Correlated ionic motion in solid electrolytes: Tests of Smoluchowski dynamics and conductivity relations

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The conductivity of a one-dimensional model for solid electrolytes of framework type is calculated using both the Langevin and Smoluchowski equations. The Smoluchowski conductivity is generally larger than that from the (more general) Langevin approach; they become identical only in the strong damping limit. The inversion of computed or observed carrier densities to obtain an effective potential is generally straightforward for one dimension, but the derivation of the conductivity from this potential is easy only in the strong-damping extreme. The vibrational spectra of most ionic conductors indicate that the quantititve validity of the Smoluchowski equation is dubious for them.

I. INTRODUCTION

Framework solid electrolytes are materials in which an ionic species diffuses in a covalently linked framework lattice at rates comparable to those observed in dilute electrolyte solutions.[1] Typical frameworks consist of group III or IV metal oxides (aluminas, titanates, zirconates, silicates) and the mobile ions are often group I monocations (Ag^+, K^+, Na^+), although solid electrolytes with H^+, as well as some dication species (Ca^{2+}, Sr^{2+}) have been[2] prepared and studied. Experimental probes of quasione-dimensional tunnel-structure framework solid electrolytes such as K hollandite ($K_{1.54}Mg_{.77}Ti_{7.23}O_{16}$) or β eucryptite ($LiAlSiO_4$) have shown that ion interactions are quite important in the disordered, conductive regime. In particular, Beyeler has shown,[3] from analysis of the diffuse x-ray scattering in K hollandite, that some ions are significantly shifted off of their crystallographic sites due to ion–ion repulsion, that a model based on a distribution of ion clusters can successfully reproduce the diffuse scattering spectrum, and that the ion–ion interaction may be stronger than the periodic potential of the host crystal.

Theoretical efforts to deal with ion–ion interactions in these materials were originally based upon lattice-gas or simple hopping models.[4] These have proven extremely valuable; for example, Kimball and Adams showed[5] that for any hopping model the conductivity must increase with frequency at low frequencies, and Richards[6] has been able to describe magnetic resonance line shapes and thermal and stoichiometric effects on the conductivity using a hopping model, while the early lattice-gas path-probability method of Sato and Kikuchi[7] has provided both the conceptual framework for much of the discussion of conduction mechanisms and the starting point for recent illuminating Monte–Carlo work by Murch and Thorn.[8] The above comments by Beyeler,[3] however, coupled with the facts that liquidlike behavior has been observed in some solid electrolytes[9] and that the observed activation barriers for ionic motion are often comparable to $k_B T$, argues that a lattice-gas model might be inadequate, and that a more fully dynamic calculation would be needed to examine the mechanistic details of ionic motion.[4] Indeed, Beyeler concludes[3] 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 crystallographic sites". Accordingly, a number of dynamical treatments, both formal and numerical, have appeared. Essentially, all of this work takes advantage of the timescale separation which exists between motions of the framework where the ions vibrate on a timescale of 10^{-13} s, and the much slower diffusion timescale of the mobile cations. This permits the use of Langevin dynamics, rather than full molecular dynamics, and makes numerical study practical.

In the case of strong frictional interactions between the framework and the mobile ions, the velocity distribution of the latter relaxes to its equilibrium Maxwellian form more rapidly than the average jump time. Under these conditions the Langevin equation (or the equivalent Fokker–Planck form) can be simplified by integrating out the velocity variables so that a Smoluchowski equation describing many-particle diffusion in coordinate space is obtained.[10] Many theoretical discussions of framework ionic conductors are couched in terms of the Smoluchowski equation,[11,12] although the physical requirements for its validity may not hold in many realistic physical cases. One particularly fascinating result which holds exactly for a noninteracting one-dimensional system in the Smoluchowski limit is that the zero-frequency conductivity is determined by the equilibrium, one-particle, static distribution function $\rho(x)$, an elegant result derived for ionic conductors by Dieterich *et al.*[13]

The present study arose from a combination of this last result and the fact that recent x-ray studies using anharmonic refinements seem capable in some cases of providing an experimental determination of the static distribution $\rho(x)$.[14] We wished to investigate the domain of validity of the Smoluchowski equation, the qualitative and quantitative accuracy of the Dieterich form for the conductivity, the relationship between bare lat-

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tice barriers and observed activation energies, and that among the observable density $\rho(x)$ and the bare lattice potential. We have chosen a one-dimensional model because of the observed strong correlation effect in one-dimensional hollandite systems, and the availability for comparison of the results of Langevin dynamics studies.

We report the values of conductivity and of density based on Langevin dynamics. The Langevin and Smoluchowski equations are presented in Sec. II, along with the Dieterich form for the conductivity and its relation to $\rho(x)$ and the effective one-particle potential. Section III contains our results for the conductivity calculated from the Dieterich form and directly (via calculated correlation functions) from the Langevin dynamics. Comments appear in Sec. IV.

II. LANGEVIN, FOKKER-PLANCK, AND SMOLUCHOWSKI EQUATIONS

We consider the dynamics of carriers (mobile ions) moving in a static potential due to the equilibrium structure of the framework lattice; because of the large masses, classical mechanics is used[15]; we work in one dimension. The total potential consists of a one-particle periodic part V_1 and the ion–ion interactions V_2. Thus,

$$V=\sum_{i=1}^{N} V_1(x_i)+\sum_{j\neq i}^{N} V_2(x_i-x_j)\ , \tag{1}$$

where x_i is the displacement of the ith ion. The limit of free carriers occurs when $V_2=0$; this then becomes the problem of Brownian diffusion in a periodic potential, for which some general results are available.[16] Because the mobile ions are charged however, we expect (and experiments[3] and simulations[17,18] have shown) that the Coulomb term in Eq. (1) is of substantial importance. For simplicity then we choose

$$V_1(x_i)=\tfrac{1}{2}V_0\cos(2\pi x_i/a)\ , \tag{2}$$

$$V_2(x_i-x_j)=q^2/|x_i-x_j|\ . \tag{3}$$

Thus, the lattice potential is sinusoidal and the short-range and long-range van der Waals forces (which have been shown to have minimal effects in these species[17,18]) have been omitted. The effective charge q is expected to be less than the formal ionic charge due to screening and charge-transfer effects. The potential (1) defines a classical many-body problem with long-range, nonseparable, nonuniform potentials; the solution of this problem yields the carrier dynamics.

Because of the timescale separation cited above between ion and framework motion (or, equivalently, because the strong covalent forces in the oxide lattice lead to high Debye temperatures), there is no significant memory effect from the lattice on the ion dynamics. Thus we can, to an excellent approximation, describe ion motions by Langevin equations. For the one-dimensional case, these are

$$m\ddot{x}_i=-m\Gamma\dot{x}_i-\partial/\partial x_i\{V\}+R_i(t)\ , \tag{4}$$

where Γ is a damping frequency, m is the ion mass, and the random force term $R_i(t)$ satisfies the fluctuation-dissipation theorem in the form

$$\langle R_i(t)R_j(0)\rangle=2mkT\Gamma\delta(t)\delta_{ij}\ . \tag{5}$$

The effects of the framework on the mobile ions are thus manifested in three terms: the static framework provides a background potential $V_1(X)$, while the framework vibrations both provide a random force or "kick" $R(t)$ and thermalize the ion velocity through the damping term containing Γ. Since the random force and damping terms arise from the same physical origin, their amplitudes must be related; the relation is (5). The Langevin equations (4) describe the evolution of the ion trajectory in both displacement and velocity. The distribution function $P(x,\dot{x},t)$ corresponding to this trajectory satisfies the Fokker–Planck equation

$$\frac{\partial p(x,\dot{x},t)}{\partial t}+\dot{x}\frac{\partial p}{\partial x}-\frac{1}{m}\frac{\partial V}{\partial x}\frac{\partial p}{\partial \dot{x}}=\Gamma\frac{\partial}{\partial \dot{x}}\left[\dot{x}p+\frac{kT}{m}\frac{\partial}{\partial \dot{x}}p\right]\ . \tag{6}$$

When the ions collide with the lattice so often that the mean-free path becomes smaller than a typical range over which the potential V_1 changes, the velocity relaxation will be so rapid that the distribution function $p(x,\dot{x},t)$ for the velocity and displacement at time t can be factorized as[10]

$$p(x,\dot{x},t)=\exp(-m\dot{x}^2/2kT)f(x,t)\ , \tag{7}$$

here the (Maxwell) equilibrium form describes the velocity distribution. Then the Fokker–Planck equation for $p(x,\dot{x},t)$ simplifies to the Smoluchowski form:

$$\frac{\partial f(x,t)}{\partial t}=\left(\frac{kT}{m\Gamma}\right)\frac{\partial}{\partial x}\left[\left(\frac{\partial V}{\partial x}\right)\left(\frac{f}{kT}\right)+\left(\frac{\partial f}{\partial x}\right)\right]\ , \tag{8}$$

(when $V=0$ and the substitution

$$D=kT/m\Gamma \tag{9}$$

is made, Eq. (8) reduces to the ordinary diffusion equation).

One expects that the form (8) represents the dynamics of Eq. (4) properly when the damping is large, so that[18]

$$\left|\frac{\partial^2 V}{\partial x^2}\right|\ll m\Gamma^2\ . \tag{10}$$

Physically this means, as stated above, that the damping frequency Γ is larger than the frequency $(m^{-1}\partial^2 V/\partial x^2)^{1/2}$. Typical parameter values for framework conductors, however, may not satisfy Eq. (10). In particular, when the ions are fairly light (Li^+, Na^+) and the framework potential V_1 becomes substantial, Eq. (10) may cease to hold, as the ion mean-free path grows. Then Eq. (8) becomes a poor representation of the Fokker–Planck equation (which is equivalent to the Langevin equation). One aim of our work is to examine the parameter range for which the dynamics show that replacement of Eq. (4) by Eqs. (7) and (8) is reasonable.

The replacement of Eq. (6) by Eqs. (7) and (8), when it is valid, is a major simplification. For example, for simple sinusoidal potentials and noninteracting particles, an exact solution is available for Eq. (8), but not for Eqs. (4) or (6). Of perhaps more interest, it can be shown that if Eq. (8) holds, a rigorous form for the mobility of independent particles in one dimension

is given by Dieterich's result

$$\frac{\mu(0)}{\mu(\infty)} = \left[\frac{1}{a^2}\int_0^a \exp[\beta V_{\text{eff}}(x)dx]\int_0^a \exp[-\beta V_{\text{eff}}(x)\,dx]\right]^{-1} . \tag{11}$$

where a is the unit cell dimension and the effective potential is V_{eff} and $\beta^{-1} = kT$. This can in turn be related to the local ion density, for thermal equilibrium, by

$$\rho(x) = A\exp[-\beta V_{\text{eff}}(x)] , \tag{12}$$

where A is a normalization factor. The value $\mu(\infty)$ in Eq. (11) is just the free Brownian mobility $(m\Gamma)^{-1}$. Thus, we can rewrite Eq. (11) as

$$\mu(0) = a^2(m\Gamma)^{-1}\left[\int_0^a dx\,\rho(x)\int_0^a dx\,\frac{1}{\rho(x)}\right]^{-1} . \tag{13}$$

The result [Eq. (13)] has some important implications: the mobility will be strongly reduced whenever a point or region occurs for which the particle density is very small (close to zero), since then the second integrand in Eq. (13) will blow up. Interpreting $\rho(x)$ via Eq. (12), this means that when the local potential is very repulsive, it can significantly reduce the overall mobility. For interacting systems, an important feature is that the density is determined not from the bare lattice potential V_1 but from the full potential V [Eq. (2)]. If $V_2 = 0$ then for the sinusoidal potential (2) the usual activated form $T\mu(0) \sim \exp(-\beta V_0)$ follows from Eq. (13), if $\beta V_0 > 1$. However, the relevant activation barrier in interacting cases will be determined from V, not from V_1. It should be noted that while Eq. (13) is exact for noninteracting particles, its applicability to the interacting particle case, while reasonable, is not assured.

In the next section we compare Smoluchowski and Langevin results for a series of system parameters and particle densities. The Langevin results were obtained via numerical solution (stochastic trajectories[17,19]) of Eq. (4) to obtain the velocity and displacement autocorrelation functions, from which the transport properties can be derived via linear response theory.

III. RESULTS: COMPARISON OF LANGEVIN AND SMOLUCHOWSKI DYNAMICS

A. Noninteracting case

To test how sensitive the applicability of the Smoluchowski equation is to the criterion (10), we compared the conductivity $\sigma(\omega = 0)$ computed from stochastic trajectories (Langevin) to the exact Smoluchowski result for sinusoidal potentials. The latter is[11]

$$D = [I_0(V_0/2kT)]^{-2}\cdot\frac{kT}{m\Gamma} , \tag{14}$$

where I_0 is a modified Bessel function and the diffusion coefficient D is related to the conductivity σ via

$$\sigma = \frac{N(\text{Ze})^2 D}{kT} , \tag{15}$$

where Ze is the ion charge.

The Langevin equation (4) with V_2 equal to zero and physically reasonable parameters has been solved with several values of Γ. The diffusion coefficients calculated from stochastic trajectories are compared to those calculated using Eq. (14) in Table I. The data show: (1) as the damping constant increases, the two results become closer together, and at high damping the two solutions agree; (2) the Smoluchowski solution varies strongly with varying damping constants, whereas the stochastic Langevin dynamics results are less sensitive to changes of the damping constant; and (3) the Smoluchowski diffusion coefficients are too high when the system is not in the high damping limit.

TABLE I. Comparison of diffusion coefficients determined by stochastic Langevin dynamics and the Smoluchowski equations.[a]

$\Gamma\times10^{-12}$ Hz	Langevin[b] ($D\times10^5$ cm^2/s)	Smoluchowski[c] ($D\times10^5$ cm^2/s)	$\left\lvert\frac{\partial^2 V}{\partial x^2}\right\rvert\frac{1}{m\Gamma^2}$
0.135	15.7	120.1	1000
1.35	5.5	12.1	10
3.0	3.6	6.5	2
4.5	2.6	3.6	0.91
6.0	2.3	2.7	0.51
10.0	1.5	1.6	0.18

[a] $V_0 = 0.1$ eV, $T = 453$ K, $a = 3.1$ Å, $m = 1.776\times10^{-22}$ g.
[b] Computed from stochastic trajectories, Ref. 17.
[c] From Eq. (14). All results for $V_2 = 0$.

The deviations at low damping arise since the Smoluchowski solutions in some sense underestimate the effect of the external force. That is, the strong damping means that the large accelerations which should be produced by the external (lattice) potential are substantially reduced. For this system, the sinusoidal external force localizes the particles and is responsible for lowering the diffusion constant (compared to the case when V_1 is zero). Therefore, Smoluchowski results obtained using small damping constants yield too high a value for D. Alternatively, one can understand the fact that the Smoluchowski result for σ is too large by noting that for a real system which does not obey Eq. (10), the average velocity at the bottom of a potential well is higher than that on the top while the absolute average of the velocity (over all positions) should be $\propto kT$, independent of the damping strength. Therefore, the real velocity near the barrier top will be smaller than that predicted by Eq. (7), and thus the conductivity (rate of crossing barrier tops) will be lower in actuality than predicted by Eq. (8). Table I includes values for the validity criterion (10). When agreement between the Langevin dynamics and the Smoluchowski results is obtained, this smallness parameter is ~0.20. However, when $\Gamma = 1.35\times10^{12}$ Hz, the value inferred from spectroscopy of α AgI,[20] the diffusion coefficient calculated from the Smoluchowski result [Eq. (14)] is about two times too high. As pointed out long ago[10] by Chandrasekhar, one expects Eq. (8) to be useful only for distances greater than $(kT/m\Gamma^2)^{1/2}$ and times greater than Γ^{-1}. The fact that the Smoluchowski prediction overestimates the conductivity for superionic conductors has been noted previously.[13]

B. Interacting particles

When $V_2 \neq 0$, there are no available exact results for the Smoluchowski equation or the Langevin equation.

TABLE II. Comparison of diffusion coefficients for an incommensurate system of interacting charged particles ($\rho_0 = 0.75$) determined by Langevin dynamics and the Dieterich form.[a]

$\Gamma \times 10^{-12}$ Hz	Temp. (K)	Barrier height (eV) V_0	Barrier height (eV) V_{eff}	E_a (eV)[b]	Diffusion coefficient $\times 10^5$ (cm^2/s) Dieterich[c]	Diffusion coefficient $\times 10^5$ (cm^2/s) Langevin[b]
1.35	453	0.3	0.113	0.10	8.45	2.46
13.5	453	0.3	0.111	0.10	0.89	0.98
13.5	300	0.3	0.099	0.10	0.29	0.23
13.5	700	0.3	0.133	0.10	2.03	2.02

[a] $a = 3.1$ Å, $m = 1.776 \times 10^{-22}$ g.
[b] Computed from Langevin dynamics, Eq. (4).
[c] Computed from Eq. (13).

We have, however, completed stochastic Langevin calculations for a one-dimensional system with 30 mobile ions and periodic boundary conditions, and the results both for the conductivity $\sigma(\omega)$ and for the time average density $\rho(x)$ are available from them.[17,18,21]

The density function obtained from these stochastic trajectories is correlated over several sites; however, the density function is periodic with lattice constant equal to the period of V_0 because each site in the system is equivalent. This allows the density function to be calculated as follows:

$$\rho_a(x) = \frac{1}{N} \sum_{n=0}^{N-1} \rho(x+n) \quad 0 < x \leq a \,, \quad N \gg 1 \,, \tag{16}$$

where N is the number of sites in the system. Using the density function in Eq. (16) we can compute the effective potential.

$$V_{eff}(x) = -kT \ln \rho_a(x) \,. \tag{17}$$

The diffusion coefficients calculated using the Dieterich expression (11) are then compared to the diffusion coefficients calculated from the stochastic trajectory. The system density ρ_0 is the average number of mobile ions per minimum in V_1 of (2). The results for an incommensurate system, $\rho_0 = 0.75$, are presented in Table II, and the effective potential computed from Eq. (17) using ρ_a from Langevin dynamics, is compared to the bare potential in Fig. 1. These results indicate that: (1) The effective potential barrier height is approximately equal to the activation energy determined by Langevin dynamics, independent of the damping constant; (2) The interionic forces in the incommensurate system cause the effective barrier height to be lower than the bare potential; (3) the Dieterich solution is only valid in the high damping case; and (4) The diffusion coefficient calculated using the Dieterich equation is too high in the lower damping case. Items (3) and (4) are similar to the results of the noninteracting case; item (4) has been noted previously, while item (3) is expected, since Eq. (11) is derived from the Smoluchowski equation, which is valid only in the high damping limit.

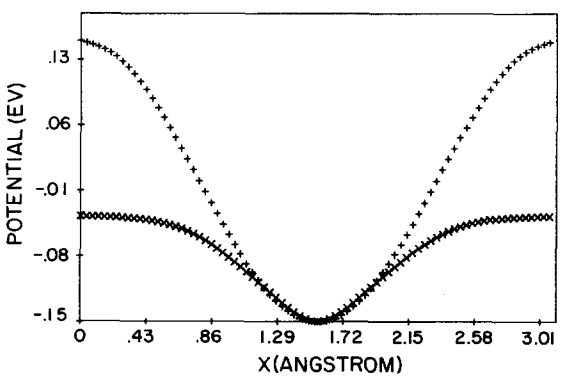

FIG. 1. The bare one-particle potential $V_1(x)$ [Eq. (2)] and the effective potential $V_{eff}(x)$ [Eq. (17)], for a system with $q = 0.6$, $a = 3.11$ Å, $V_0 = 0.3$ eV, $\rho_0 = 0.75$, $T = 453$ K. For this incommensurate system, the effective barrier is far lower than the one-particle barrier, so that correlation promotes conduction.

For the commensurate case ($\rho_0 = 0.5$), the activation barrier is higher than V_0, due to ion–ion repulsion. This means, in turn, that the second derivative (force constant) in Eq. (10) is larger, so that for the Smoluchowski limit to hold, Γ must be still larger. Using the parameters of Table II, the activation barrier derived from the Langevin dynamics simulation is larger than that associated with V_{eff} derived from Eq. (17). This may arise from the formation of a sublattice (full–empty–full–empty site occupancy) characteristic of the commensurate stoichiometry. This case is in fact uninteresting from the practical point of view since commensurate systems are poor ionic conductors.

IV. CONCLUSIONS

Much of the formal work concerned with ionic conductivity is couched in terms of the Smoluchowski equation.[4,11,12,16] Our results, for both the interacting and noninteracting cases, indicate that unless the criterion (10) is in fact satisfied, the Smoluchowski calculation will always predict conductivities that are too large. We find that Smoluchowski behavior holds, and the Dieterich expression gives the correct conductivity, when the damping is indeed strong. For weaker damping, the Dieterich results fail quantitatively, although the qualitative effects of correlation and commensurability are seen by studying $\rho(x)$. The effective barrier height calculated using Eq. (17) is lower than V_0 for incommensurate systems, since, as has been previously noted,[17,18] the effect of the Coulomb repulsion between carriers is to push them out of the bottoms of the periodic potential, thus lowering the effective activation

energy below V_0. The effective barrier calculated from Eqs. (16) and (17) using the correct (Langevin) density yields the correct barrier regardless of Γ, but only when Eq. (10) is satisfied will the density alone correctly determine σ from Eq. (13).

The criterion (10) is equivalent to saying that the frequency for the mobile-ion mode at the well bottom must be smaller than the linewidth. For most ionic conductors this is not true; for example, the frequency/linewidth ratios in Na β alumina,[22] Ag β'' gallate,[23] α AgI,[24] and NASICON[25] are roughly 61/40, 40/15, 110/50, and 60/40, respectively. Thus, in none of these cases is the criterion (10) for the validity of the Smoluchowski equation satisfied.

Recently Schultz and Zucker[14] have calculated V_{eff} from x-ray and neutron diffraction data of Li_3N and silver halide conductors. They find that the calculated V_{eff} barrier height agrees with experimentally determined activation energies. We find that our calculated V_{eff} barrier height agrees with the Langevin dynamics activation energy. Thus, the simple relationship between $\rho(x)$ and the effective barrier height seems to be a general result; however, the relationship between the measured $\rho(x)$ and the conductivity is not expected to hold in general, but only in the very high damping case; most ionic conductors are not in this limit in the important temperature range.

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