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CHARGE CARRIER CORRELATIONS IN FRAMEWORK SOLID ELECTROLYTES

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Stochastic Langevin dynamics is employed to simulate correlated charge carrier diffusion in framework solid electrolytes. We include realistic coulombic ion-ion interactions, as well as static and dynamic effects of the framework lattice. Ionic conductivity and correlation factors are calculated for several model systems. These transport properties characterize the diffusion mechanism as either liquid-like or correlated hopping. For systems in which the charge carrier density is incommensurate with the period of the lattice, ionic motion can be either liquid-like or hopping depending on the system parameters. The transition from correlated hopping to liquid-like diffusion induced by variation of these parameters is discussed.

I. INTRODUCTION

In framework ionic conductors highly mobile ions diffuse through a crystalline sublattice. These materials often exhibit ionic conductivity greater than 10^{-3} $(\text{ohm-cm})^{-1}$, and therefore function as solid electrolytes. Recent studies have demonstrated the importance of ion-ion correlations in solid electrolytes. For example, experiments measuring tracer diffusion and d.c. conductivity in Na-β-alumina[1] indicate that charge carrier motion is correlated. Diffuse X-ray scattering data[2] for the one-dimensional ionic conductor hollandite is also indicative of strong ion-ion correlations. Theoretical studies have shown that these ion-ion interactions cause the d.c. conductivity to be stoichiometry dependent.[3,4] When the charge carrier density is commensurate with the period of the lattice, the repulsive coulombic inter-ionic forces augment the periodic barrier, decreasing the conductivity. However, for incommensurate systems competing effects of the static lattice potential and the coulombic potential can lead to enhanced conductivity.

In this paper, we focus on the effects of ion-ion interactions and charge carrier correlations by examining ionic diffusion at the individual particle level. We calculate correlation factors which provide a quantitative measure of the correlations, and then discuss mechanisms of ionic diffusion in terms of these ion-ion correlations.

We employ stochastic Langevin dynamics[5] to simulate one-dimensional correlated ionic diffusion in framework solid electrolytes. The interaction between the mobile ions and the framework sublattice is represented by a sum of sinusoidal, damping, and stochastic forces, and correlated ionic motion is represented by realistic interparticle forces. These equations of motion are written as follows:

$$m\ddot{x}_i = -m\Gamma\dot{x}_i - \frac{A\pi}{a}\sin\left(\frac{2\pi}{a}x_i\right) + \phi(i)_{int} + R(t)$$

$$\phi(i)_{int} = \sum_j \left(\frac{7C}{r_{ij}^{8}} + \frac{(q\,e)^2}{r_{ij}^{2}}\right) \qquad (1)$$

where Γ is the damping constant, A is the height of the periodic potential due to the static framework, $\phi(i)_{int}$ is the ion-ion interaction force and R(t) is a correlated Gaussian random variable. The time correlation function of R(t) is related to Γ and the temperature by the fluctuation dissipation theorem[6] $\langle R(0)\ R(t)\rangle = \delta(t)2m\Gamma k_B T$. Equation (1) is solved numerically with periodic boundary conditions, yielding stochastic trajectories from which the desired transport property is calculated.

The subscript i refers to the ith particle and the notation $\langle\cdots\rangle$ refers to the average of many trajectories.

II. HAVEN RATIO

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.

$$H_r \equiv D_{Tr}/D_0 \qquad (2)$$

Here D_{Tr} and D_0 are the experimentally observed tracer and bulk diffusion coefficients. Consider the interstitialcy mechanism in which a mobile ion jump causes the neighboring ions to move as well. Here, D_0 is usually greater than D_{Tr}. However, if the system is infinitely dilute each ion moves independently so D_0 equals D_{Tr}. Thus H_r is unity for uncorrelated motion while $0 < H_r < 1$ when correlations are present.

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The diffusion coefficient for a one-dimensional system is calculated from mean squared displacement $(\Delta x^2)^1$ via the Einstein relation:

$$D = \lim_{t\to\infty} \frac{\Delta x^2(t)}{2t} \qquad (3)$$

where

$$\Delta x_{Tr}^2(t) = \frac{1}{N} \sum_{i=1}^{N} \langle [x_i(0) - x_i(t)]^2 \rangle$$

and (4)

$$\Delta x_0^2(t) = \frac{1}{N} \sum_{i=1}^{N} \langle \left(\left[\sum_{i=1}^{N} x_i(0) \right] - \left[\sum_{i=1}^{N} x_i(t) \right] \right)^2 \rangle$$

Figure 1 is a plot of the $\Delta x_0^2(t)/t$ and $\Delta x_{Tr}^2(t)/t$ (bulk and tracer) as a function of time. In the long time limit the bulk mean square displacement is proportional to t as expected from the Einstein relation (3); however, the mean squared displacement of tracer ions asymptotically varies[7] as $t^{1/2}$

$$\Delta X_t^2(t) \alpha t^{1/2} \text{ (large t)} \qquad (5)$$

The expression for the Haven ratio can be rewritten combining equations (2) and (6)

$$H_r = \lim_{t\to\infty} \frac{\Delta X_{Tr}^2(t)}{\Delta X_0^2(t)} \qquad (6)$$

From equations (5) and (6) H_r for ionic diffusion in a one-dimensional channel is zero; however, we can define a finite time Haven ratio, or alternatively a correlation factor which is finite and decreases when ionic motion becomes more correlated

$$F \equiv \Delta X_t^2(t')/\Delta X_0^2(t') \qquad (7)$$

where t' is chosen arbitrarily to be 5.12 psec.

Table I lists values of the diffusion coefficient and the correlation factor for an incommensurate system as a function of ion-ion interaction strength. As the latter increases the correlated nature of ionic diffusion increases (i.e., F decreases). Thus, the value of F is a quantitative measure of correlated motion and can be used to relate these correlations to the mechanism of ionic diffusion; decrease in the value of F reflects increased correlation.

III. MECHANISM OF DIFFUSION: LIQUID-LIKE VERSUS CORRELATED HOPPING

Correlated hopping is characterized by $\tau_R >> \tau_F$, where τ_R is the residence time of an ion in a site, and τ_F is the time of flight from one site to the next. When a hopping mechanism is dominant, ion-ion correlations are most important during the hopping event (not when the mobile ions are localized). Thus because $\tau_F << \tau_R$, the correlation factor (F) will be large (close to unity). On the other hand, liquid-like ionic motion is strongly correlated at all times and is characterized by small values of F. Therefore, values of F calculated from the stochastic trajectories characterize hopping vs. liquid-like behavior.

Consider a system with no periodic barrier. Here the stochastic forces tend to disorder the mobile ions, while the repulsive coulombic force with periodic boundary conditions tends to order them. When the mobile ions are equidistant, the

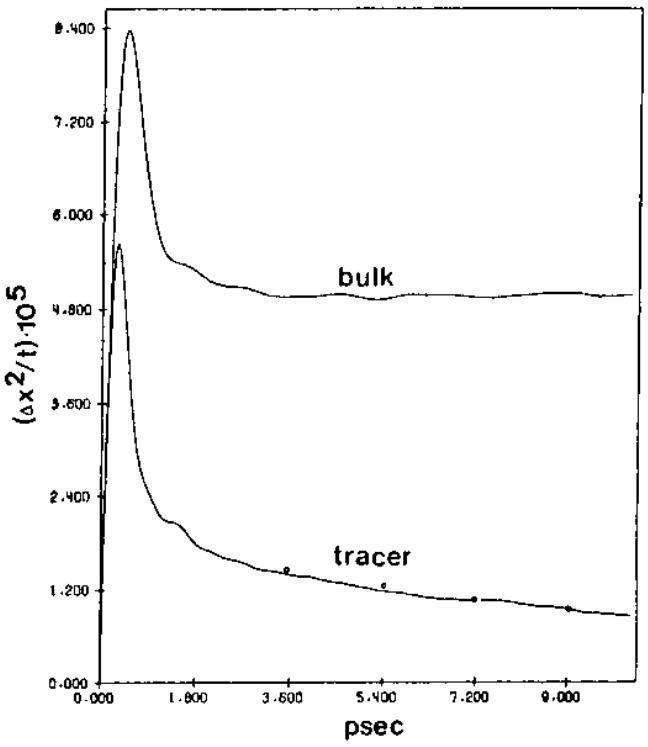

Figure 1. The mean squared displacement of bulk and tracer ions, for a model system with A = 0.05 eV, a = 3.1 Å, q = 0.4, ρ = 0.5, Γ = 1.35×10^{12} Hz, T = 453°K. Circles are the $t^{-1/2}$ behavior.

Table I. Correlation Factor as a Function of Charge for an Incommensurate System

T = 453°K; ρ = 0.75; A = 0.2 eV, m = 1.776×10^{-22} grams, Γ = 1.35×10^{12} Hz; a = 3.11 Å

q	F x 100	D_0 $cm^2/sec \times 10^5$
0	-	0.63
0.4	39.4	3.38
0.6	12.2	10.2
0.8	6.2	20.66
1.0	2.9	25.3

coulombic potential energy is minimum. This behavior is evident from the data in Table II.

As the strength of the interionic forces increases, ionic motion becomes more correlated (F is seen to decrease), while the bulk conductivity remains constant. This indicates that at low frequency when the interionic forces are dominant the mobile ions move in unison (provided $k_BT < \langle\phi_{int}(i)\rangle$).

Now consider diffusion where the density of mobile ions is commensurate with the period of the lattice. Table III lists F as a function of periodic barrier height for commensurate density. Compared to trajectories with no lattice barrier the value of F is five times greater when the barrier height is 0.06 eV (approximately k_BT). As the barrier height is increased at constant T, F is increased. Moreover, when a periodic barrier is present (.05 eV ≤ A ≤ .1 eV) F is independent of q (0.4 ≤ q ≤ 0.8); however, the bulk and tracer d.c. conductivities decrease as q is increased. This suggests the following scenario: the periodic barrier keeps the ions separated and local motion of the ions in the bottom of the potential wells is largely uncorrelated. When the mobile ion gets enough thermal energy to approach the top of the periodic barrier, coulomb repulsions take over, inducing either backwards correlations (the mobile ion migrates back to its original lattice site) or forward correlations (the mobile ion and its neighbors migrate to a vacancy). Comparison of stochastic trajectories with and without coulombic forces indicates that back correlation is more frequent, hence σ is decreased as the coulomb interaction strength increases. The bounceback dominates the caterpillar. Thus the correlation factor calculated from these simulations characterizes two types of motion;[8] liquid-like diffusion occurs when there is no periodic barrier, and correlated hopping occurs when A ≠ 0 and the mobile ion density is commensurate with the period of the lattice.

When the mobile ion density is incommensurate with the period of the lattice, ionic motion can be either liquid-like or hopping, depending on the values of A, q and ion density (ρ_0). In contrast to the commensurate systems, F shows strong q dependence: as q varies from 0.4 to 1.0 (A = 0.2 eV and ρ_0 = 0.75, Table I) F decreases from 0.394 to 0.030 and σ increases by a factor of ~ 8. Figures 2 an 3 are the stochastic position vs. time trajectories for systems with q = 0.4 and q = 0.8, respectively. Examination of Figure 2 shows vibrations within a potential well (the amplitude of these oscillators fluctuates due to random thermal effects) and large sharp changes in the position which correspond to hopping from site to site. In the weak coupling limit ($\langle\phi(i)\rangle \ll A\pi/a$) correlation effects ensure single site occupancy. In the strong coupling limit ($\langle\phi(i)\rangle > A\pi/a$) no hopping is observed (Figure 3). The mobile ions diffuse like a charged liquid. Large changes in position (for example, 15, 38, and 55 psecs) manifest themselves in all the mobile ions.

Table II. Charge Dependent Correlation Factor (No Periodic Barriers)

T = 453°K, ρ = 0.5; a = 3.11 Å; A = 0, m = 1.776×10^{-22} grams; Γ = $1.35\times10^{+12}$ Hz

q	F x 100	D_{Tr}
0.4	15.6	3.95
0.6	10.1	2.56
0.8	7.3	1.74

Table III Correlation Factor as a Function of Barrier Height for a Commensurate System

T = 453°K; a = 3.11 Å; q = 0.6; ρ = 0.5; m = 1.776×10^{-22} grams; Γ = 1.35×10^{12} Hz

A	F x 100	D_0
0	10.1	25.4
0.05	47.6	3.05
0.1	60.3	0.61

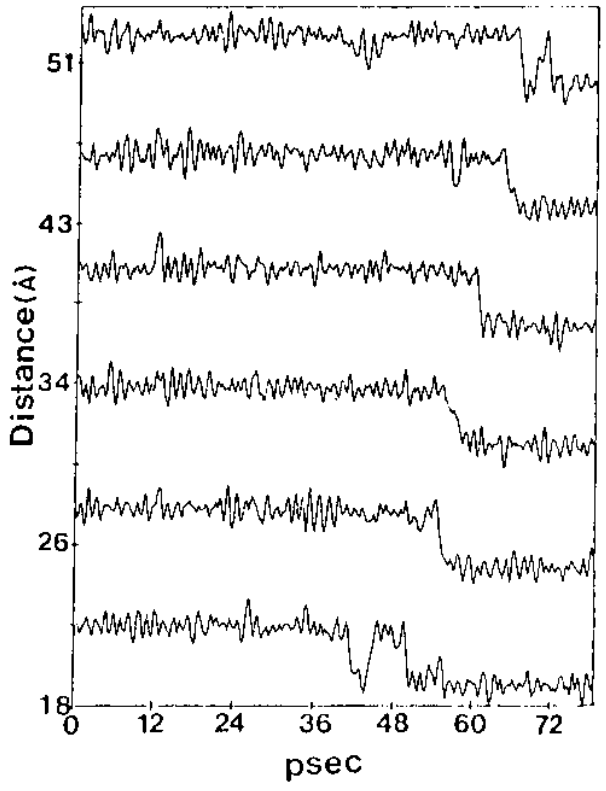

Figure 2. Position vs. time for six mobile ions; q = 0.4, A = 0.2 eV, T = 453°k; ρ = 0.75; a = 3.1 Å; Γ = 1.35×10^{12} Hz. The correlated motion is of hopping type.

Table IV gives F as a function of A (q = 0.6 and ρ = 0.75); F increases by 60% when A changes from 0 to 0.1 eV for a system with incommensurate mobile ion density; however, F increases by 500% when similar change is imposed on systems with commensurate density (Table II). In all of these model systems the periodic barrier tends to keep the mobile ions localized, but this effect is much greater when the mobile ion density is commensurate with the period of the lattice. The values of F in Table IV change from 7.9 when A = 0.1 eV to 24.8 for A = 0.3. These F values are indicative of liquid-like diffusion for A=0.1 eV and hopping when A=0.3.

IV. SUMMARY

The correlation factor characterizes the mechanism of ionic diffusion as either correlated hopping or liquid-like. In a hopping mechanism the time of ionic flight is much less than the residence time. This results in large values of the correlation factor because the ion-ion interactions are most important during a hopping event. On the other hand, in liquid-like diffusion correlations are important all the time and F is small. Incommensurate systems can exhibit either correlated hopping or liquid-like diffusion depending on the temperature, periodic barrier height, density and interaction strength. In the weak coupling limit, $\langle\phi_{int}\rangle$ is much less than $A\pi/a$, correlated hopping results. Here the interaction insures single ion site occupation. In the strong coupling limit, $\langle\phi_{int}\rangle$, is greater than or approximately equal to $A\pi/a$ and diffusion is liquid-like. Increasing the effective charge can change the mechanism of diffusion from hopping to liquid-like. Thus the particle interactions can completely determine the diffusion mechanism in these reduced-dimensionality, strongly-interacting systems.[11]

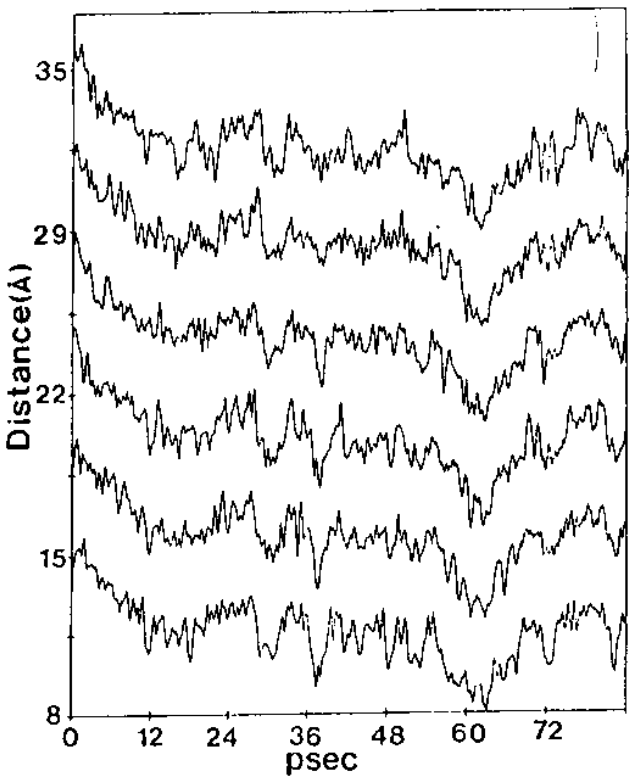

Figure 3 : Position versus time for six mobile ions; q = 0.8, A = 0.2 eV, T = 453°K, ρ = 0.75; a = 3.1 Å; $\Gamma = 1.35\times10^{12}$ Hz. The motion is liquid-like.

Table IV. Correlation Factor as a Function of Barrier Height for an Incommensurate System

Incommensurate T = 453°K, ρ_0 = 0.75; q = 0.6; $\Gamma = 1.35\times10^{12}$ Hz; m = 1.776×10^{-22} grams

A	F x 100	D_0
0	5.04	25.4
.05	7.6	20.4
.1	7.9	18.5
.2	12.2	7.65
.3	24.8	2.46

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