the nearest neighbor harmonic force exerted on particles separated by the equilibrium distance ( $r_e = a/\rho_0$  where  $\rho_0$  is the mobile-ion density per site), equaled the force due to nearest neighbor Coulomb interactions for the same distance.

The long range Coulomb forces for both commensurate and incommensurate stoichiometries exhibited the largest changes in the DC conductivity when compared to results obtained from an independent particle calculation. On the other hand, the nearest neighbor harmonic forces induced the smallest changes in the conductivity. The correlation factors for NCC and NNH systems with  $\rho_0 = 0.75$  are about equal. For  $\rho_0 = 0.5$  these correlation factors and conductivities vary more significantly with different interionic potentials.

The interionic forces of commensurate systems are responsible for diminishing the conductivity since they pin the mobile ions to their lattice sites. The conductivity data in Table I indicate that the NNH forces do not pin the mobile ions so well as Coulomb forces, yet values of the correlation factor indicate larger overall correlation for NNH than the Coulomb case. In order to describe this behavior, the local correlation function of Eq. (7) must be examined

The maximum and minimum values of  $C_n(t)$ ,  $C_n^{\text{max}}$ , and  $C_n^{\text{min}}$ , respectively, ( $n = 2, 3, 4, 5$ ) for systems with long range Coulomb interactions are compared to results for systems with nearest neighbor harmonic and nearest neighbor Coulomb interactions in Tables II and III, for incommensurate and commensurate systems, respectively. (We call a system commensurate if  $I\rho_0 = 1$  for integer  $I$ . For such systems, the equilibrium positions are the same independent of the strength of  $V_2$ .) The most striking result in Table II is that the correlations in the NNH system fall off more rapidly as a function of ion-ion separation than either the NNC or Coulomb systems. On the other hand, the Coulomb systems exhibit the longest-ranged correlations (Fig. 1). The correlation factor (Table I) for the incommensurate Coulomb case is about half the value of the NNC system, yet values of  $C_n^{\text{max}}$  for the NNC and Coulomb systems are similar when  $n$  is small. This difference in  $F$  must

TABLE II. Local correlation as a function of distance between ions for commensurate systems.

$\phi$	$N$	$C_n^{\max}$	$C_n^{\min}$
C	2	0.164	-0.199
	3	0.075	-0.065
	4	0.053	
	5	0.039	
NNC	2	0.117	-0.168
	3	0.068	-0.065
	4	0.031	
NNH	2	0.088	-0.068
	3	0.012	-0.005

then be due to the long range correlations from the Coulomb force.

The NNH incommensurate system (Table III) has the weakest local correlations, negligible for distances greater than the nearest neighbor separation, whereas the long range Coulomb system has the strongest correlations, persisting over many sites. For commensurate Coulomb systems  $C_2$  is dominated by negative values, while for commensurate NNH systems  $C_2$  is dominated by positive values. Inspection of Figs. 2 and 3 shows that  $I_2$  in Eq. (8a) will be negative for commensurate Coulomb systems and positive for commensurate NNH. This large negative term is responsible for the large value of  $F$  and is indicative of strong local correlations.

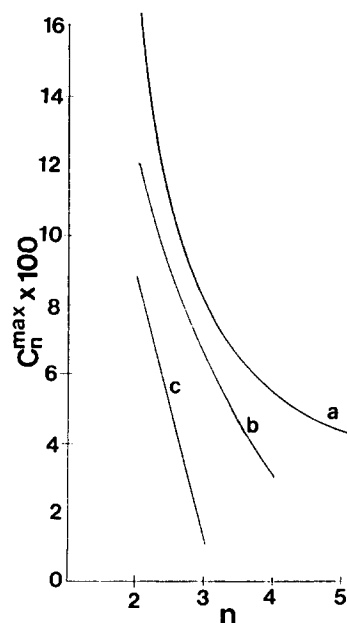


FIG. 1. Distance dependence of maxima in the local correlation function. (a) Coulomb interaction of Eq. (5). (b) Nearest neighbor Coulomb interaction of Eq. (9a). (c) Nearest neighbor harmonic interaction of Eq. (9b). The  $C_n$  is defined by Eq. (7) parameter values as in Table II.

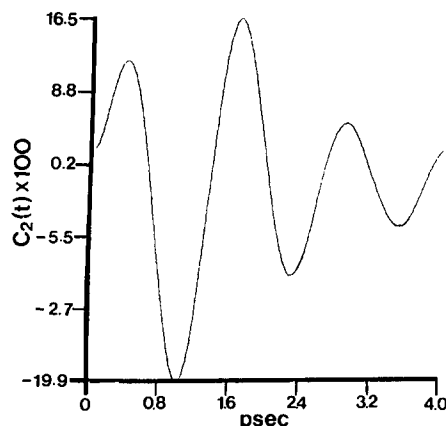


FIG. 2. The local correlation function  $C_2(t)$ , for a Coulomb system with  $q=0.6$ ,  $\rho_0=0.5$ , other parameters as in Table I.

These results demonstrate that it is possible to have strong local correlations (i.e., values of  $C_n$ ) and weak overall correlations (i.e., large values of  $F$ ). The local correlations are mainly due to the interionic forces whereas the overall correlations include the effects of the periodic barrier and charge carrier density as well as ion-ion interactions.

#### IV. THE COULOMB CASE: TRANSITION TO LIQUIDLIKE BEHAVIOR

For commensurate systems, the role of interionic repulsion is straightforward: it lowers the overall conductivity, raises the effective barrier, pins the ions to their lattice sites, and blueshifts the local ionic vibration frequency. For incommensurate systems, the repulsions generally raise the conductivity, lower the effective barrier, push the ions off their lattice sites, and split the vibrational frequency.<sup>25</sup> Moreover, the favored interion spacing to minimize the one-particle

TABLE III. Local correlations in incommensurate Stoichiometry. Variation with strength of Coulomb potential.

$q=0.4$	$\rho=0.75$	$A=0.2$ eV	$\Gamma=1.35 \times 10^{-12}$ Hz	
		(other parameters as in Table II)		
	$n$	$C_n^{\max}$ <sup>a</sup>	$C_n^{\min}$ <sup>b</sup>	$I_n^c$
$q=0.4$	2	0.131	-0.138	0.488 E-6
	3	0.026	-0.032	-0.223 E-5
	4	0.180	-0.081	-0.178 E-5
	5	0.040	-0.048	-0.40 E-5
	$q=0.6$	2	0.191	-0.148
3		0.0939	-0.0956	2.26 E-5
4		0.0502	-0.0278	0.241 E-5
5		0.0467	-0.397	0.106 E-5
$q=0.8$	2	0.296	-0.181	0.481 E-5
	3	0.157	-0.138	0.449 E-5
	4	0.105	-0.078	0.429 E-5
	5	0.069	-0.054	0.487 E-6

<sup>a</sup>Defined in Eq. (7); the maximum value of  $C_n(t)$ .

<sup>b</sup>Defined in Eq. (7); the minimum value of  $C_n(t)$ .

<sup>c</sup>Defined in Eq. (8).

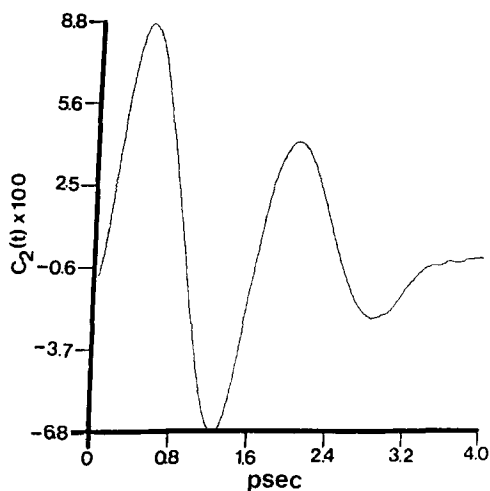


FIG. 3. The local correlation function  $C_2(t)$ , for a nearest neighbor harmonic system, with  $\omega^2 = 1.94 \times 10^{24} \text{ s}^{-2}$  and other parameters as in Table I.

potential (2) (which is an integer multiple of the lattice constant  $a$ ) will differ for incommensurate stoichiometries from the spacing favored by the Coulomb repulsion (3) (which is just  $L/n$ , where  $n$  is the number of ions in the box of length  $L$ ). The competition be-

tween these two spacings will be determined by the minimization of the total free energy of the system. As the height  $A$  of the lattice potential is increased, the first spacing should dominate, while if the density  $\rho$  or the charge  $q$  increase, the second term should be most important.

Thus we observe from the Langevin dynamics, that if the effective charge  $q$  is increased from 0.4 to 0.8 (for  $\rho_0 = 0.75$  and the parameters of Table IV), then the motion goes from correlated hopping ( $\tau_0 \gg \tau_1$ , with many oscillations occurring around each lattice before the particle jumps, and with fairly strong correlations) to liquidlike ( $\tau_0 \sim \tau_1$ , oscillations superposed on flowlike behavior and very strong correlations). Figure 4 shows a slice of the trajectories for several neighboring particles at the intermediate situation, with  $q = 0.6$ . For this choice, the Coulombic potential is still much greater than the lattice potential, but the forces due to them are roughly similar, at  $0.1 \text{ eV/\AA}$ . By comparison, for  $q = 0.4$  (correlated hopping behavior), the Coulomb forces are smaller than those due to  $V_1$ , while for  $q = 0.8$  (liquidlike motion) the Coulomb forces are larger. For  $q = 0.6$ , the behavior is intermediate; while specific residence times can be identified for particles at minima of  $V_1$  (such as those at  $57.535 \text{ \AA}$  and at  $69.975 \text{ \AA}$  in Fig. 4), still the overall behavior

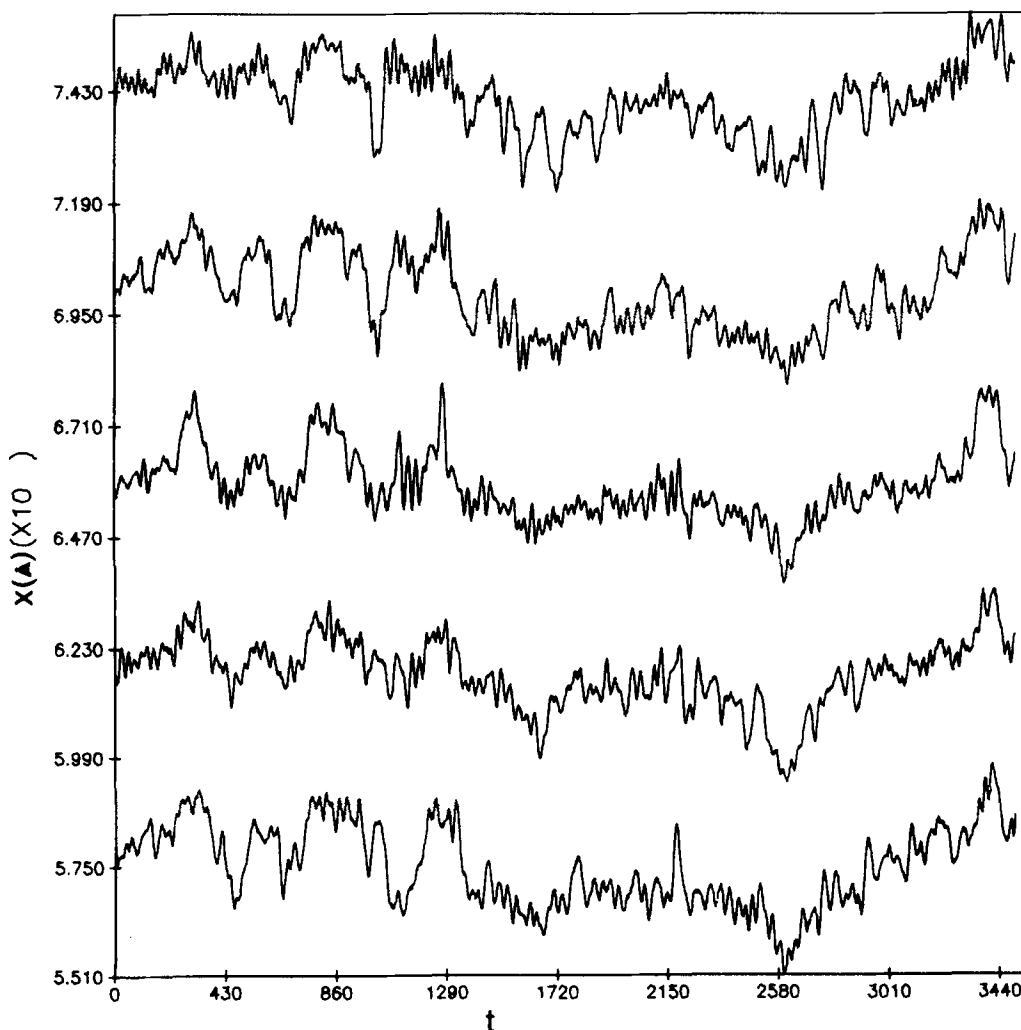


FIG. 4. The displacement-time trajectories, as calculated from Langevin dynamics, for an incommensurate system with intermediate ion-ion repulsion strength.  $\rho_0 = 0.75$ ,  $q = 0.6$ , other parameters as in Table I. The behavior is intermediate between the liquidlike ( $q = 0.80$ ) and correlated hop ( $q = 0.4$ ) behavior of Ref. 15. Note the hop at  $t = 600$  units, but the generally liquidlike profile (particles not restricted to lattice sites). Units on  $t$  axis are  $0.02 \text{ ps}$ .

is more continuous than in the weak-coupling ( $q=0.4$ ) case, and correlated hops *per se* can no longer be identified.

Very rough visual estimates, based on Fig. 4 and data presented earlier,<sup>15</sup> indicate that the ratio or residence time  $\tau_0$  to hopping time  $\tau_1$  is approximately 30 for  $q=0.4$ , 3 for  $q=0.6$ , and close to zero (no real residence) for the liquidlike  $q=0.8$ .

Thus the visual appearance of the trajectories, as well as the correlation factors (which decrease from 0.39 at  $q=0.4$  to 0.062 at  $q=8$ )<sup>12,15</sup> and residence times, indicate that the behavior can change from correlated hopping to liquidlike as the Coulomb forces increase. In the limit of very strong Coulomb repulsions, the activation energy for conductivity will vanish, as the ions form a rigid lattice whose spacing is incommensurate with that of the framework. The total effect of  $V_1$  then is constant as the ions move in lockstep, so that there is no activation. This behavior is very much like the incommensurate sliding charge density wave which has been studied for electronic conduction in one dimension.<sup>26</sup> In that case, the wave can be pinned either by the presence of defects or by disorder in the (framework) lattice: we expect the same to be so for the ionic motion situation. Effects of Coulomb trapping by counterions in framework ionic conductors will be reported elsewhere.

When the Coulomb forces greatly exceed the lattice forces, the interionic potential may be expanded about the equally-spaced minimum. When the expansion is cut off at harmonic terms, the Frenkel-Kontorova model is obtained. For this model, Geisel has shown<sup>25</sup> the commensurability effects, and has also demonstrated that, at least in the strong-damping limit, the full sliding charge-density wave behavior is not obtained, as the correlations weaken considerably after six or so neighbors. Coulomb forces, however are longer-ranged than the (near-neighbor harmonic) Frenkel-Kontorova ones, and one might therefore suspect longer-ranged correlations. Once again, it is of interest to investigate both  $c_n$  of Eq. (7) and  $I_n$  of Eq. (8). Table III shows both the extremal values of  $C_n$  and the  $I_n$  for Coulomb forces in an incommensurate stoichiometry. As the charge increases, the dominant local ( $n=2, 3, 4$ ) correlations change from smaller and negative to larger and positive. Both size and sign are understandable: the behavior becomes more like a sliding wave or caterpillar collective motion as charge and correlation strength increase. If one particle is moving to the right at time zero, most probably nearby particles at short times are also moving to the right; this is reflected in the  $C_{n,\max}$  behavior. From the fact that  $F < 1$ , we deduce that, if  $I_n$  is negative for small  $n$  (as is for  $q=0.4$ ), then it must be positive for larger  $n$  (otherwise the  $D_0$ , from Eq. (8), will be smaller than  $D_{\text{tracer}}$ ). For very large  $q$ , as seen in Table III, the  $I_n$  are positive, and decrease slowly with  $n$ .

This behavior (conduction enhancement by correlation effects in incommensurate situations) has one interesting implication for experimental investigation. Groups in Philadelphia<sup>27</sup> and in Evanston<sup>28</sup> have prepared frame-

work ionic conductors in which the mobile ions are divalent. If the compensator trapping and cage potentials ( $V_1$ ) can be overcome, we would predict that such systems have higher conductivity than monovalents. Such an argument may help explain the anomalously high conductivity of  $\text{Pb}^{2+}$  in  $\beta'$  alumina.

## V. DAMPING, CORRELATION FORCES, AND THE EFFECTIVE POTENTIAL: THE MICROWAVE CONDUCTIVITY

A few microwave conductivity results have been reported for superionic conductors. The limiting behavior of  $d\sigma(\omega)/d\omega$  as  $\omega \rightarrow 0$  has been of particular interest, since Kimball and Adams<sup>8</sup> showed that the effects of correlation, if treated in a hopping model, will always be to make the conductivity *increase* for increasing  $\omega$  away from the origin. Physically, this means that the "bounceback" effect should dominate the caterpillar effect in the low frequency limit. They demonstrated this by calculations on short commensurate chains.

Although the hopping models have many serious difficulties for solid electrolyte applications, other results, based on Brownian motion models, have also demonstrated increasing conduction in the microwave. Formally, one can show (see the Appendix) that

$$d\sigma(\omega)/d\omega|_{\omega=0} = M\omega, \quad (10)$$

but the sign of the constant  $M$  is undetermined. For interacting-particle systems, we are aware of no work, either formal or numerical, which yields negative  $M$ . For noninteracting particles, one can show that so long as the restoring force at the well bottoms acts for a long enough time,  $M$  will be positive. This holds, in particular, no matter how large the damping  $\Gamma$  may become. Using the approximate solution provided by the Brown-Boveri group<sup>29</sup> for the problem of an ion diffusing in a periodic potential, one can show that the value of  $M$  can become negative if the memory time over which the restoring force effectively acts is smaller than the inverse frequency at the well bottom.

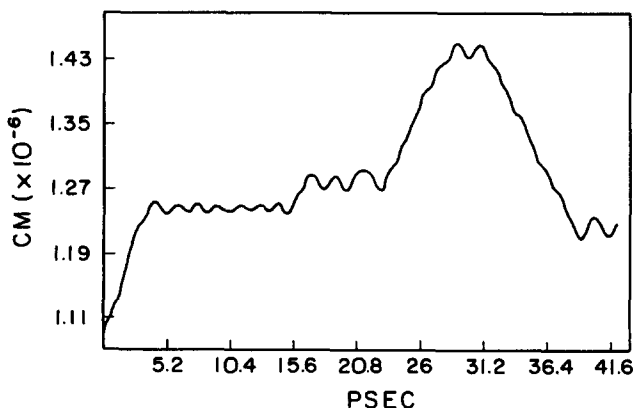


FIG. 5. Typical trajectory in the case of weakly damped, non-interacting particles. Parameters in Table I, except  $\Gamma=1.35 \times 10^{11} \text{ s}^{-1}$ . Note the oscillatory regions (between 5 and 15 ps), and the quasifree motion (such as from 0 to 4 ps). These result in harmoniclike and Drude-like behavior, respectively.

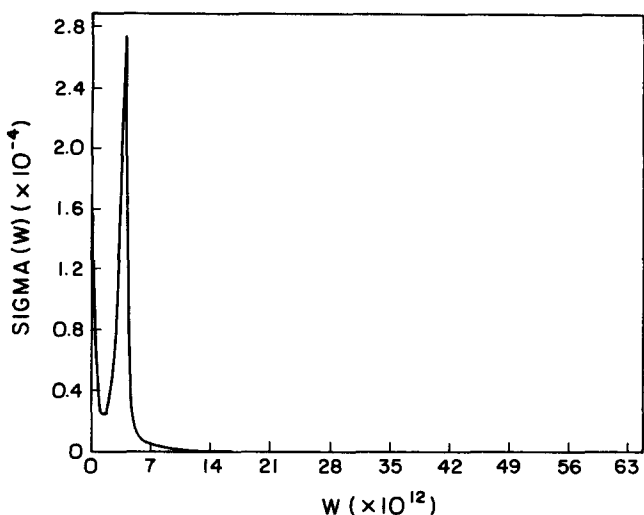


FIG. 6. Computed conductivity for noninteracting particles (as in Fig. 5). Note decrease of conductivity with frequency (quasifree, Drude-like) at low frequency, oscillatory peak for  $\omega \approx 4 \times 10^{12}$  Hz.

When the particle-particle repulsions  $V_2$  are absent, an ion, once thermally promoted above the barrier energy  $A$ , can diffuse a fairly long distance if  $\Gamma$  is small compared to thermal frequencies. Thus, one should be able to observe in this regime, both diffusive character (peak at  $\omega=0$ ) and harmonic character (peak at  $\omega = (k_{\text{eff}}/m)^{1/2}$ , for a local effective force constant  $k_{\text{eff}}$ ). This behavior is in fact observed in our Langevin dynamics for very dilute systems, as shown in Figs. 5 and 6; it was proposed in an early model by Huberman and Sen,<sup>30</sup> who argued that the restoring forces acting on the ions should be harmonic at short times but absent at long times. This behavior is not expected to be common, since ion-ion repulsion will generally prevent the free motion over more than one or two lattice sites.

In experimental practice, most superionic conductors exhibit oscillatorlike behavior ( $M > 0$ ) rather than Drude-like behavior ( $M < 0$ ). The only well-documented case for which this fails is  $\alpha$ -AgI, for which Funke and others<sup>7</sup> have observed negative  $M$ .

## VI. REMARKS

Liquidlike behavior has been invoked previously for solid electrolytes of molten-sublattice type, such as  $\alpha$ AgI. Our simulations, coupled with observations of sublattice spacings in hollandite and with formal results available in the Frenkel-Kontorova (strong-coupling)<sup>25</sup> and Smoluchowski (strong-damping)<sup>10,11,16</sup> limits, indicate that simple correlated hopping, which is an appropriate dynamical model for framework solid electrolytes in the commensurate or weak-interacting cases, may begin to fail seriously for strongly interacting, incommensurate cases, such as Pb- $\beta'$  alumina. For these instances, the theory and the simulations indicate that the ionic displacements are strongly correlated, that the flight time and time between jumps are no longer easily differentiated, and that the dynamics is truly

liquidlike. It would be of considerable interest to search for this behavior experimentally, either employing inelastic scattering to get at  $\rho^{(2)}(x, x')$ , or anharmonic fits to the x-ray data to look for broadened behavior in  $\rho(x)$ , or, perhaps, from  $M < 0$  behavior (negative slope at origin) in the microwave conductivity.

In glass framework conductors, or in frameworks with strong compensatorcharge trapping, effective incommensurability may be provided by disorder in  $V_1(x)$ . This can then lead to *enhancement* in the conductivity, compared to the untrapped, perfectly ordered case. More work on these materials, both experimental and theoretical, would be of real value, to study the competing effects of disorder in  $V_1(x)$ , the unperturbed, periodic  $V_1(x)$  and the ionic interactions. Glassy materials can in fact demonstrate fairly substantial ionic conductivity,<sup>31</sup> and the mechanistic understanding of that process, in terms similar to those developed here and elsewhere for ordered frameworks, remains a challenge.

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## APPENDIX

The frequency dependence of the microwave conductivity. We wish an expression for

$$d \operatorname{Re} \sigma(\omega) / d\omega \Big|_{\omega \rightarrow 0} \equiv d\sigma / d\omega. \quad (\text{A1})$$

Apart from constant term  $A_0$ , we have from the correlation expression

$$\sigma(\omega) = A_0 \int_0^\infty e^{i\omega t} \sum_n \langle J_1(t) J_n(0) \rangle dt. \quad (\text{A2})$$

Thus

$$d\sigma / d\omega = A_0 \int_0^\infty e^{i\omega t} it \sum_n \langle J_1(t) J_n(0) \rangle dt. \quad (\text{A3})$$

For small  $\omega$ , this becomes (real part)

$$d\sigma / d\omega = -\omega \int_0^\infty \sum_n \langle J_1(t) J_n(0) \rangle t^2 dt. \quad (\text{A4})$$

Since the integral in Eq. (A4) is a real number independent of  $\omega$ , we can rewrite Eq. (A4) as

$$\operatorname{Re} \frac{d\sigma}{d\omega} \Big|_{\omega \rightarrow 0} = M\omega,$$

where  $M$  is a real number. Thus the slope of the conductivity near the origin is directly proportional to frequency.

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