FAST ION CONDUCTION: SOME THEORETICAL ISSUES

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Recent progress in the theoretical understanding of fast ion conduction in solids is discussed, with emphasis placed on mechanistic behavior and on the characteristic features of particular sorts of solid electrolytes. We consider soft framework materials such as α-AgI, and hard framework materials such as β″-alumina. In each case, we discuss which theoretical methods have been used to investigate mechanisms of conductivity and diffusion, and some of the physical insights which have been gleaned on the mechanism of ionic conductivity. Comments are also made on glassy conductors such as glassy lithium aluminosilicate, and polymeric ionic conductors such as polyethylene oxide/lithium triflate. Since different characteristic timescales, and characteristic energies, are appropriate for these different classes of materials, varying theoretical methods have been used, and should be used, to understand the ionic motion. Particular concepts, such as dynamic percolation in polymer electrolytes, strong memory effects in soft framework materials, strongly correlated liquid-like diffusion in hard framework materials and disorder-induced weakening of correlations in glassy materials are pointed out. We speculate briefly on the role of very strong interionic correlations in causing possible domain-wall conduction, a process that goes well beyond any hopping description. We briefly discuss some special behavior observed in certain classes of solid electrolytes, such as fractal behavior, "universal dielectric response", the mixed alkali effect in glasses, and the "Liang effect", which is the enhancement of ionic conductivity by inclusion of an insulating second phase. Remarks are ventured both on theoretical methodology and on the usefulness of models for understanding, predicting and designing solid electrolyte behavior.

1. Introduction

Although fast ion conductors, or solid electrolytes, were first discussed by Faraday well over a century ago [1], modern work in the area really began with Ketelaar's investigations of Ag_2HgI_4 in the 1930s [2], and with the important work, beginning at the Ford Laboratories, on the β-alumina structure in the 1960s [3]. Solid electrolytes are generally defined as solids that exhibit a characteristic ionic conductivity more typical of liquids, lying in the range from 10^{-6} to 10^{-1} Ω^{-1} cm^{-1} near ambient temperature. Although the original discoveries of solid electrolytes were certainly fortuitous, within the past decade or so, theory has played an increasing role in helping to understand, and to predict, the behavior of characteristic solid electrolyte materials.

The fundamental problems involved in discussing fast ion conductors are exceeding complex. One deals with strongly disordered solid materials, in which Coulombically charged particles move rapidly either among sites or within a disordered host medium. Characteristic concentrations of charged species are far higher than normally seen in aqueous solutions, and indeed these strong Coulomb correlations comprise one of the most challenging aspects of the theoretical interpretation of fast ionic conductivity. Nevertheless, a great deal of progress has in fact been made in the theoretical understanding of solid electrolytes, and a number of important conceptual and mechanistic ideas have evolved from these theoretical studies.

Since facile ionic charge transport is the hallmark of solid electrolytes, the great preponderance of the-

oretical studies concern themselves with conduction or diffusion. Other properties of solid electrolytes, such as structural regularities, thermodynamics or optical properties have not been extensively investigated theoretically. Given this situation, we will concentrate in this overview on theoretical treatment of ionic conductivity and of charge transport mechanisms.

Several excellent reviews have been published outlining the theoretical treatment of solid electrolytes [4-7]. In general, these reviews have been structured in terms in the techniques employed for understanding the materials. For example, in the landmark review of Dieterich et al. [5], the distinction was made between hopping models, in which ions are assumed to be localized at a given set of sites and no inertial motion of the carriers is included, and dynamical models, in which the ionic motion is described by Newton's equations with proper interaction potentials, and approximations are utilized to solve for the conductivity. Dieterich et al. [5] cite a number of theoretical advances made using both hopping models and dynamical treatment. The reader is referred to this review for a still very current discussion of the methodologies employed and of some of the results obtained.

We focus in the current overview on the systems involved in the study of solid electrolytes. These can be fairly well divided into very highly disordered materials including glassy and polymeric conductors, and framework crystalline materials, including soft ionic crystals such as α-AgI and Ag_2HgI_4 and hard covalent crystals such as β-alumina, $LiAlSiO_4$ and the hollandites. Section 2 presents some general theoretical notions on polymeric and glassy electrolytes. It also includes a qualitative discussion, based on recent work of Angell, Torell and co-workers [8,9], on the relationship of ionic motion to lattice motion in the highly disordered electrolytes. This provides a unique and valuable conceptual picture upon which an understanding of the mechanisms of charge transport in these materials can be based. Section 3 discusses soft framework crystals. This is probably the class of solid electrolytes that is best understood theoretically, and a general picture of a liquid-like charge-carrier array moving in a nearly harmonic bath provided by the immobile counterions seems essentially correct; correlations both among carriers

and between carrier ion and counterion cage are important, and are briefly discussed. This is also the only area of solid electrolyte research in which electronic structure studies have been published, and some discussion of those results is given. Sections 4 and 5 are devoted to some very recent work on the hard, covalent framework conductors; section 4 is based on recent theoretical analysis by Boughaleb et al. on the use of effective potentials for discussion of correlation effects in ion transport in framework materials. Section 5 discusses the question of strongly correlated ion motions in covalent frameworks, in the light both of new experimental work on the β-alumina materials and hollandites and of simulation studies of a quite different class of problems, the structure of rare-gas overlayers on graphite. It contains some speculation on domain structures and conductivity. Section 6 very briefly mentions some special topics that have been treated theoretically, including activation entropy, enhanced transport along interfaces and retarded transport through interfaces, fractal studies of some dynamical conductivity effects and the mixed alkali effect. Finally, section 7 presents some overall comments.

Theoretical work on solid electrolytes is now a rich and extensive area, and no attempt at completeness can even be attempted here. The aim of this article is, rather, to give the flavor of current theoretical work in the area. We apologize in advance both for the incompleteness of this article and for the omission of some very important and illuminating theoretical work, especially in the area of hopping models.

2. Highly disordered electrolytes: polymers and glasses

2.1. Generalities

Polymeric and glassy solid electrolytes comprise the newest, and one of the most challenging, areas of solid-state ionics research. Even an overview of current theoretical research in these materials involves both more detail, and more speculation, than are really appropriate here. Two features of these electrolytes distinguish them from the crystalline materials: Firstly, while all solid electrolytes require disorder to some degree, or else no simple pathways

for ion motion are available, the disorder in glasses and polymers far exceeds that in crystals. There is no long-range order of any type in glasses and polymers; by contrast, in α-AgI or β-eucryptite, the mobile ions are disordered over the available sites, but the immobile-ion array exhibits crystalline order. A second distinction in fact follows: glasses and polymer electrolytes are, in a definite sense, not solid electrolytes at all but rather, at least to some extent, liquid electrolytes.

Any glass, conductive or not, can be viewed as a supercooled liquid; thermodynamically, it has undergone a glass transition in which configurational motions of a certain type are locked, but it has not undergone the liquid → solid, first-order freezing transition that produces crystals. The entropy of the glassy state, like that of the liquid state, is correspondingly high. Solvent-free polymer electrolytes, which were first described by Wright et al. only fifteen years ago [10], conduct well only above their glass transition temperature T_g. Above this temperature, the local environment of the mobile ions is in fact liquid-like; the disorder is dynamic as well as static, with the coordination environment about any given ion evolving on a timescale (10^{-9}–10^{-11} s) similar to that of ordinary liquids. These materials appear macroscopically as solids, because their viscosities are very high, orders of magnitude higher than those of ordinary liquids. In polymers, this high viscosity is due to entanglement of the long polymeric chains, while in glasses it arises from the immobile structure caused by the network-forming component.

Several excellent recent reviews of polymer electrolytes [11–15] and glassy [8,16] electrolytes are available, and the reader is referred to them for extended discussion of theoretical treatments. In fact, theory has been far less successful in these areas than it has been in crystalline electrolytes, due largely to the structural complexity of the materials. We will present a very brief discussion of some of the salient features that a theory must contain, and then mention a classification scheme, due to Angell [8,9], that permits qualitative understanding of important factors in the ion transport in these materials.

2.2. Polymer electrolytes: some features

A typical polymer solid electrolyte, such as $P(EO)_6LiCF_3SO_3$, can exist in several morphologies (here P refers to poly, EO means ethylene oxide – CH_2-CH_2-O–, the 6 indicates six repeat units per salt, and $LiCF_3SO_3$ is the complexed salt). Although early models suggested otherwise [17,18], a large number of experimental data have now shown conclusively [11–15,19–21] that the region of high conductivity is the homogeneous elastomeric amorphous phase, and that the presence of partly crystalline phases inhibits conduction. It has also been demonstrated quite convincingly that the motion of the mobile ions is strongly linked to those of the polymer segments [11–15,22,23]; below T_g, where these chain segment motions become frozen, the ionic conductivity drops to extremely low values. Finally, it appears quite certain that both anions and cations are mobile in ordinary polymer/salt electrolytes of the type $P(B)_n \cdot MX$ [11].

All of these observations can be explained qualitatively using free-volume models, and accordingly the free-volume theory has been very broadly applied to these materials [11–15,22–25]. Free-volume theories are based [26,27] on the notion that the mobile species can in fact move only when, locally, a void opens which is large enough to accommodate that species (subsequent work by the authors of ref. [27] considers kinetic effects). In the case of polymer electrolytes, the rough independence of mobility on ion size [28–31] and the very strong correlation of ionic conductivity with chain segment motion imply that it is chain segments, rather than the ions themselves, that must move if conduction is to occur. Free-volume theory then uses simple statistical ideas to maximize the number of ways in which a given amount of free volume can be distributed, and eventually results in an expression for the mobility of the form [26,27]

$$\mu \propto v_t \exp(-\gamma V^*/V_f), \qquad (1)$$

where v_t is a thermal velocity of the chain segments, γ is a parameter of order unity accounting for overlap of free volumes, V^* is a characteristic van der Waals or hard-sphere volume of the segment and V_f is the free volume. If the concentration of carriers is constant, and if the free volume is expanded about

some temperature T_0 at which the free volume vanishes, one obtains for the conductivity

$$\sigma = \sigma_0 \exp[-B/R(T-T_0)] , \qquad (2)$$

where σ_0 is a prefactor containing charges, carrier concentrations and constants, B is a constant inversely proportional to expansivity and proportional to V^*, and R is the gas constant. The form (2) is identical to that of the empirical Vogel–Tammann–Fulcher (VTF) equation [32,33], which fits the thermal dependence of many polymer electrolytes exceeding well. Cheradame [23] suggested that the form can be improved by including an activation energy term accounting for the production of free ion carriers from the added salt, resulting in the expression

$$\sigma = \sigma_0 \exp[-E_a/RT - B/R(T-T_0)] , \qquad (3)$$

which describes the conductivity reasonably well for a number of polymer electrolytes.

While the free-volume picture is intuitively attractive, and can be used to derive the VTF equation, there are some significant disadvantages associated with its use [34,35]. Firstly, it is a quasithermodynamic theory, and therefore not based on microscopic description of the materials; this is a major drawback to its use as a vehicle to interpret and/or predict variations in conductivity with such experimental variables as concentration, ion size, ion charge or coordination environment. Secondly, no dynamics or kinetics is included in the simple free-volume model; in particular, the free volume is assumed to move instantaneously with no constraints [27], and no effects of ion–ion correlation or ion–polymer complexation are included. Finally, there are some quite straightforward experiments, such as a maximum in the conductivity as the ion concentration is varied [29,36], that cannot be simply explained using free-volume theories.

One alternative model is the configurational entropy model of Gibbs and co-workers [37,38]. This is another quasithermodynamic picture, this time based on entropy rather than volume as the important parameter. Although it is preferable to free-volume models for several reasons, and has been broadly applied to problems in glasses, polymers and molten salts [34,35,39], it has not yet been applied extensively to polymer electrolytes.

More microscopic approaches to problems involving polymer electrolytes have been presented; these have generally been based on percolation theories. Ordinary static percolation theory has been used to interpret the dependence of conductivity on the extent of crystallinity in partly crystalline, inhomogeneous polymer electrolytes (cf., e.g. ref. [20]). A more unusual construction, called dynamic percolation theory (DPT), has been presented, developed and applied by the Northwestern group [11,12,40, 41]; some recent results using this model are presented in this volume by Granek et al. [42]. The DPT model takes account of the facts that the disorder in polymer electrolytes is dynamic, rather than static, and that the motion of the ions depends strongly on those of the polymer host, to generalize the usual percolation picture as follows: in percolation theory [43], one usually considers hoppers moving about on a lattice, and writes, for the motions of these hoppers,

$$\frac{dP_i}{dt} = \sum_j (-W_{i \to j} P_i + W_{j \to i} P_j) , \qquad (4)$$

where P_i is the probability to find the hopper on site i and $W_{j \to i}$ is the hopping probability per unit time from j to i. The percolation aspect enters in the assignment of the W, which are normally chosen as

$$W_{i \to j} = 0, \quad \text{probability } 1 - f,$$
$$= w, \quad \text{probability } f, \qquad (5)$$

where f is the percentage of open, or available, jump routes (usually called "bonds", but not chemical bonds). Dynamic percolation theory generalizes [40] the percolation model of (4) and (5) by reassigning the routes as open or closed, the reassignment occurring on a characteristic timescale τ_{ren}, corresponding to a "renewal" of the hopping situation for the ions. The DPT model has been studied formally and applied to understanding the frequency-dependent conductivity, the viscosity, the Walden product, and the thermal dependence of conductivity in polymer electrolytes [41,42].

All of these theoretical pictures, at their current levels of development, are quite inadequate for discussion of real polymer electrolytes, in that none of them appropriately consider ion–ion interaction. Characteristic polymer electrolytes have ion concen-

trations in the range 1–10 molar, corresponding to average interionic separations of 5–8 Å. Clearly, it will be necessary to include interionic Coulomb interactions to obtain any real, quantitative understanding of the conduction. Although experiments are now being reported that detail quite well [11,12,29,36,44] the concentration dependence of the conductivity, no convincing theoretical approach has yet dealt with these problems. The challenge is a severe one, since one deals here with strong electrolyte solutions in a structured solvent. This is an outstanding problem for theoretical approaches to solid electrolytes.

2.3. Glasses

The conceptual understanding of transport in glassy electrolytes appears to be even less well developed than that in polymers. This is largely because some absolutely vital principles remain unresolved experimentally. Perhaps the most important of these involves glass structure, and the relation of structure to ion transport. The simplest model for glass structure, Zachariasen's continuous random network model [43,45,46], pictures glasses as being formed simply by random orientational disorder of bond angles, starting with a single crystal. Such a glass would be homogeneous in all physical properties, including density, if observed on a distance scale of several lattice spacings. Several recent studies of glasses, including ion-conductive glasses, discuss the structure of the glass in terms of this Zachariasen model, and present structural and/or spectroscopic evidence for its appropriateness. There are, however, a series of theoretical and experimental reports indicating that glasses in general, and glassy electrolytes in particular, are inhomogeneous on distance scales of order 10–100 Å. The causes suggested for such inhomogeneities include nonuniform densification on quenching from the melt and selective cluster bonding. Whatever the cause, several recent reports discuss ionic conduction in glass in terms of intracluster and intercluster jumps in such an inhomogeneous structure.

Clearly, the nature of the conduction mechanism can differ from a hopping-like picture in a disordered random framework potential to a percolative pathway involving higher mobilities in a particular

region of an inhomogeneous glass, with slower motions in the intervening structure. Pechenik et al.'s work on β-eucryptite glass [47,48], where the structure is taken as a continuous random network but the glassy structure reduces the ordering effect on the Li ions and therefore increases the conductivity (reduces the activation energy) compared to the comparable crystal, and Mundy and Jin's work [49] on Na^+ transport in sodium aluminogermanate glasses, in which transport is discussed in terms of barriers to individual jumps determined by strain energies and correlation factors among mobile ions, both relate to transport within a continuous random network. On the other hand, Malugani et al.'s recent work on Ag_2PO_4/AgI glass [50] interprets the conduction using a percolation model, with high mobilities in the α-AgI clusters. Clearly, it is difficult to suggest a theoretical picture of ion transport if the results for glass structure are so tenuous. Part of the difficulty may arise from oversimplification: just as solid electrolyte crystals should be divided into classes including hard frameworks, soft frameworks, plastic crystals and rotator phases, just so different glasses might well be expected to exhibit different structural motifs and transport mechanisms. Mundy and Jin [49] suggest just such a difference between the aluminogermanates, which remain homogeneous, and the aluminosilicates, which exhibit phase separation [51].

Despite the confusion arising from different structures, several important generalities do appear useful in discussing charge transport in glassy electrolytes. For covalent, hard glasses, one might employ a modified hopping model, in which the parameters of the usual hopping model for hard frameworks are reinterpreted as averaged values in the glass. The significant disorder in the framework structure largely removes the complications resulting from commensurability effects in covalent framework electrolytes [52–56]. One then writes

$$\sigma = (Nq^2/2dk_B T)\beta a^2 \nu_0 \exp(-G_m/k_B T) , \qquad (6)$$

where N, q, d, β, ν_0, a and G_m are, respectively, carrier concentration, charge, the dimension of the problem, the fraction of mobile ions, the effective attempt frequency, the mean jump distance for the ion and the free energy barrier to migration [49,56]. The G_m term contains an entropy factor, relating to

correlations among the ions and to the geometry of conduction paths, and an enthalpy term, usually interpreted in terms of hopping enthalpy.

A major debate concerns the β factor, the percentage of mobile ions. One school of thought, originally suggested by Ravaine and Souquet [57], is that most ions are in fact bound, and therefore immobile, in glassy structures. According to this "weak electrolyte model", only a small fraction of carriers can contribute to the conduction, a function fixed by the ratio $\beta = \exp(-G_d/k_B T)$, where G_d is the free energy needed to dissociate the alkali ion from an original site in which it is Coulombically bound (trapped) by a charge compensator or by a defect like a non-bridging oxygen. The other approach is to take $\beta = 1$, and attribute the activation terms solely to mobility effects.

Martin [58] has presented a clear description of the weak electrolyte picture, and has shown that the $\beta = 1$ and $\beta \approx \exp(-G_d/k_B T)$ pictures might not be so diametrically opposed as first appears. Fig. 1 is his representation of alkali motion in a generic aluminosilicate glass. In the weak-electrolyte-type model, there is a shallow second local minimum in the activation curve, representing an intermediate, bound alkali, while in the strong-electrolyte picture there is no such intermediate. Nevertheless the activation process corresponds to the overall height of the free-energy barrier, whether or not the secondary, weak-electrolyte minimum occurs. The weak-electrolyte picture is very useful for correlation of ionic conduction with thermodynamic properties, and will probably continue as an extremely useful conceptual tool for explaining glassy conduction. Indeed, when concentrations of charged species become very high in any electrolyte, solid or liquid, factors involving carrier trapping by counterions become highly relevant. Armand [59] has recently stressed the utility of the weak-electrolyte idea in interpretation of polymer electrolytes.

Glassy electrolytes can be usefully thought of as statically disordered frameworks, so that many of the ideas important in framework conduction are relevant; examples include the importance of ionic correlations, the hop-like nature of ionic excusions and the promoting role of immobile-ion vibrations. A number of simulations have been reported on glassy frameworks [60–62]. They show results that are, in
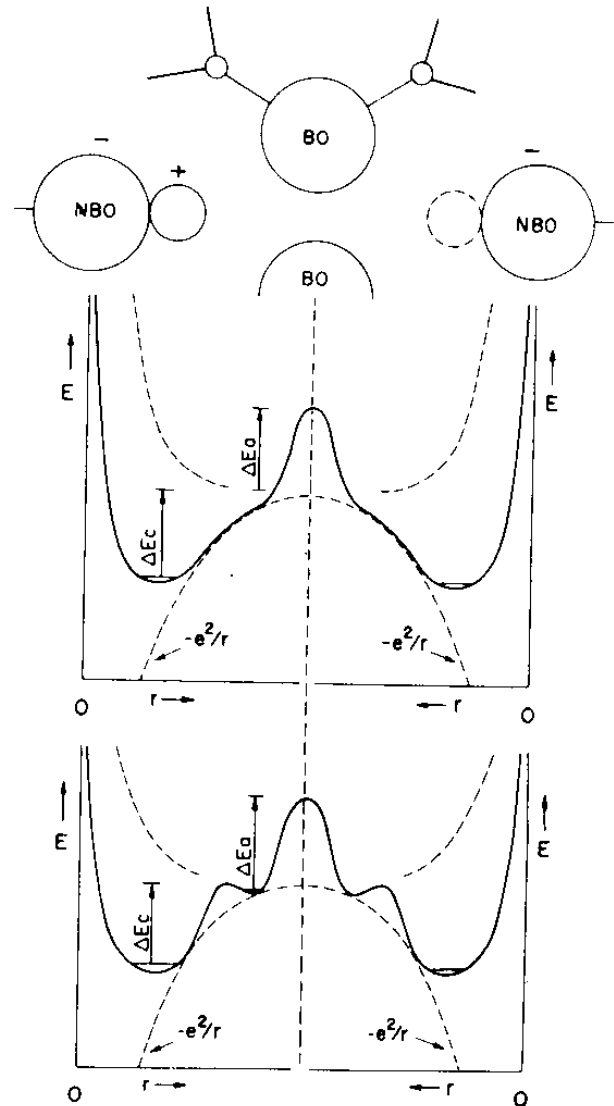

Fig. 1. Schematic representation of the weak-electrolyte and strong-electrolyte pictures for conductivity in glasses. The strong-electrolyte picture above shows no local minimum in the potential, while the weak-electrolyte theory does postulate an equilibrium concentration of unbound species, with Coulomb bonding energy ΔE_C, and relative concentration $\exp(-\Delta E_c/RT)$, whose further activation barrier to diffusion, ΔE_a, is relatively small. BO and NBO denote bridging and non-bridging (charged) oxygen. From ref. [58].

many ways, quite similar to framework crystals. Some important differences do, however, occur. One is the reduced role of commensurability (due to the random ion/lattice potential) already discussed. A second difference involves the packing density, which is a relevant parameter in glasses, but not in crystalline frameworks, where the structure determines the density. Mundy and Jin have shown [49] that

substantial changes in the activation enthalpy occur as the packing density increases and the sizes of the aluminogermanate rings that determine local barrier heights increase also. Simulation studies on glasses indeed show that larger densities will generally produce substantially lower conductivities, as the free volume and the space available for ionic diffusion are reduced [8]. Clearly, more work correlating structure and conduction in glassy electrolytes is badly needed.

2.4. The relationship of relaxation and conduction: decoupling indices

In dilute liquid electrolyte solutions, the viscosity of the liquid can be related to the diffusivity of dissolved ions either by the empirically based Walden rule [63]

$$D_i\eta = \text{constant}, \tag{7}$$

or by the Stokes–Einstein form (obtained for a spherical particle in a continuum)

$$D_i = k_B T / 6\pi\eta r_i. \tag{8}$$

Here D_i, η and r_i are the diffusion coefficient of the i species, the viscosity and the radius of the i species. In framework crystalline solid electrolytes, neither (7) nor (8) are really meaningful, since these solids have enormous (essentially unmeasurable) viscosities, which do not vary significantly with temperature (as D does). The glassy and polymer electrolytes are, as stated above, in some sense liquid, and thus it becomes an interesting issue whether or not the D_i $\propto 1/\eta$ result applies to them.

Angell has generalized this concept considerably [8,9], and has defined a decoupling index R_τ as the ratio of mechanical and electrical relaxation times:

$$R_\tau = \tau_s/\tau_\sigma, \tag{9}$$

where τ_s and τ_σ are the relaxation times for structural and conductive processes. They may be obtained either from direct measurement, from the definitions

$$\langle \tau_\sigma \rangle = \epsilon_\infty e_0/\sigma_{dc}, \tag{10}$$

$$\langle \tau_s \rangle = \eta/G_\infty. \tag{11}$$

Here e_0, ϵ_∞, σ_{dc}, η and G_∞ are respectively permit-

tivity of free space, optical dielectric constant, dc conductivity, shear viscosity and shear modulus. Remembering the Nernst–Einstein relationship, we observe that R_τ is proportional to the Walden product.

Angell uses the values of R_τ to discuss several properties of glassy and polymeric electrolytes [8,9]. Some of the interesting observations include:

(1) For glasses, the ratio changes very rapidly from the high-temperature melt to the service temperature (below T_g). For example, in $CsAg_4I_xCl_{5-x}$, the conductivity decreases by a factor of 10^3 on going from 139°C to T_g at -21°C. The viscosity change over this same interval exceeds a factor of 10^{15}. Thus R_τ in the ionic glass at its service temperature is of order 10^{12}; the electrical relaxation is far faster than the mechanical, in this frozen, supercooled material. The large value tells us that mechanical response is entirely decoupled from electrical response.

(2) For polymer electrolytes, one must use for τ_s the time appropriate for the relaxation of a single bead on the polymer chain. This local relaxation time corresponds to that seen in light scattering.

(3) For typical polymer electrolytes, the decoupling ratio R_τ can be smaller than, though roughly of order, unity. This means that local mechanical stress relaxes more quickly than does electrical field. Values of ≈ 0.02 are found for PPG4000–LiCFSO$_3$ (16 : 1), roughly independent of temperature. Angell and Torell draw two inferences from this [9]: structural rearrangements are not always accompanied by charge migration, and ion–ion interactions might slow the ionic motion, thus decreasing both σ_{dc} and R_τ.

The values of R_τ are suggestive, and quite helpful in deducing the important mechanistic effects on ion motion. One trouble, as Torell and Angell note, is that τ_s in fact is very broadly distributed; one very important issue is then just which *parts* of the relaxation spectrum are in fact relevant to ion motion. The success of WLF relationships [22–24] in correlating thermal dependencies and mechanical and conduction properties certainly implies strong correlation between the sections of the response spectrum responsible for conduction and for mechanical properties such as viscosity, but since each is given, in linear response [64], as an integral of a correlation function, it is some distributed average of the

relaxation processes that in fact is described by the WLF relationship.

The values of R_τ provide intriguing hints into the conduction mechanisms in these highly disordered electrolytes. More microscopic work, both structural and theoretical, is needed to provide more specific insights.

3. Soft framework materials

Relatively soft crystals, often containing heavy metals such as Ag^+, Hg^{2+}, Pb^{2+} or Tl^+, constitute a large class of solid electrolytes. Historically, these are the first solid electrolytes to be studied carefully, and indeed the early observation that the conductivity of AgI and related materials actually decreases at the melting point was one of the earliest indications that ionic motion in fairly well-defined channels in the solid was partly responsible for the high conductivity in the solid. From a theoretical viewpoint, these soft framework substances are probably better understood than any of the other classes of solid electrolyte.

3.1. Electronic structure considerations

Since solid electrolytes are electronic insulators or wide-gap semiconductors, since their unit cells are often quite large, and since good ionic conductivity requires disorder at least in the site occupancy, the prospect of performing electronic structure studies on these materials is a daunting one and, accordingly, very little electronic structure work has been reported on any solid electrolyte. In the case of heavy-metal superionics, however, some work on electronic structure has been reported, and the results are intriguing.

Kleppmann and Bilz [65] suggested long ago that quadrupolar polarizability of mobile metal ions should reduce the energy barrier, associated with the motion along mobile-ion pathways from the minima at sites of high symmetry (tetrahedral, in Ag_2HgI_4) to barrier sites of lower symmetry (trigonal in Ag_2HgI_4).

This would imply that, for isostructural materials, mobile ions with higher quadrupolar polarizability should be relatively more mobile than ions with lower

Table 1
Activation energies for conduction in $M_2M'I_4$ salts, with comparable energy changes from electronic structure studies on MI_4^{2-} species (from ref. [67]).

Salt	Cation radius (Å)	ΔE_a [a]	ΔE_{calc} [a]
Ag_2HgI_4	1.26	36	
Ag_2ZnI_4	1.26	42	
Cu_2HgI_4	0.96	60	
In_2ZnI_4	1.32	72	
NaI_4^{3-}	0.95		80.25
KI_4^{3-}	1.33		85.08
AgI_4^{3-}	1.26		54.77
HgI_4^{2-}	1.10		98.18
InI_4^{3-}	1.32		101.32
CuI_4^{3-}	0.96		71.66

[a] In kJ/mol. Details in original references.

quadrupole polarizability. More generally, if the charge cloud of the mobile ion is deformable (that is, if the polarizabilities are relatively high), one anticipates that the energy barriers associated with changes in coordination environment, as the particle moves along the conduction path, will be smaller. This criterion is complementary to such obvious considerations as ion size (very large ions cannot move well) and ion charge (higher charged species are generally far less mobile). The concept is an interesting one: as one proceeds from "hard", non-polarizable [66] metal ions such as Li^+ or K^+ to "soft", polarizable [66] ions such as Ag^+ or Pb^{2+}, the relative importance of covalency increases, so that a description in terms of electrostatics becomes less tenable. Nevertheless, the rationalization of barriers, and therefore relative mobilities, in terms of ion electrostatics is both of heuristic value and conceptually attractive.

Table 1 contains some measured activation energies for ionic conductivity in a family of heavy metal iodide conductors. It is, of course, important to remember that conductivity activation energy can contain contributions from carrier number activation since

$$\sigma = \sum n_i q_i \mu_i , \qquad (12)$$

where σ, n, q and μ are respectively conductivity, carrier concentration, ion charge and mobility; observed activation behavior of σ can derive from μ or

from n or from both. In addition, a number of dynamical studies (vide infra) as well as simple considerations of conduction path geometry, indicate that strong correlation effects can occur in the actual dc conduction process, so that the activation energy measured for the mobility μ can, and generally will, include ion correlation effects, and thus the observed activation energy will not be simply the single-ion barrier. Nevertheless, table 1 strongly implies that the barrier to single-ion motion surmounting the barrier between minima is lowest for the Ag^+ ion, and does not correlate well with the ion size (larger Ag^+ has lower activation energy than smaller Cu^+ or Na^+). This indeed suggests that Bilz's proposal for quadrupolar polarizability as an important factor in reducing the barrier to ion motion might be valid.

Accordingly, McOmber et al. [67] carried out electronic structure studies on a small cluster of MI_4^{n-} where n is 2 for M $= Hg^{2+}$, and $n=3$ for Ag^+, Cu^+, Na^+, Tl^+. They used basis-set self-consistent-field methods, with pseudopotentials used to represent the inner-shell electrons both on iodine and on the metal atom. They calculated the change both in fragment total energy and in electronic wavefunction as the metal ion is moved from the centered, tetrahedral site to the in-face trigonal site. Structural relaxation effects were not included. These electronic structure studies predict that Ag should have the lowest barrier. More interesting than the

energy changes are the calculated differences in electronic structure. In going from T_d to C_3 symmetry of the iodides about the central metal, the change in ligand field corresponds to a $\Delta l= \pm 2$, 0 change in angular momentum. Thus only mixing of the type s↔s, d, p↔p, f, d↔s, d, g for the angular momentum of the atomic orbitals on the metal should occur along the $T_d \rightarrow C_3$ path. Since the basis set on the metal contains only s, p and d functions, contributions from $l=3$, 4 symmetries, which would require f or g basis functions, are not seen. Nevertheless, population analysis of the fragment indeed suggests that the electron cloud changes shape in exactly the way suggested by quadrupole polarizability or crystal-field considerations, to accommodate the ion to the change in iodine environment. For example, the Ag^+ ion moves a considerable amount of charge out of the p_x and p_y orbitals, the $d_{x^2-y^2}$ orbital and the d_{xy} orbital and into the p_z and d_{z^2} orbitals, upon attaining the C_{3v} geometry (table 2). This corresponds to $\Delta l=0$, ± 2 for the electrons involved. Qualitatively, crystal-field considerations suggest that the metal ion should change its shape to become more "wasp-waisted" upon attaining the C_{3v} site; that is, density should be squeezed out of the plane containing the (negatively charged) iodides. This is in accord both with the behavior suggested by the quadrupolar polarizability argument and with the results of the ab initio electronic structure studies.

Table 2
Mulliken population analysis.

Species	Position	Metal orbitals [a, b]										Total population
		s	x	y	z	xx	yy	zz	xy	xz	yz	
NaI_4^{3-}	tet.	0.506	0.401	0.401	0.401							1.709
	in face	0.502	0.369	0.369	0.460							1.700
KI_4^{3-}	tet.	0.416	0.360	0.360	0.360							1.496
	in face	0.412	0.327	0.327	0.439							1.505
CuI_4^{3-}	tet.	0.616	0.420	0.420	0.420	1.330	1.330	1.330	1.997	1.997	1.997	11.857
	in face	0.656	0.390	0.390	0.452	1.303	1.303	1.368	1.996	2.000	2.000	11.858
AgI_4^{3-}	tet.	0.580	0.417	0.417	0.417	1.330	1.330	1.330	1.997	1.997	1.997	11.813
	in face	0.615	0.394	0.394	0.437	1.283	1.283	1.406	1.994	2.000	2.000	11.806
HgI_4^{2-}	tet	1.173	0.134	0.134	0.134	1.333	1.333	1.333	1.997	2.000	2.000	11.569
	in face	1.186	0.142	0.142	0.091	1.301	1.301	1.387	1.997	1.999	1.999	11.550
InI_4^{3-}	tet.	2.0	0.474	0.474	0.474	1.333	1.333	1.333	2.000	2.000	2.000	13.421
	in face	1.897	0.496	0.496	0.589	1.337	1.337	1.324	2.0	2.0	2.0	13.468

[a] Linear combinations of the xx, yy, and zz orbitals form the x^2-y^2 and z^2 orbitals.
[b] The three-fold axis along which the metal is moved is taken as z. From ref. [67].

The results of table 1 (lower barrier Ag^+ than for Hg^{2+}, Cu^+, Na^+ or In^+) are then understandable in terms of the atomic energy levels of the separated ions. Na^+, and indeed all the alkalis, have a closed-shell structure – they are very "hard", and have very low polarizability or quadrupole polarizability. Tl^+ or In^+ are "softer", but have no low-lying d-levels into which electron density can be shifted upon change in coordination environment. Both Ag^+ and Cu^+ have $d^{10-n}s^n$ levels available ($n=0, 1, 2$) within reasonable energy of one another. These terms are closer in Ag^+ than in Cu^+, thus qualitatively explaining both why Cu^+ and Ag^+ (as well as iso-electronic Hg^{2+}) are good mobile ions in these soft iodide crystals and why Ag^+ is better than Cu^+ (or Hg^{2+}). If the d orbitals are omitted from the basis set, the calculated changes are very large, exceeding 40 kJ/mol, for Ag^+, but negligible for K^+ or In^+; the d-type behavior is needed.

Andreoni and Maschke [68] have used local-density electronic structure techniques, also involving pseudopotentials, to study chemical bonding in the silver halides. They find that the bonding is in fact more covalent than might have been suspected, and that a fully ionic picture is not appropriate for description of these species. These covalency effects might perhaps explain why the phonon dispersion curves in the silver halides, as opposed to the alkali halides, require the introduction of directional forces. They also point out that the use of pairwise ionic potentials for simulating ionic conduction in these materials cannot be justified on the basis of their results.

A great deal more electronic structure work should be done on superionic conductors. Calculations of this type should be of value not only for understanding electronic changes upon ion migration, but also for interpreting structure, and, most importantly for gaining information on potentials for ionic interaction, potentials that are badly needed for accurate dynamical studies.

3.2. Studies of ion motion

Framework solid electrolytes consist of ordinary Bravais-type lattices in which a substantial amount of disorder is present. In most frameworks, this disorder arises from partial occupation of lattice sites. For example, Ag_2HgI_4 undergoes an order–disorder

phase transition at 50°C [2,65–68]. In the lower-temperature) β-phase, which is not a fast-ion conductor, the eight tetrahedral sites in the double unit cell contain four Ag^+ ions, two Hg^{2+} ions and two vacancies, but the structure is fully ordered (space group I_4). Above the phase transition, the color changes from yellow to orange, the ionic conductivity increases by four orders of magnitude and these eight sites are occupied randomly by the two vacancies and the six ions (space group $F\bar{4}3$). Similarly, in AgI, the high-temperature, conducting phase contains Ag^+ ions and vacancies randomly occupying a collection of sites in the unit cell. Theoretical work on ionic conduction in the soft framework electrolytes has concentrated on elucidation of the conduction mechanism and on the details of the fast-ion motion.

The most detailed and precise description of these soft solid electrolytes is gleaned from full molecular dynamics (MD) simulation of the ion motion. Early pioneering studies, especially of CaF_2 and AgI, were reported by Vashishta and Rahman [69,70]. More recently, groups at London, Argonne [71], Harwell [72] and Keele [73] have presented molecular dynamics studies of a number of solid electrolytes, of both soft-mode and hard-framework type. (The soft-mode electrolytes are characterized by relatively low Debye temperatures, sharp order–disorder phase transitions, largely ionic bonding and, generally, "soft", polarizable, heavy mobile ions such as Ag^+ or Cu^+.) The MD method consists of solving the classical (Newton) equations of motion for the ions, subject to given ion–ion potentials:

$$-\nabla_i\{V_{tot}(x)\} = m\ddot{x}_i, \tag{13}$$

with m_i and x_i the mass and the position vector of the ith ion. Eq. (13) is solved numerically using fully periodic (Born–von Karman) boundary conditions and starting from some arbitrarily chosen initial condition. After an initial annealing period the integration is continued forward in time, and properties of the material are obtained from the calculated ionic trajectories, either from a direct computation of the desired property or from computation of an appropriate correlation function. For example, the (ii) component of the static tracer diffusion coefficient is obtained as

$$D_{ii} = \tfrac{1}{6} \lim_{t \to \infty} [x_i(t)]^2 / t , \tag{14}$$

or, alternatively, as

$$D_{ii}(\omega) = \int_0^\infty e^{-i\omega t} \langle \dot{x}_i(t) \dot{x}_i(0) \rangle dt , \tag{15}$$

where $\langle\ \rangle$ denotes an average over the sampled system. The correlation-function result of eq. (15) has several advantages compared to the simpler form of (14), including a general form for finding the frequency dependence and straightforward generalization to quantum systems. For finding dc ionic conductivity, however, the limiting form of (14) is more generally used. This is because the upper time limit in the integral of eq. (15) is finite for any real simulation. Indeed, most simulations have been limited to at most several hundreds of picoseconds. For relatively small numbers of trajectories for these short time intervals, convergence of (15) is poor, so that (14) is in fact preferable. If the sampling statistics are adequate, the two computed results should agree [55,70].

The most serious problems encountered in MD simulations are the expense of the computation and the selection of an appropriate potential $V_{tot}(x)$. For most crystalline materials, the time increment used in MD studies is fixed by the period of the highest-frequency vibration: normally the time increment is about one tenth of the period, so that for a frequency of 10^{13} s^{-1} (typical of ionic crystals), a sampling time of 10^{-14} s should be adequate. Thus a trajectory of 10 ps will require 1000 time integrations. The problems in selecting the potential are quite serious. Ordinarily, the potential is approximated by a pair form

$$V(x) = \sum_i \sum_{j>i} V_{ij}(x_i, x_j) , \tag{16}$$

and the pair potentials V_{ij} are chosen to include such parts as Coulomb interaction, dispersion forces, short-range repulsions, polarizability terms, etc. Most potentials are selected to reproduce such parameters as harmonic frequencies or geometric and metrical structure. The limitation to local, pair-wise forces is insufficient for many systems in which three-body and/or non-local forces are relevant.

Molecular dynamics studies of ionic conduction were surveyed by Gillan in 1983 [72] and by

Vashishta [74] and Catlow [75] more recently. A typical mechanistic insight is illustrated in fig. 2, taken from an MD study of Li$_3$N by Wolf et al. [73,76]. It shows a six-ion migration process of the mobile Li$^+$ ions. This is to be distinguished from the independent hops of interstitials or vacancies generally invoked for explaining conduction or diffusion in such low-conductivity materials as NaCl or LiF. Wolf discusses this six-ion slippage in terms of a "solitary-wave-type propagation of vacancies or interstitials at high velocity by means of slippage of regions of the mobile sublattice over a nearest-neighbor separation". The shortest-timescale "snapshot" of fig. 2c indicates that the motion is indeed nearly simultaneous, and thus is to be distinguished from independent hops or the "caterpillar" mechanism of consecutive nearest-neighbor ion hops [77]. The motion of fig. 2c is more like an incommensurate charge-density wave, or even like a fragment of a one-dimensional solitary wave, or soliton excitation [78]. Such transport schemes had been discussed formally several times, using non-linear wave equations in one dimension [78]. The clear demonstration of such a collective, strongly correlated motion event in the MD run lends support to the idea of collective transport. Ordinarily, one expects that the relative importance of such highly correlated motions, as compared to single-ion hops or correlated hops, will be highest in one-dimensional systems and smallest in three dimensions, where dissipation is more facile.

The correlation function $\phi(t) = \langle \dot{x}_i(t) \dot{x}_i(0) \rangle$ is itself of interest. It describes how the averaged dynamical behavior of a given ion evolves in time. For immobile ions, such as iodide in AgI, the correlation function $\phi(t)$ shows multiply periodic behavior, corresponding to damped oscillations in position. For example, notice in fig. 3a [70] that the forward correlations (positive $\phi(t)$) is effectively cancelled by the backward correlations (negative correlations), resulting in a series of Lorentzian-like curves for $D(\omega)$ of eq. (15), with a value of nearly zero at the origin (no dc conduction). Conversely, fig. 3b shows the correlation function for the mobile ion [70]. Here the dominant positive hump at short times results in an average value of the integrand that exceeds zero, so that the dc conductivity, given as the $\omega \to 0$ limit of eq. (15), is finite. Nevertheless, the large negatively signed region of $\phi(t)$ for the mobile ion shows

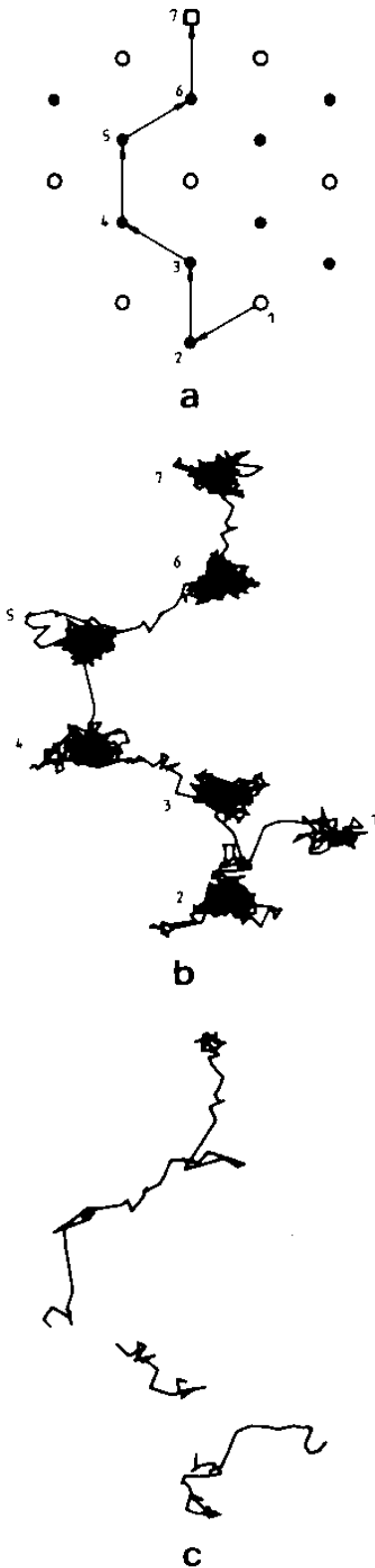Fig. 2. A collective six-ion migration process, obtained from molecular dynamics study of Li_3N. The three figures show a schematic of the process, the MD results for 7 ps, and the MD results for 0.5 ps. From ref. [73].
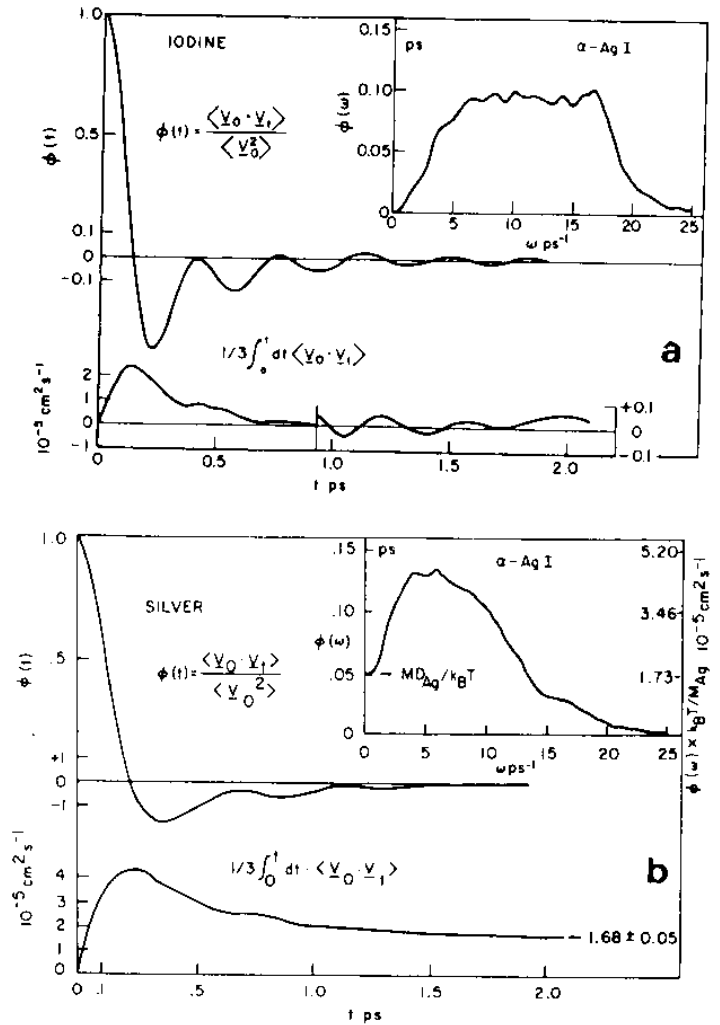

Fig. 3. Results of molecular dynamics study of α-AgI at 450 K (from refs. [69,70]). Note that the autocorrelation function $\phi(t)$ contains far more order for the immobile I^- than for the (disordered, mobile, conducting, liquid-like) Ag^+. The asymptotic value of the lower curve gives the diffusion coefficient, which is finite for Ag^+, vanishing for I^-.

the importance of "bounceback"-type behavior, in which the mobile ion returns to the site whence it originated with higher-than-random probability, even for good solid electrolytes.

A recent diffraction study by Tsuchiya et al. [79], both underscores the accuracy of the MD study of AgI and indicates some important differences between soft and hard framework solid electrolytes. Fig. 4 shows the effective partial pair correlation functions deduced from the neutron study. Note the excellent agreement between the observed correlation function and the MD result. Note also that the mobile ion $(Ag^+...Ag^+)$ correlation function decays quite quickly, showing only first-neighbor and sec-
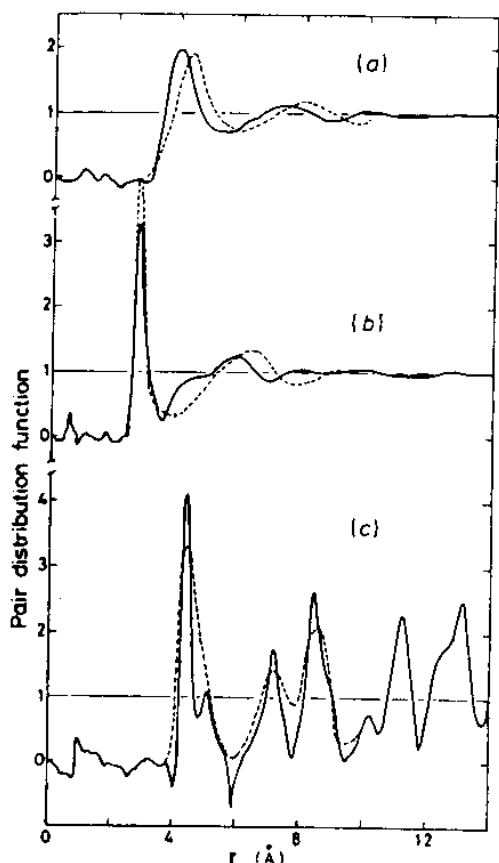
Fig. 4. The pair correlation functions of α-AgI, as deduced from neutron scattering [79] and from molecular dynamics simulation [69,70]. Note the good agreement, for Ag...Ag (a), I...Ag (b) and I...I (c). Note also, as in fig. 3 the far more pronounced structure in the immobile I^- array than in the mobile Ag^+.

ond-neighbor well-defined peaks. This is indicative of short-range correlations, resulting from Coulombic and short-range potentials in the Ag^+ subsystem as well as interactions between Ag^+ and I^-. Comparison with pair distribution functions for hard-framework, covalent crystals [52–55], such as that shown in fig. 7, or with autocorrelation functions $\phi(t)$ [79], shows that the correlations are considerably stronger in the latter system, especially at commensurate stoichiometries. We suggest two reasons for this stronger structure: the first is that the covalent bonds between the framework species in hard crystals (such as Al...O bonds in β-alumina or Al...O and Si...O bonds in β-eucryptite) prevent large-amplitude motion of the immobile sublattice in covalent materials, as opposed to the larger excursions found for the immobile ions in soft, ionic crystals in which the restoring forces are far weaker. Large-amplitude motions of the immobile framework in species such

as AgI both promote ionic motion and lead to breakup of longer-range correlations (other effects also arise from the relatively weak interparticle forces in ionic crystals – see section 4.3). The second factor reinforcing structure in the covalent, hard framework is reduced effective dimensionality – in the hollandites and eucryptites and NASICON, the ions are restricted to move in channels, while in the β-aluminas and gallates conduction occurs on a slab. Correlation effects are always stronger in lower dimensionality (fewer opportunities for disorder), so that the structural correlations extend farther in the more covalent electrolytes.

Overall, the picture discussed extensively by the Brown–Boveri group a decade ago [80] for soft frameworks like AgI seems essentially correct: above the Faraday transition, which can be thought of as a sublattice melting process and like other melting transitions is of first order and associated with a substantial increase in disorder (entropy), transport occurs in an effectively melted sublattice moving in a potential established by the immobile counterion lattice. Given this picture, it is very tempting to treat the immobile species (I^- in AgI, S^{2-} in Ag_2S) as a harmonic heat bath, and to characterize the mobility process by reduced dynamics of the mobile ions alone.

Such a description is offered by a kind of generalized Langevin dynamics, in which the equation of motion for the ions is just

$$m_i\ddot{x}_i(t) = -m_i\gamma\dot{x}_i$$

$$-m_i\omega_i^2 \int_0^t d\theta\, M(t-\theta)\,\dot{x}(\theta) + R(t) . \qquad (17)$$

Here the suffix i numbers the mobile ions, of mass m_i at position vector x_i. The first term on the RHS is just a damping. The first and last terms both arise from the motion of the immobile counterion lattice: the last term is a random force acting on the mobile ions, the first term is a generalized viscous drag force. If an effective timescale, or frequency, separation exists between the vibrations of the immobile ions and the motions of the mobile ions, then one can take

$$M(t-\theta) \simeq \delta(t-\theta) , \qquad (18)$$

and (17) becomes the Langevin equations exten-

sively used in the study of many processes [81], including ion motion in covalent framework electrolytes (section 4). As written, eq. (17) describes a harmonic oscillator with a time-dependent restoring force: if $M(t-\theta)$ is taken as an exponential, then the restoring force is harmonic at short times, but vanishes at long times. Generalized Langevin equations were first used by the Brown–Boveri group, to study Ag^+ ionic conductors [80]. This followed earlier suggestions by Huberman and Sen [82] that Ag^+ ion motion in α-AgI could be considered in two time regimes: at short times, the Ag^+ vibrate in place, while over longer timescales they diffuse. The form (17) was used by the Brown–Boveri group to discuss the frequency-dependent conductivity of AgI, and by the Northwestern group [83] to understand the changes in Raman linewidth accompanying the Faraday transition in Ag_2HgI_4 and related materials.

Olson and Adelman [84] have recently used a generalized Langevin description to discuss ionic motion in AgI. The actual equation set they use resembles (17), but is slightly more elaborate in that a molecular-timescale generalized Langevin procedure [85] is employed. The essential idea of the technique, developed by Adelman, is that the system of interest (in this case the Ag^+ ions) is coupled to the harmonic bath not directly, but rather indirectly through one or more intermediate species, each of which can be treated approximately as a coupled oscillator. In the present case, this approximation is justified physically: locally, any given Ag^+ ion interacts with a "cage" of neighboring I^- ions. The dynamics of this interaction should not, in general, be replaced by stochastic average, since strong instantaneous correlations exist between the motions of neighbor Ag^+ and I^-. (This is a very different situation from that in the covalent structures such as the β-aluminas. There the local vibrations of the Al–O host occur so rapidly, due to the strong covalent bonding and resulting high frequency, that over the characteristic timescale of the alkali ion many Al–O vibrations have occurred, and thus the Al...O motions can be treated as a stochastic variable.) In Adelman's scheme, one writes a series of coupled Langevin-type equations, one for the Ag^+ ions, one or more for the motions of the local cages, and a final one for the last cage species coupled to the stochastic lattice.
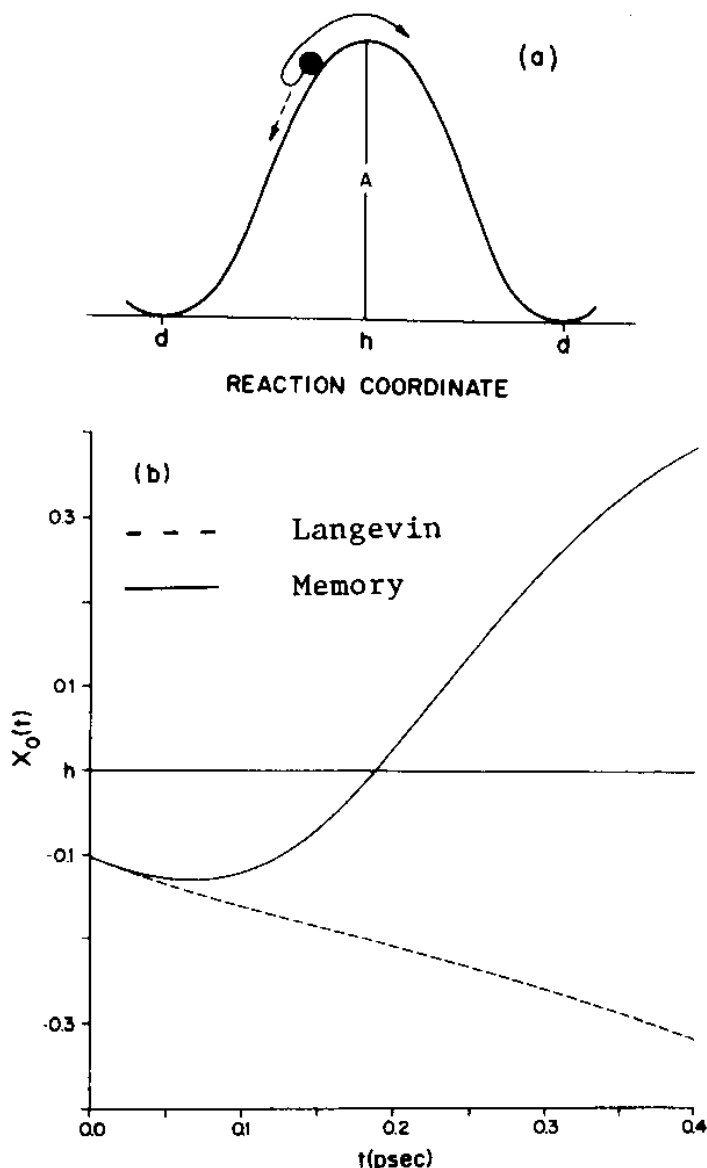

Fig. 5. The "whipback" effect observed in generalized Langevin dynamics study of α-AgI [84,85]. The dashed line shows the result (at $T=0$ K) from Brownian dynamics, the solid line that of generalized Langevin behavior. The lower curve shows the trajectory. The reversal of the Ag^+ ion motion, to go back uphill, is caused by slow cage relaxation.

The solution to this set of coupled Langevin equations reproduces quite well the results of the full MD calculation. Mechanistically, the local correlations produce an interesting dynamical behavior. Since the Ag^+ ion is coupled to the overall lattice only through the local ion cage, memory effects are observed that would not be seen in simple stochastic (Langevin or Brownian) dynamics. The most interesting of these is the "whipback" effect, illustrated in fig. 5. A given Ag^+ ion, if it is instantaneously in a region of high potential, will, according to simple Brownian dy-

namics, drop to a lower potential position in a straightforward damped motion. In fact, correlation with the local cage of I^- ions can cause the Ag^+ to whip back to the high-potential region, due to local repulsion effects caused by the (correlated) iodide. This is clearly indicated in the lower part of fig. 5, which shows the actual trajectories of the Ag^+ ion according to Brownian and generalized Langevin dynamics.

The role of these local correlations, which will be strong in soft frameworks like the heavy-metal conductors, means that both hopping models and simple Brownian dynamics models should be used only with great care for these systems, since they may well ignore some important dynamical features. For example, Jacucci's group has recently shown, using full molecular dynamics, that the Ag^+ motions in AgI can be accurately described by a hopping model only at times longer than that for strong Ag...I dynamical correlations [86].

The MD and generalized Langevin calculations, as well as hopping model studies, are actually simulations, rather than theoretical constructs, in the sense that equations of motion are integrated numerically. More conceptual theories for ionic motion have also been advanced, and some of them have been of great value. Very recently, Dieterich and co-workers have used density functional theory both to calculate the density distribution of the mobile ions and to study the ionic conduction in Ag_2S.

In their study of the density distribution, Roman and Dieterich [87] assume that the S^{2-} ions are rigid, providing only a static potential for the liquid like Ag^+ array. Gillan has reported a similar study for CaF_2 [88]. Essentially, the idea is to expand the interaction among fluid particles to second order in the density. One then obtains the integral equation

$$\rho(x) = N\exp\left(-\beta V(x) \right.$$

$$\left. + \int dx'\ C_0(x-x';\rho)[\rho(x') - \bar{\rho}] \right), \qquad (19)$$

where $\rho(x)$ is the ion density at position x, $\bar{\rho}$ is the average density, N a normalizing constant, $V(x)$ the static potential from the S^{2-} array acting on the Ag^+ ions, $\beta^{-1} = k_B T$, and C_0 is the Ornstein–Zernike di-
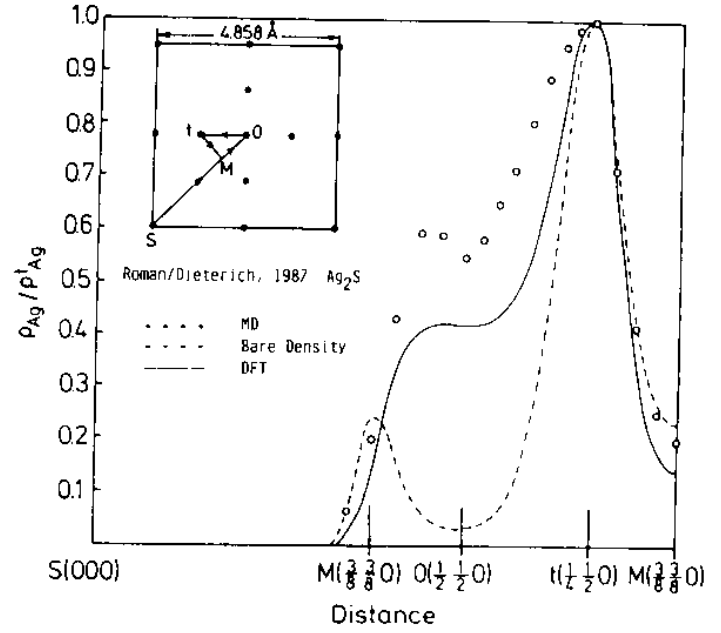

Fig. 6. The calculated Ag^+ ion density in Ag_2S, from ref. [89]. The results using only the potential set up by the bare S^{2-} potential are very largely corrected using an approximate interionic repulsion obtained from density functional theory.

rect correlation function. The equation is solved by iteration, starting with the guess $\rho_0(x) \approx \exp[-\beta V(x)]$ that is the solution for noninteracting Ag^+ ions. The form chosen for C_0 is that of a one-component plasma.

The results of this study are fascinating. As fig. 6 shows, the ion density calculated for Ag_2S at 46 K agrees quite well with the MD result as well as with the experimental result of Cava et al. Moreover, comparison of the result for Ag_2S with that for α-AgI suggests that Coulombic correlations among Ag^+ ions are far more important for Ag_2S (this is reasonable, as we argued above, based on the more open and disordered structure of AgI).

A very sophisticated calculation of conductivity in Ag_2S has been reported by Dieterich's group [90], based on the use of Langevin dynamics, dynamic mean-field theory and density functional methods. Discussion of the details of that calculation goes well beyond the scope of our overview, but several observations can be made. The first is that, in agreement with results discussed in section 4 for covalent frameworks, ion motion at high frequency is largely determined by bare interaction between ion and lattice species, but the dc conduction is strongly influenced by interionic interactions. The essential features of commensurability behavior, rise in $\sigma(\omega)$

at small ω and well-defined vibrational structure are obtained satisfactorily. While some details of the behavior are not correctly given for arbitrary damping strength (or friction), this work represents the best approximation yet made to the construction of an effective potential for ionic conduction. As will be detailed in section 4, the general multi-ion diffusive behavior cannot be described well (quantitatively) with any effective potential (unless it is frequency dependent). For qualitative purposes, however, the use of effective potentials is of great value.

The heavy-metal, or soft ionic, solid electrolytes can thus be thought of as exhibiting liquid-like motion of the mobile ion array in the vibrating potential set up by the immobile counterions. This motion is in fact quite similar to that occurring in the molten phases of the same materials. Indeed, upon melting, the ionic conductivity first drops, since in the melt the counterions are no longer immobile and therefore do not decouple so effectively from the mobile ions, at long times, as they do in the solid phase. Correlation effects, both among the mobile ions and with the cage motions, are quite important in determining the conductivity. In this sense, the mobile array is a correlated Coulomb fluid, similar in some senses to the ions in polymeric electrolytes. The latter situation is more complicated for several reasons (both cations and anions are mobile, there are three species (cation, anion, polymer) rather than two, and the polymer host has its own dynamical behavior), but the idea of a correlated Coulomb fluid describes, qualitatively, soft-mode electrolytes, concentrated polymer electrolytes, molten salts and solvated molten salts. It is not such a good description of hard, covalent crystalline solid electrolytes, to which we now turn.

4. Covalent framework materials

4.1. Generalities. Hopping models and effective potentials

The covalent framework crystalline electrolytes, usually oxides, differ from the soft frameworks that we have just discussed in several ways. They have much higher frequencies and Debye temperatures, and generally do not exhibit the $\beta \rightarrow \alpha$ Faraday phase

transition, corresponding to sublattice melting and accompanied by large increases in conductivity, enthalpy and Raman linewidth, seen in the soft ionic framework such as CuI or AgI. These materials are of great technological interest as battery electrolytes, are stable to quite high temperatures, and can often be grown as large single crystals. Accordingly, they have been subjected to very extensive study. We concentrate here on two issues of major theoretical importance: what is the role of interionic correlation in determining the mobility mechanism in these materials, and what relationships can be established between the structure of the materials, including the distributions of the mobile ions, and the conductivity. In this section, we discuss studies of the effects of correlation on structure and conductivity; in the next section we offer some speculations on possible strongly correlated behavior in β-aluminas.

Many workers have used site hopping models to discuss ionic motion in these ceramic electrolytes. A good overview is provided in Murch's book [91]. Hopping models are based on the idea that ions spend most of their time executing relatively low-amplitude vibrations about equilibrium lattice positions, and much less time in jumps among these allowed sites. Hopping models completely ignore any inertial effects, and solve master equations of the type

$$\dot{P}_i(t) = \sum_{j \neq i} [-P_i W_{i \rightarrow j}(P) + P_j W_{j \rightarrow i}(P)], \qquad (20)$$

where the probability $P_i(t)$ of occupying lattice site i at time t is fixed by the probabilities $W_{j \rightarrow i}(P)$ for jumping from site j to site i; the correlations among the ions enter in the dependence of the hopping rates W on the ionic occupations P. For simple materials such as (nonconductive) alkali halides and metals, hopping models are well justified, and provide a very accurate picture of diffusive motions.

4.2. Langevin dynamics

While simple site-hopping models of ionic conductivity [91–94] have proved very useful for explaining conductivity and some dynamical properties in framework systems, these experimental observations, as well as related features in the ionic distribution in K-hollandite [95] and results of Brownian dynamics simulations [53–55,96] and full molecu-

lar dynamics [97] argue that the hopping picture cannot be fully valid in these materials, because the hopping and residence times can become comparable. This is particularly clear in older Langevin simulation (fig. 7) of the one-dimensional case with Coulomb repulsions, where simply doubling the effective ionic charge in a situation where the framework and the pair potential compete [98] changes the motion from correlated hopping (ions on sites) to liquid-like diffusion (ions moving continuously). Although the hopping picture is not generally valid for covalent frameworks, one can use Langevin (Brownian) dynamics to study the ionic dynamics, because, as discussed in section 3, the substantial timescale separation between vibrational periods of the framework and the far slower diffusive and vibrational times of the mobile ions permit the former to be treated as stochastic variables affecting the motion of the latter.

We will focus here on the one-particle density $\rho(r)$ of N interacting Brownian particles subject to an external periodic potential, and explore the limits of the validity of the one-particle dynamic description embedded in an effective potential (deduced from

$\rho(r)$) which includes the effect both of the external potential and of the interaction between mobile particles. Such effective potentials have been deduced experimentally for a number of materials [89,95,99] and previous theoretical studies have discussed their role in controlling the conductivity [55]. We study the forms of these effective potentials, their variation with the microscopic parameters of the system such as ion density and interaction potential, and their usefulness as a suggestive or even accurate predictor of dynamical properties.

4.3. Model: interacting Brownian particles

Numerical studies which treat the many-body dynamics include both molecular and Langevin dynamics. To pinpoint the effects of ionic correlation, we discuss the case of one-dimensional (tunnel) electrolytes such as eucryptites or hollandites, employ stochastic Langevin dynamics, and treat explicitly only the mobile sublattice. In real systems, the ions of the rigid sublattice oscillate around their equilibrium positions, giving rise to two phenomenological forces acting on the mobile ions: the dis-
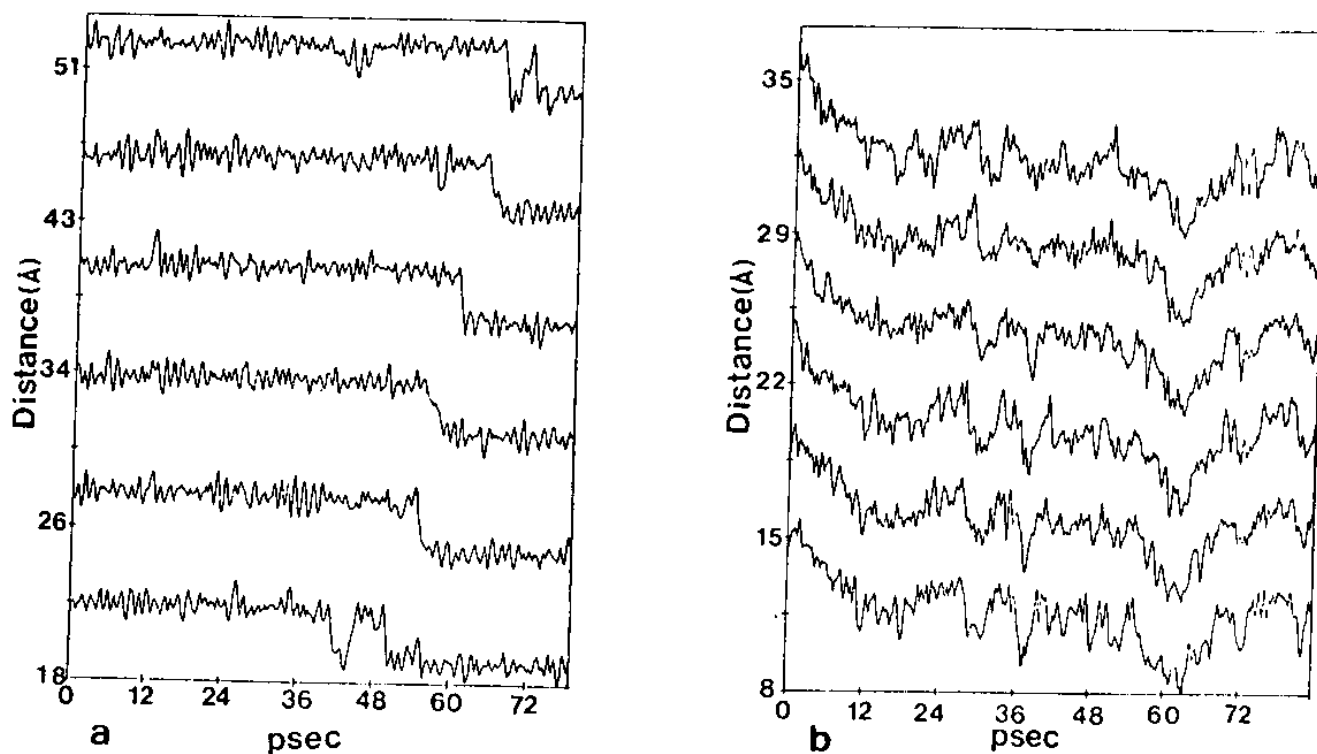

Fig. 7. Langevin simulation of the motion and mechanism for a one-dimensional covalent framework electrolyte such as hollandite. The interionic potential is Coulombic, the density is incommensurate, $C = 0.75$. (a) The case of correlated hopping; (b) the case of liquid-like, very strongly correlated diffusion. The only difference is that the charge of the mobile ion array is doubled in (b). From ref. [98].

sipative force $-m\gamma v$ and the random force $R(t)$.

The model consists then in solving N coupled Langevin equations:

$$m\ddot{x}_i = -m_i\gamma v_i - \nabla_i V_{\text{tot}}(\{X\}) + R_i(t) , \qquad (21)$$

where m, x_i, v_i represent respectively the mass, the position and the velocity of the mobile ion i. Since both the friction coefficient γ and the random force $R_i(t)$, assumed to have a white noise spectrum, have the same physical origin, they are related via the second fluctuation–dissipation theorem as follows:

$$\langle R_i(t) \rangle = 0 \quad \text{for all } i ,$$

$$\langle R_i(t) R_j(0) \rangle = 2m\gamma k_B T\delta_{ij}\delta(t) . \qquad (22)$$

Potential energy along the conduction path due to all ions other than the conducting ones is represented by the periodic static framework potential

$$V_1(x_i) = \tfrac{1}{2}V_0[1 - \cos(2\pi x_i/a)] , \qquad (23)$$

where V_0 is the activation energy in the absence of interaction between mobile particles. The coupling of the diffusing species with the framework is characterized by the dimensionless quantity: $\Gamma = 2\pi\gamma/\omega_0$, where $\omega_0 = (2\pi^2 V_0/ma^2)^{1/2}$ is the vibration frequency of the single particle at the bottom of the well. This Brownian motion model in a periodic potential has been used extensively for solid electrolytes [52–55,98,100,101].

Assuming pair interaction, the total potential energy may be written as

$$V_{\text{tot}}\{X\} = \sum_{i=1}^{N} V_1(x_i) + \sum_{i>j} V_2(x_i - x_j) , \qquad (24)$$

where $\{X\}$ denotes the configuration of the system in the real space

$$\{X\} = \{x_1, x_2, ..., x_N\}$$

and V_2 represents the pair potential, and contains several parts. Since the mobile particles carry charges, Coulomb interaction seems most appropriate. We discuss two different pair interaction potentials and determine for each of them the static and dynamic properties. We consider both the Coulomb potential

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

(Q is an effective charge expected to be less than a formal ionic charge because of screening effects) and

the Frenkel–Kontorova potential. Due to its simplicity, the Frenkel–Kontorova (FK) potential has been employed extensively in different physical contexts. The interaction between the conducting particles, when strong enough, tends to keep them separated by a distance $b = a/C$, where a is the lattice spacing and C is the concentration (ions/site). The expansion of the pair potential up to harmonic terms around the average interparticle distance leads to the FK potential [22]

$$V_2 = \tfrac{1}{2}\alpha \sum_{i=1}^{N} (x_{i+1} - x_i - b)^2 . \qquad (25)$$

The FK potential model consists then of a harmonic chain subject to the periodic potential V_1. The force constant α is given by

$$\alpha = 2\pi^2\kappa^{-1}k_B T/b^2 , \qquad (26)$$

where κ^{-1} represents the correlation length (in units of b) and α measures the interaction strength.

The model system consists of N coupled Brownian particles confined to a one-dimensional channel. Periodic boundary conditions are applied to eliminate the boundary effects. The forces acting on an ion i then include the sum of the forces exerted on it by all the other mobile ions including those of the image boxes, the one-particle periodic potential due to the static framework and the viscous drag and random forces of eq. (21), arising from fast-timescale vibrations of the framework. Numerical solutions to the coupled Langevin equations have been applied successfully to solid electrolytes [52–55,98,102], they enable us to probe the evolution of the diffusion process at the microscopic scale.

4.4. Static properties and decoupling approximations

The static properties of the system are drastically affected by interactions among the diffusing ions. Experiments performed on the one-dimensional ionic conductors β-eucryptite [100] and potassium hollandite [95] showed pronounced structures in the static structure factor $S(q)$ due to strong short-range interaction between the conducting ions. If the pair interaction is strong, as the experimental results for K-hollandite seem to suggest, it creates an almost regular arrangement of the ions by forcing some of

them to move away from the minima of the periodic potential. Such situations may result in an effective potential with complicated structure [103,106].

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

$$\rho(x) = \sum_i \langle \delta(x - x_i) \rangle , \qquad (27)$$

$$\rho^{(2)}(x, x') = \sum_{i \neq j} \langle \delta(x - x_i) \delta(x' - x_j) \rangle , \qquad (28)$$

where $\langle \ \rangle$ means the average over the canonical ensemble. We also define the pair correlation function $g(x, x')$, related to $\rho^{(2)}(x, x')$ by

$$\rho^{(2)}(x, x') = \rho(x) g(x, x') \rho(x') . \qquad (29)$$

The pair correlation function $g(x, x')$ reflects the static correlation between the mobile ions arising from the interaction potential V_2. In inhomogeneous systems such as ours, the explicit dependence of $g(x, x')$ on both x and x' has to be considered: this makes it a very difficult quantity to derive analytically [101,104]. The knowledge of $\rho(x)$ and $g(x, x')$ is essential for the computation of the transport properties and the structural features such as the static structure factor $S(q)$, which can be measured experimentally by X-ray diffraction. The mutual repulsions of the diffusing ions induce an effective single-particle potential which can have a completely different shape from the bare framework potential V_1.

A common procedure consists in approximating the pair correlation function $g(x, x')$ for the inhomogeneous system by the homogeneous pair correlation $g_0(x - x')$ obtained by putting $V_1 = 0$: this represents the homogeneous approximation. It has been used by many authors, especially in the context of surface effects in liquids. Recently, Radons et al. [105] have employed a normalized homogeneous pair correlation function $g_0(x - x')$/constant, to calculate the dynamical structure factor. Here the constant has been chosen such that the static structure factor $S(q)$ is positive for all q. The results obtained using this homogeneous approximation are quite inaccurate for the one-particle density which appears in all correlation functions. Recent work of Boughaleb et al. [103,106] has been devoted to the calculation of structure functions using Langevin dynamics.

4.5. The effective potential

In analogy to the case of non-interacting particles, the one-particle density can be written in the form [107]

$$\rho(x) = \text{constant} \times \exp[-\beta V_{eff}(x)] , \qquad (30)$$

where $V_{eff}(x)$ represents the single-particle effective potential. Since $\rho(x)$ can be obtained from experiment [89,95,99,107] so can $V_{eff}(x)$. Moreover, the barrier height of $V_{eff}(x)$ can be very useful in interpreting the transport properties of the system. In particular, in the high-damping limit, it can be interpreted as an activation energy. The effective potential $V_{eff}(x)$ is the best single-variable description of the system dynamics; it is independent of the friction constant, being fixed only by the Newtonian terms in eq. (21) and by the temperature. Note that eq. (19) defines an approximate $V_{eff}(x)$ in terms of C_0, the direct correlation function. The Langevin dynamics simulation provides trajectories to calculate $\rho(x)$ and thus obtain $V_{eff}(x)$ directly.

4.6. Static properties and $V_{eff}(x)$

By varying the density of the diffusing ions, we can go from a configuration where both V_1 and V_2 assume their minimum for the same given ion spacing to a competing situation. One then distinguishes the former situation as a commensurate density, with C^{-1} = integer, and the latter as an incommensurate density, with $C^{-1} \neq$ integer (here C is the concentration measured in ions per site). For a given density the distribution of the ions over the periodic potential can best be seen by looking at the pair correlation function $g(x, x')$. Let us call the ion at the position x the test ion. For a homogeneous system, $g(x, x') = g_0(x - x')$. For an inhomogeneous system we will consider only two pair correlation functions, one where the test ion is at the bottom of the potential well ($g(0, x')$), another where the test ion is between wells at barrier top. These two functions compared to the homogeneous pair correlation function will indicate the importance of the sinusoidal potential $V_1(x)$.

In fig. 8 we show the pair correlation function $g(x, x')$ for the Coulomb potential at incommensurate density $C = 0.75$. Note that the liquid (homogeneous
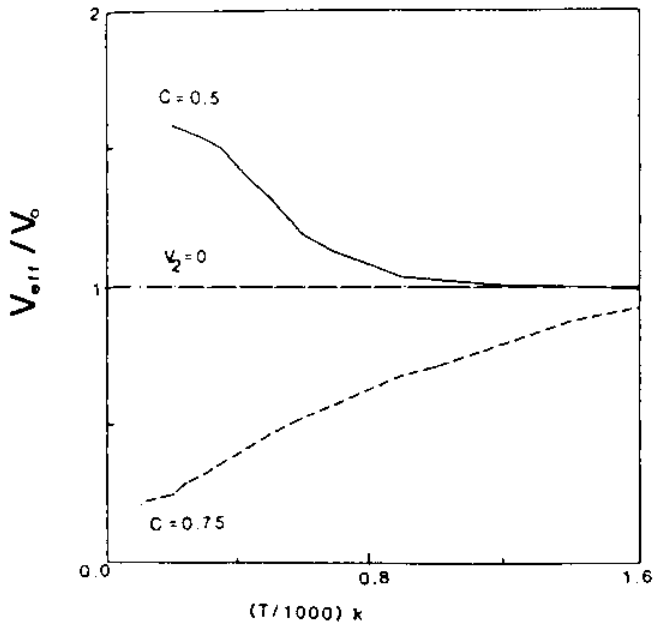
Fig. 8. Pair correlation function $g(x, x')$ for the Coulomb system, at incommensurate density $C=0.75$, at $T=400$ K. Potential parameters $V_0 = 0.1$ eV, $a = 4$ Å, $Q = 0.6$. The curves are the correlation function at well bottom (—), at well top (– – –) and the homogeneous approximation (...). From ref. [103].

Fig. 9. Effective potential of eq. (30) for the Frenkel–Kontorova potential with $\kappa^{-1} = 3$, $T = 400$ K. The curves are for the bare framework (V_1 only, solid line), for incommensurate density (..., lower barrier and higher conductivity) and for commensurate density (– – –, higher barrier and lower conductivity). From ref. [103].

approximation) and the inhomogeneous pair correlation functions are very similar: this indicates a very weak modulation of the mobile-ion density due to the periodic lattice potential; the ions act nearly like a homogeneous liquid. Since $g(x, x') = g_0(x, x')$ in this case, we expect the homogeneous approximation to be quite good. Of the six peaks representing the six nearest neighbor ions, four have an equilibrium position offset from the minimum of the periodic potential. The energy required for the shifted ions to diffuse to the next equilibrium position is therefore smaller than the bare barrier height V_0. This barrier height reduction can be reflected in an increase of the dc conductivity, computed in section. 4.7.

We present now some results concerning the effective potential derived via eq. (30), for a series of physical situations (differing frictions, densities, potentials and temperatures). Fig. 9 shows the effective potential for the FK potential and for different densities ($C = 0.5$ and $C = 0.75$). As expected the barrier height of V_{eff} increases compared to the bare sinusoidal potential for the commensurate density $C = 0.5$: the interionic interactions reinforce the periodic potential in localizing the ions at the bottom of the well. On the other hand, for $C = 0.75$, the two
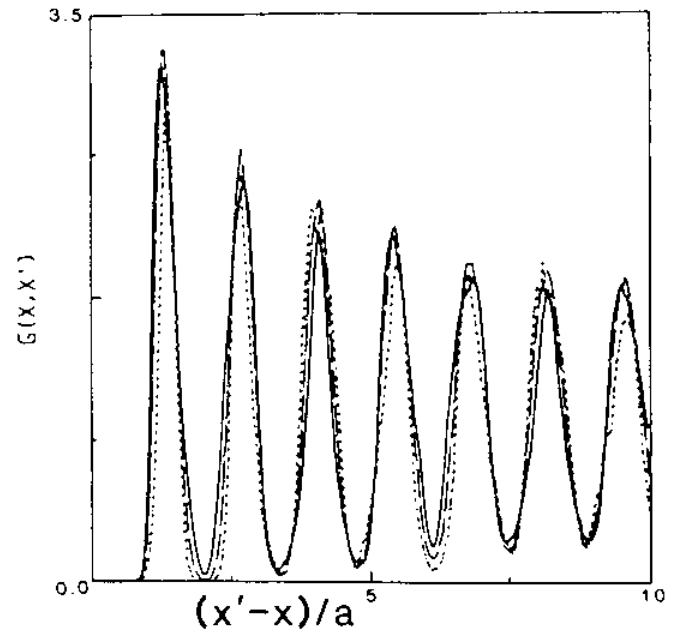
potentials compete for their own preferred spacing, giving rise to a ground state configuration where some ions are moved away from the minima of V_1. Consequently the barrier height of the resulting effective potential is lowered compared to V_0.
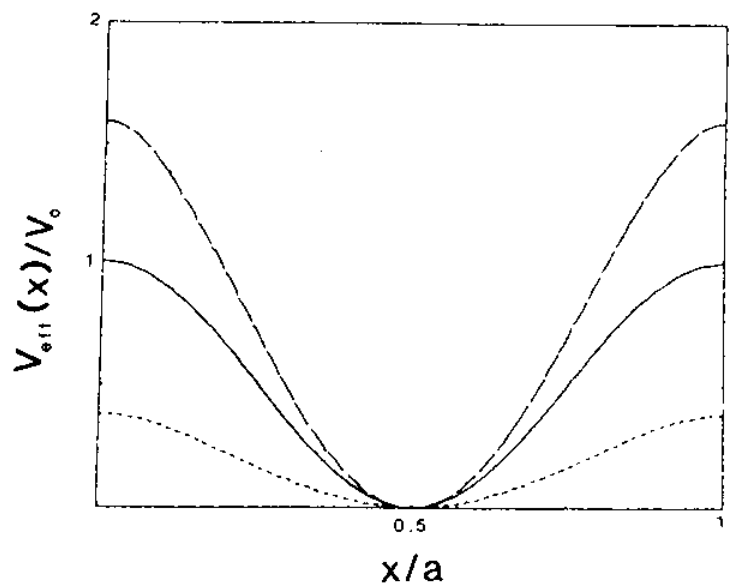

Fig. 10. Temperature effect on the barrier height of the effective potential, for the Coulomb case ($Q = 0.6$). Note different behavior of commensurate and incommensurate densities (from ref. [103]).

Fig. 10 shows the change in the shape of $V_{eff}(x)$ caused by temperature effects for the concentration $C = 0.75$. Clearly, as temperature increases, larger thermal oscillation of the mobile ions lead to smearing out the structure in $\rho(x)$ and therefore in V_{eff}. Similar structure in $V_{eff}(x)$ has been observed recently by the means of X-ray diffraction in the one-dimensional conductor potassium hollandite [107]. As the temperature increases the thermal fluctuations of the ions become important allowing the bare periodic potential to reinforce its domination over the interionic interaction. This results in an increase (decrease) of the barrier height of the effective potential for incommensurate (commensurate) density.

4.7. Dynamic properties: conductivity σ(ω)

Detailed analytical studies of the conductivity have been completed in some limiting cases such as high temperature and strong damping on the basis of the Smoluchowski equation [52,108]. Also, the dynamical properties of the many-body system have been derived using continued fraction methods truncated at a certain order [52]; the accuracy of this approximation drops with decreasing friction. In the low-friction limit, higher-order continued fractions are necessary and no analytical solutions are then available in the presence of V_2.

In the high-friction limit, the dc conductivity can be expressed in terms of the effective potential [105]

$$\sigma_0 = Q^2 D_0 P_0 \left(\frac{1}{a} \int\limits_0^a \exp[\beta V_{eff}(x)] \, dx \right)^{-1}$$

$$\times \left(\frac{1}{a} \int\limits_0^a \exp[-\beta V_{eff}(x)] \, dx \right)^{-1}, \qquad (31)$$

where P_0 is the number of particles per unit of space, and $D_0 = k_B T / m\gamma$ the bare diffusion coefficient. This formula is exact for noninteracting particles. We explore the extent to which the many-particle dynamics can be represented by the single-particle dynamics in the effective potential, for differing density, temperature, frictions and interionic interaction.

The frequency-dependent conductivity has been obtained both for the many particle system and for a single particle subject to the corresponding effective potential [55,103,106]. The calculations have

been performed for both the pair interaction potentials and a wide range of friction. Even though the effective potential is a time-averaged, equilibrium property, we find, in general, that it gives a good, qualitative indication of the many-particle behavior. In effect, as one can see from the results concerning $\sigma(\omega)$, the diffusive motion of the ions is enhanced or reduced compared to noninteracting particle system for incommensurate or commensurate densities respectively. The behaviors of the effective potential for both situations has been discussed in section 4.6. The barrier height of V_{eff} acts in a sense as an activation energy for the diffusion process. These qualitative behaviors of the dc conductivity with the effective potential hold in all friction regimes.

In the high-friction limit the conductivities are generally very close to their Smoluchowski values. For this case, the fluctuations of the interionic interactions responsible in part for the correlation between the ions, which are not included in the effective potential, are strongly damped and do not contribute significantly to the long-time diffusive behavior of the many-particle system. On the other hand, in the low-friction limit corresponding to weak dynamical coupling between the mobile ions and the rigid framework, these fluctuations persist in the system for a long time, resulting in a deviation of the low-frequency response of the many-particle system from that of the single particle in the effective potential. But even for low friction the effective potential description of the diffusive behavior seems to be quite fair if the thermal energy is larger than the barrier height of the effective potential: in effect, as the temperature increases, it reduces the correlation between the local and long-distance motion and leads to a domination of the diffusive mode over the other local modes. In all cases the Smoluchowski result of eq. (31) forms an upper limit to the conductivity found from the full Langevin simulation [103].

Most analytical studies have been performed in the high-friction (Smoluchowski) limit. But most ionic conductors exhibit a strong oscillatory peak, indicating that the intermediate or low-friction regime is more appropriate to describe the dynamics of the mobile sublattice. In the other (underdamped) limit, it is known both for continuous dynamics [109] and for lattice gas models [110] that the diffusion of a single particle subject to a periodic potential is faster

than that predicted by classical rate theory. Due to the weak dissipation process, the mean free path can be larger than the lattice spacing a if the relation $(\pi\gamma V_0/\omega_0 k_B T) \ll 1$ is satisfied. In this limit, the thermalization of the particle requires a time far exceeding one oscillation period, so diffusive jumps exceeding a in length can be observed, and mobile ions can exhibit both oscillatory and quasifree behavior [80,82,96,111].

Several studies have been presented in which a short-ranged potential $V_2(x) = B(b/x)^{\eta}$, $\eta = 7$, has been employed. Again, it is observed that commensurate stoichiometries are better ordered, and less conductive, than either noninteracting particles or incommensurate stoichiometries, which are the most conductive. The effective potential description, in this case, fails in several respects: the effective potential, defined using the computed $\rho(x)$ from simulations as $V_{eff} = -k_B T \ln \rho(x)$, predicts that the main oscillatory peak in the mobile ion spectrum will blueshift in the commensurate case; this is not observed in the simulation, which shows no shift in the position of this peak. The low-frequency behavior is also given incorrectly, at small friction, by the effective potential. Thomas and Dieterich [90] have shown that, in this regime, it is inappropriate to use effective potentials, since the ion–ion interactions are effectively unimportant and the relevant potential is given well by the bare potential. Their analysis discussed in section 3.2 leads to the conclusion that the dc conductivity of the many-particle system is close to the one obtained from the effective potential for all friction regimes, but Langevin simulation shows that this is not true for a commensurate system characterized by a weak dissipation process.

The short-range system is peculiar in the sense that the particles do not "feel" each other for moderate densities unless they diffuse over large distances. To analyze further the effect of ion correlation on the high-frequency response of the system, one has to consider a strong pair interaction potential, as Beyeler et al. [95] suggested from the analysis of X-ray data on the quasi one-dimensional conductor K-hollandite.

An attempt to study the dynamics of such systems has been undertaken in an important paper by Geisel [52]. He calculated the conductivity for harmonically coupled particles (FK) for arbitrary par-

ticle concentration $C = b/a$ directly from the Fokker–Planck equation, using a continued fraction method up to third order. The many-body averages were performed in the high-temperature limit with the help of the transfer-integral technique. The resulting static conductivity clearly shows the commensurability effects: it is reduced or enhanced compared to noninteracting-particles case depending on the commensurability of the mobile sublattice with the periodic potential. But the results concerning the ac conductivity misrepresent the effects of the friction coefficient and the strength of the interionic interactions: the oscillatory peak shifts to frequency larger than ω_0 as the friction or the interaction V_2 increases for both commensurate and incommensurate states. Langevin simulation results conflict with these results [103]. While the dc conductivity decreases as we increase the strength of the interaction, the oscillatory peak becomes sharper but stays around ω_0. Also, the position of the resonance structure does not depend on Γ, contrary to the results obtained by Geisel. The value of the friction affects the magnitude of the diffusion and the width of the oscillatory peak but not the position of the peak.

The effective potential describes quite well the low-frequency dynamics of the many-particle system in the high-damping limit [55,103,106]. The interesting results are for the low-friction regime. Even though the $V_{eff}(x)$ contains no memory effects which are important for an underdamped system, and fails to reproduce the resonance structure of the system, it still can duplicate the low-frequency behavior of the system, in all ranges of friction, in the case where the diffusion mode dominates the spectrum of $\sigma(\omega)$ such that the correlations between the oscillatory and the diffusive motion are minimal. This situation can be found at high temperatures in an incommensurate state which is relevant to most highly conductive materials, with strong interionic interaction.

4.8. Implications: correlation effects in covalent frameworks

Extensive theoretical efforts, using hopping models, Brownian (Langevin) dynamics, and decoupling approximations make it quite clear that interionic interactions strongly effect both the dc conductivity and the oscillatory behavior (frequency-dependent con-

ductivity) of covalent framework electrolytes. These correlation effects are strongest in reduced dimensionality structures. In the high-frequency regime, we found that, for commensurate states, the resonance frequency of $\sigma(\omega)$ is determined by the external periodic potential $(\omega \approx \omega_0)$ and for incommensurate densities the ac conductivity presents a very structured high frequency spectrum, with the main oscillatory peak shifts towards smaller frequency than ω_0 as the interionic interaction increases.

The very interesting theoretical question of just how to define $V_{eff}(x)$ without the simulation (or diffraction data) has been considered several times [5,87,90,102,105,108,112]. The theoretical results make it clear that these effective potentials are of real value and that their derivation using some generally valid and accurate decoupling approximation remains an objective of real interest.

5. Correlated conductivity in covalent frameworks – some experimental aspects

Several hopping-model studies [91,92,94] of β-alumina structures have suggested that strong correlations exist among the hoppers, and indeed that extended defect-type structures augment the essential site transport mechanism (interstitialcy in β, vacancy in β"). Three recent studies have shown extremely tantalizing results, that imply structures, and perhaps motion mechanisms, in covalent framework that are even more correlation-dependent than has been believed heretofore. Long ago van Gool [113] suggested that domain boundary migration might be responsible for the high conductivity of these electrolytes. While this idea is not currently popular, it perhaps is worth reexamining in the light of these new results.

Weber and Schulz [89] have studied the structure of potassium hollandites over a very broad temperature range. They obtain probability density functions for the mobile K$^+$ ion, based on painstaking anharmonic refinement of the scattering data. For our purposes here, the important result of their work is that, as the temperature increases, the occupations of various sites in the hollandite structure change markedly. Below ≈ 430 K, the ions preferentially occupy sites that are shifted off the center of the cavity
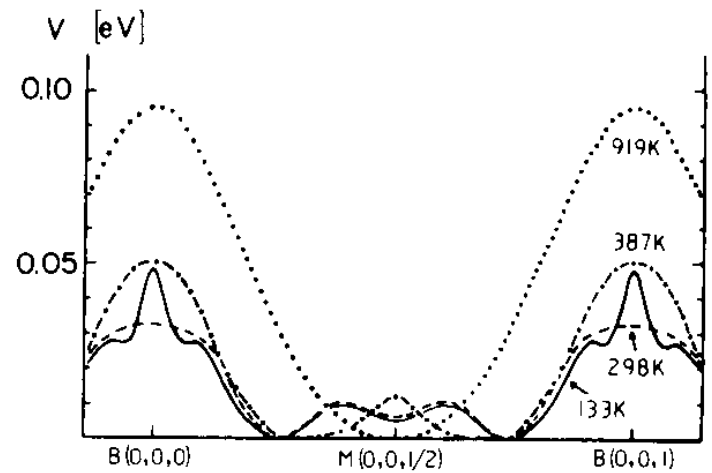

Fig. 11. The effective potential of eq. (30), deduced from densities observed in X-ray refinement of K-hollandite. Note the smoothing of the potential, and loss of smaller minima as the temperature, and thus the ion kinetic energy, increases. From ref. [89].

(formal "site") in the direction of the bottleneck. Above this temperature, the preferred location is at the cavity center. From their refined densities, Weber and Schulz determine an effective potential, using the form of eq. (30). They remark on two important features of this potential: firstly, it has a barrier much lower than the characteristic value (≥ 0.3 eV) for a bare lattice. Second, this lowering of the effective barrier is in good agreement with theoretical suggestions that in incommensurate species with strong interionic interaction, the correlation effects will act to lower the effective barrier and to introduce collective effects into the conductivity.

Fig. 11 shows the potential along the tunnel axis deduced by Weber and Schulz [89]. Notice that substantial secondary structure is found at lower temperatures, and that, as the temperature is raised, the structure simplifies, but the barrier height increases. Precisely such structure for the effective potential was seen in the Langevin simulations [103] on covalent framework tunnel conductors discussed in section 4.

These results indicate the strong role of correlations in reducing effective potential barriers and in moving the center of the ion displacement off of the formal lattice site. Just such effects were indicated in the earlier structural work by Beyeler [95], and quite extensively in the theoretical studies based on Langevin type models [52–55,96]. Since, however, both theory and experiment here involve hollandites [98,102,103,105,106], which are very poor solid

electrolytes, it might be objected that these strong correlation effects are an artifact of one-dimensional conductors, and might be restricted to such cases.

That this is probably not true is indicated by very recent work on the β"-alumina and β-alumina structures. Wolf et al. [97] have carried out an ambitious and extensive full molecular dynamic study of Na-β-alumina. They find, again, that high conductivity occurs only for incommensurate densities. More interestingly, they suggest a change in mechanism of transport, from correlated hops of low temperatures to very strongly correlated, liquid-like motion at high temperatures. Moreover, just as found experimentally for the hollandites, secondary structures in this ion distribution, observed at low temperatures, are wiped out at high temperature, when the motion is more continuous and liquid-like.

Very strong correlation effects in both β- and β"-aluminas are indicated by the extensive recent structural correlation studies reported by Collin et al. [114], who used both conventional structure determination and diffuse scattering. They deduce that the structures can be defined in terms of domains, with all domains equivalent, and each having the same composition as the average. At high temperatures, they observe for β"-alumina a high-temperature pattern that looks like a liquid distribution, quasiuniform along the whole honeycomb lattice. Finally, they observe, for β"-alumina, a room-temperature coherence length of roughly 70 Å at room temperature. At higher temperatures, the correction range drops due to thermal motion. Due to correlation effects, the formally equivalent BR and aBR sites in the β" structure are in fact different in energy, and therefore, within one domain, either BR or aBR sites, but not both, serve as the center of ionic occupancy. Domain walls exist where the preferential occupancy changes from BR$\leftrightarrow$aBR (fig. 12). At higher temperatures, the energetic distinction between BR and aBR is reduced, as a consequence of the increased disorder and drop of the correlation length. All of this behavior is qualitatively similar to that observed for hollandites both in theory [52–55,98,102,103,106] and experiment [89]; the domain structures are not observed per se in one dimension, but the role of interionic correlation in redefining the site occupancy compared to the bare potential, and the smoothing out of the structure in
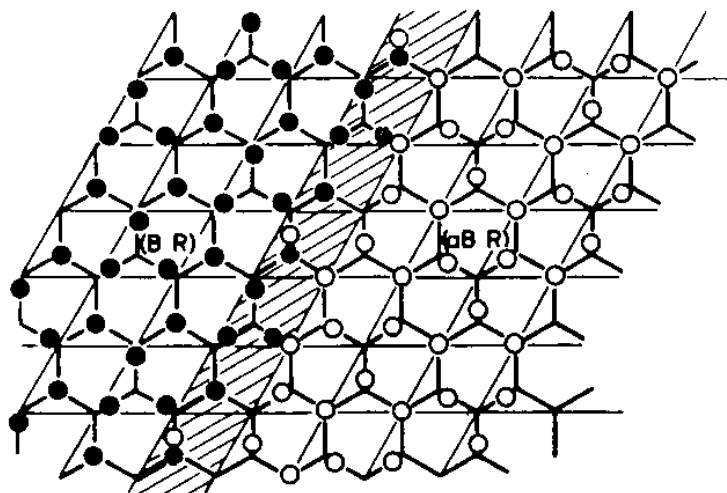

Fig. 12. Domain wall structure for Na-β"-alumina. The domain on the right shows primarily occupation of the anti-Beevers–Ross (aBR) sites, on the left the BR sites are occupied. Strong correlation effects keep the domain regions homogeneous, with a disordered, mobile wall between. From ref. [114].

the effective potential as the temperature rises, are common features of one- and two-dimensional framework electrolytes.

The strongly correlated, domain-type structures deduced for β"-alumina suggest that ion motions might occur most simply along the domain walls between the tightly ordered domains; as temperature rises, the domain walls become more extended as the domains shrink, and thus the overall average ionic mobility increases substantially. An indication of just how the interplay among lattice one-body potential, commensurability effects, domain walls and temperature works can be gained from the very elaborate and intriguing molecular dynamics simulations performed by Abraham and co-workers on the system of rare gas adlayers on graphite [115]. Here, as in β-aluminas, one deals with interacting particles moving on a (nearly) planar surface with hexagonal structure. While there are substantial differences in the two systems, notably the far weaker forces between mobile particles and surface and among mobile particles in the graphite adlayer, still the general features are expected to be similar.

Fig. 13 shows some of the fascinating results reported by Abraham and co-workers [115]. The white areas are locally commensurate, the black areas incommensurate. Note that for all coverages studied there exist commensurate domains, separated by incommensurate domain wall regions, reminiscent of

Constant Temperature T* = 0.05

$\theta = 1.013$ $\theta = 1.025$ $\theta = 1.032$ $\theta = 1.052$ $\theta = 1.086$

Constant Coverage θ = 1.013

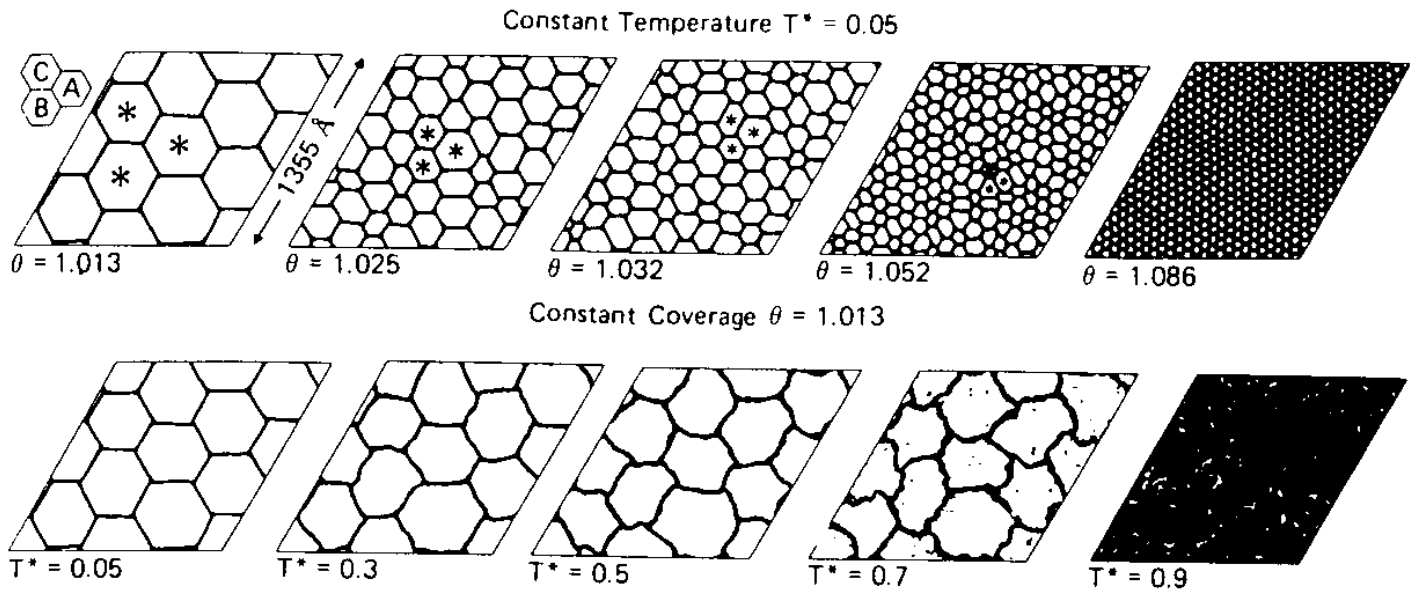T* = 0.05   T* = 0.3   T* = 0.5   T* = 0.7   T* = 0.9

Fig. 13. Structures obtained from simulation of Kr overlayer on graphite. The simulation is for 103041 Kr atoms. Note the hexagonal domains (white) and domain walls (black) of nearly constant thickness. Upper curve shows partial homogenization as density (hence interparticle correlation) increases, lower curve shows melting. From ref. [115].

the domain walls suggested for the β-aluminas by Collin et al. [114]. The domain wall thickness, for the Kr/graphite system, is roughly constant (with varying coverage at fixed temperature), lying near a value of 18 Å. The striking hexagonal structure of the domains mirrors that of the hexagonal graphite net, but at far larger scale (for comparison, remember that the thickness of the domain walls, or black line, is ≈ 18 Å). As the coverage increases, the domains shrink in size, but the structure does not convert into a fully homogeneous array, so long as the temperature remains low.

As temperature ($T^* = k_B T/\epsilon$, where ϵ is the Lennard-Jones energy of interaction between two Kr atoms) increases, the domains do start to break up, as the thermal energy overcomes the ordering imposed by the periodic framework and interaction potentials. Eventually, a homogeneous liquid is obtained for $T \gtrsim 1.0$.

Abraham et al. [115] did not calculate mobility or diffusion. But the ordering and domain structure seen in their simulations for incommensurate densities, combined with the suggestion of similar structures in the β-aluminas, constitute an intriguing possibility for structure/mobility correlations in β-aluminas. Hopping-type theories appear simply inappropriate for dealing with the domain wall structure, and more continuum work, along the lines of Langevin or MD

theories, will be needed to sort out the real importance of domain behavior in covalent framework conductivity.

6. Some special theoretical issues

Although most theoretical effort has been devoted to understanding the dc conductivity, theoretical progress has also been made in understanding other areas of the solid electrolyte field. We will simply point out a few recent research reports in these related areas, as indicative of the directions in which theory is proceeding.

6.1. Transport with dispersed second phase, "Liang effect"

In many soft framework electrolytes, notably LiI [116,117] and in some glasses [118], it has been demonstrated that the presence of a dispersed insulating second phase of a hard crystal, such as α-Al_2O_3 or silica, can lead to quite large (up to a factor of 10^3) enhancements in the observed ionic conductivity. Several mechanisms have been discussed for this behavior, including transport along dislocation loops or grain boundaries and high strain fields at the interface. Jow and Wagner [119] suggested

that the enhancements might arise from formation of a space-charge layer along the interface between the two phases, thus giving rise to increased charge density and conductivity along the interface.

Roman et al. [120] have used a three-component percolation-type model to discuss the increased conductivity. They include three regions: a conductive phase corresponding to the bulk electrolyte, a highly conductive phase describing the interface and the insulating phase itself. They find two different thresholds, and can fit the observed behavior for LiI/Al_2O_3 nearly quantitatively with the percolation model.

Wang and Dudney [121] have presented a calculation based on a representation of the composite materials as an arrangement of cubic particles, with the center of each cube constituting insulating phase, and with concentric cubic layers about this insulating cube representing areas of enhanced conductivity. Outside of these layers, the conductivity is uniform, fixed at the value of the pure electrolyte. To fit the experimental concentration dependence, they required a conductivity in the cubical sheath region that exhibits a relatively sharp maximum at a distance of roughly 600 Å from cube center. They suggest that this behavior is a combined result of carrier concentration and mobility.

Dudney [122] has considered the possible mechanism underlying the enhancement. She suggests that there is a noticeable space-charge effect in interfacial systems, and that it is adequate to explain small enhancements in systems like AgCl. But larger enhancements in systems like LiI/Al_2O_3 cannot be explained by simple space charge effects.

6.2. Mixed-alkali effect

One of the most startling observations in the ionic conductivity of glasses is the so-called mixed-alkali effect: in, say, sodium silicate/potassium silicate glass, the conductivity exhibits a very sharp minimum as a function of mole fraction, with local maxima at each pure phase [123]. There have been several theoretical treatments presented for this phenomenon, which can also be observed, though less spectacularly, in hard frameworks like β''-alumina [124]. The most common explanation involves the ad hoc assumption that unlike alkali ions exert a weak binding force

on one another; that is, that the equilibrium constant for such a reaction in the glass as

$$Na^+...Na^+ + K^+...K^+ \rightarrow 2K^+...Na^+ \qquad (32)$$
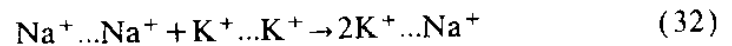
is considerably larger than the expected statistical value of 4. If this assumption is made, then several levels of treatment of the mixed-alkali effect are possible.

Ingram [125] suggested that the mixed alkali effect could be easily explained in terms of weak electrolyte theory: since only a few of the ions are free in a weak electrolyte, even a relatively small further trapping according to a scheme like (32) would lead to a substantial dropoff in the conductivity, just as is observed. Since weak electrolyte effects are usually considered to be larger in glasses than in crystals, it is not surprising that the mixed alkali effect is stronger in the glasses.

More recently, Harder et al. [126] [*2] have used a percolation-type model to discuss the mixed-alkali effect. They assume that the ions move on a lattice, and that the formation of pairs according to (32) simply blocks two neighbor lattice sites. Within this model, a very sharp mixed-alkali effect is calculated; indeed, there are two percolation thresholds, between which the percolation paths are blocked by the resultant two-atom structures, and the conduction goes to zero.

The unsatisfying feature behind these "explanations" of the mixed-alkali effect is the lack of any convincing argument in favor of an unstatistically-high equilibrium constant for (32). Until one understands how such binding is to occur, one is left with good combinatoric or analytical arguments resting on somewhat shaky ground: prediction of such atom–atom binding in a glass seems to constitute another challenge for electronic structure theory.

6.3. Dielectric response: fractals and Debye–Hückel models

Many experimental measurements on solid electrolytes involve behavior at a highly irregular interface. The most obvious examples are ordinary complex impedance measurement of the conductivity, in which the conductive sample is contacted by

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[*2] Cf. ref. [127].

electrodes, normally either spring-loaded or sputtered onto the surface. The actual interface across which the charge then passes is a highly nonplanar, irregular set of tight and loose contacts. In recent years a number of investigators have concerned themselves with the issue of how these dimensional irregularities can effect charged particle motion and response to applied signals. In particular, the concept of fractal dimension has been used both to study the dielectric response of the material and, more generally, to examine both independent-particle and correlated ion motion in disordered media. Pioneering, extensive investigations of solid electrolytes using fractal ideas have been completed by Sapoval, Gouyet and co-workers [128–130], who have shown both some of the conceptual advantages of the idea of fractal dimension and its relevance to generalized ion motion problems.

One particular area of interest involves dielectric response. Jonscher [131] has emphasized that many solid electrolytes (and other comparable systems) exhibit so-called constant phase angle (CPA) response, in which the usual complex impedance plot ($Y(\omega)$ versus $X(\omega)$) shows a straight line or spur behavior, with a "constant phase angle" $\phi(\omega)$ the between the line and the X axis. While several other explanations for this behavior have been advanced, two of the most convincing involve either Debye–Hückel-type correlations [132] or fractal behavior at the electrode [133] (or both) [134]. Le Menhaute and Crepy [135] were the first to suggest the importance of fractal behavior in determining dielectric response. The Oak Ridge group [136] has studied the response of fractal networks of cantor bar geometry. Sapoval [133] has recently examined the response of fractal electrodes of different fractal types, including the Koch island and finite Sierpinski carpet. He has shown that a high-frequency CPA behavior is indeed observed, but that at lower frequencies a second, differing constant phase angle can be found; the response can be nicely described in terms of the fractal geometry of the interface.

Funke [132] has used a generalized Debye–Hückel-type model to explain another feature of the "universal dielectric response". This consists of a high-frequency arc, whose center is depressed below the axis, and corresponds to a power-law dependence of the conductivity. Funke argues that following an initial forward jump of a mobile ion, the most probable behavior is either a "bounceback" reverse jump (cf. sections 3, 4) or a forward motion of the surrounding "defect cloud". This behavior is quite similar to that discussed for ordinary liquid electrolytes by Debye and Hückel.

Funke uses the linear-response form for the frequency-dependent conductivity (essentially eq. (15) to calculate the conductivity in the presence of these events. He is then able to show that this model, under fairly general conditions, can reproduce the "universal dielectric response", including the power law behavior and the temperature dependence. Physically, the two assumed behaviors seem reasonable: bounceback effects are omnipresent in hopping models, and indeed should be a major feature of ionic conduction in any solid electrolyte, except perhaps in the very strongly correlated, liquid-like regime. The second process, corresponding to relaxation of the "cage" around the new site, will be especially important in soft, heavy metal frameworks such as those discussed in section 3. The whipback effect seen by Olson and Adelman [84] is just that part of the bounceback caused by the failure of the cage to respond to the new position of the mobile ion. Funke's use of these correlation processes to explain the dielectric properties seems cogent and useful, though the actual relaxation process might be oversimplified in his model.

Blender and Dieterich [134] have considered the Debye–Hückel problem on random fractals. They have shown that the screened potential decays asymptotically according to an exponential of a fractional power of distance, as measured in the relevant fractal geometry.

6.4. Transport across interfaces

The Liang effect (section 6.1) involves transport along interfaces within a given solid electrolyte. In actual applications, one encounters transport phenomena across interfaces, both the electrode/electrolyte interface and, possibly, internal interfaces within the electrolyte. Dieterich's group has recently modeled [138] the interface transport problem, using a site hopping model with a locally differing hopping rate representing the interface. Interactions among the mobile ions were included using hard-core re-

pulsions. Both simulations and approximate decoupling methods were used to study the diffusion profile. It was observed that both the density of ions and the conductivity can be (not surprisingly) strongly influenced by the impurity-type hopping feature at the interface. The dc conductivity, in particular, can be substantially reduced, and the profiles of ion density can vary quite sharply in the neighborhood of the interface. Direct probing of such interfacial profiles, using either Rutherford backscattering or perturbed angular correlation spectroscopy, should prove valuable both in studying the ionic concentration gradients at interfaces and in correlating such density features with conductivity and with overvoltage effects.

6.5. Activation entropy effects

Although, as we have pointed out in sections 2–5, the hopping model must be used very carefully in discussion of ionic conduction, nevertheless it is of real conceptual value in nearly all circumstances, and can describe low-frequency conduction quantitatively in many systems. In addition, it provides a number of qualitative notions, including attempt frequency, correlation factor and mean hopping distance, that are of great value in characterizing ionic motion in electrolytes. Almond and West [139] have delineated how the concept of activation entropy may be used to distinguish differing sorts of ionic conduction, both in framework electrolytes and in glasses. They show that the so-called Meyer–Neldel rule, a frequently observed behavior in which the prefactor in the Arrhenius expression for ionic conductivity increases as the activation energy increases, can be rationalized in terms of thermodynamic relationships between enthalpy and entropy of activation. Finally, and intriguingly, they conclude that mobile ion concentrations have far less influence on the conductivity than had been previously assumed, and that two ranges of ionic conduction can be distinguished, a high-temperature situation in which a large fraction of the ions is mobile with low activation energy, and a low-temperature situation, in which the mobility is entropically enhanced. There are similarities between this picture and the strong versus weak electrolytes viewpoints discussed in section 2, similarities that could be in-

terestingly illuminated by proper study both of microscopic models and of dynamical structure.

7. Remarks

Theoretical treatments of solid state ionic materials have made great strides. The structural disorder and complexity of these materials, coupled with the Coulomb nature of interactions both among the ionic carriers and between ion carriers and charge compensating species, combine to make either numerical or formal description quite complicated. Nevertheless, very substantial understandings have been reached. As one example, our picture of how ions move in polymer electrolytes has evolved from the early picture of independent ions hopping on a lattice to the current picture of correlated diffusive motion of ions in a solvated Coulomb fluid.

This article has, very incompletely and selectively, overviewed the progress that has been made in theoretical study of solid electrolytes. It is worthwhile to point out areas in which progress has not been made, and which stand as possible areas for fruitful and useful theoretical work:

(1) Mixed conductors. Both electrode and composite materials can exhibit conductivity of both ions and electronic carriers. The interactions will then be quite strong, with intriguing behavior both at dc and in the optical range. Nearly no theoretical work has been done here, despite the obvious importance of the area and an increasing number of high-quality experiments.

(2) Stability and structural studies are still quite rare. The geometric and phase behavior of electrolytes as a function of composition and of temperature is, again, important both for applications and for the intrinsic value of the problem – how does one describe a phase diagram theoretically.

(3) Electronic structure work, as noted in section 3, has been very limited. An understanding of potentials, of pathways, of energetics and of structure may be obtained from proper accurate studies of this type, even relatively simple theoretical studies such as complexation and ion-pair energetics in polymer electrolytes remain to be completed.

(4) Though continuous models have been used for crystalline frameworks, and to a lesser extent in

glasses, a vast amount remains incomplete. For polymers, no proper microscopic continuous modeling has been done at all. Continuous (inertia-including) models are needed to understand the dynamics of ion motion [5]

(5) Relationships of structure and properties are still quite incomplete. For example, some of the questions discussed in section 5 involving commensurability effects, domains and diffusion require more detailed consideration, both formal and numerical.

(6) Langevin dynamics, especially in connection with effective potentials, represents an effective way to study continuous models without the complications of full molecular dynamics simulation. Use of such reduced dynamics for highly disordered electrolytes is an unmet challenge.

(7) The most difficult challenge lies in the development of new mechanistic, qualitative concepts for understanding behavior of ionic solids. Such concepts as optical basicity, weak-electrolyte models, commensurability effects, effective potentials or caterpillar mechanisms are of real conceptual value; others, as good or better, might be developed to help in the understanding of these important and unusual materials.

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