Polymeric Solid Electrolytes: Dynamic Bond Percolation and Free Volume Models for Diffusion

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Polymeric solid electrolytes offer a difficult problem from the viewpoint of under-standing the charge transport mechanism. While quasithermodynamic theories (config-urational entropy, free volume) are useful for rationalizing the behavior of these materials, they do not really amount to a microscopic picture. We have developed a dynamic bond percolation (DBP) model to describe ionic conductivity in these materials. The DBP model is based on a master equation describing ion hops among sites. The percolation aspects are included by making the bonds between sites ran-domly open or closed. The dynamical aspect is due to the configurational motions of the polymer, and results in the variation of the bond assignments as open or closed. The relationship of DBP to free volume theory is sketched; this involves a specific consideration of kinetic effects on free-volume motion.

I. Introduction

Since their discovery by Wright [1] and early exploration by Armand [2], polymeric solid electrolytes have been the focus of intense investigation in several laboratories. Many interesting observations have been reported, including vibrational spectra leading to a solvation scheme for the cations [3], thermo-chemical studies implying a salt lattice energy threshold for complex formation [2,4], network studies showing the increase of conductivity with decreasing glass transition temperature [5], electrochemical studies showing both negligible electronic conductivity [6] and significant anionic and cationic motion [7], microwave conductivity data indicating simi-larity of free polymer and polymer-salt complex response for frequencies above 0.5 GHz [8], morphological and thermal analysis studies indicating mesophase behavior [9], activation studies showing an important role for salt-free polymer in the conductivity [10], viscoelastic studies showing an increase in glass transition temperature with salt concentration [2,11], and a number of new polymer hosts [11,12] in addi-tion to the original materials, polyethylene oxide (PEO) and polypropylene oxide. The interpretation of the conductivity in these largely amorphous polymeric materials, which are generally studied well above their glass transition temperatures T_g, is nearly always given, following Armand [13], in terms of the Vogel-Tammann-Fulcher (VTF) equation of glass science [14] or, more extensively, in terms of the free volume theory (FVT) of Cohen and Turnbull [15,16].

The VTF equation itself is of empirical origin, though it can be derived [15] straightforwardly in the context of FVT. The VTF equation for the conductivity σ of a polymer/salt complex may be written

$$\sigma = A_0 T^{-1/2} e^{-E_A/k(T-T_0)} \qquad (1)$$

Here A_0 is a (weakly) temperature dependent prefactor, and T_0 is the so-called equilibrium glass transition temperature [17,18]; E_A has the form of an activation energy. Equation (1) predicts precisely the type of curved activa-tion plot ($\ln \sigma T$ vs T^{-1}) actually observed for many [13] of these complexes, though hysteresis [11] and complications due to uncomplexed polymer [10] may be observed in certain temper-ature and stoichiometric regimes. Because eq. (1) may be derived from FVT [15], and since it characterizes the conductivity of most PEO-salt complexes fairly satisfactorily, it is now quite standard to use FVT to discuss the ionic conductivity of polymeric solid electroltytes. There are, however, several drawbacks to the FVT approach. Most importantly, it is not intended to apply to the diffusion of small ions within a solid comprised of much larger polymeric chain segments (nor, originally, to polymers themselves, for which a configura-tional entropy model [19-22] is in several senses preferable); rather, it is used to describe viscosity, thermodyanmic data, and relaxation behavior of glass-forming materials [15,16,23-25]. While its extension to neat polymers may, with caution, be carried out, its extension to ionic motion within polymers is more problematic. In particular, one of the fundamental assumptions of FVT, the facile and rapid redistribution of the free volume, may fail to hold in the case of polymer electro-lytes with low fluidity.

We have recently presented a microscopic theo-retical treatment of ionic motion in polymers [26], based on a dynamic bond percolation theory (DBP) model. This model takes cogni-zance of the fact that ionic hopping can occur on time scales faster than typical reorganiza-tion times of the polymeric host, and that the

polymeric host itself occupies a position somewhere between that of the covalent framework host in typical framework solid electrolytes such as β alumina and the rapidly reorganizing liquid host of aqueous electrolytes. That is, there are three typical timescales in the problem, one corresponding to the observation time t_{obs}, one to the intrinsic ion hopping time $\tau_h = w^{-1}$ where w is an ion hopping rate between neighboring sites, and one being a polymer reorganization time τ_{ren}, which is the timescale on which the characterization of jump paths between sites changes between open and closed. This DBP theory is dynamic, which can be an advantage, compared to FVT, for describing the polymeric electrolytes. In the present manuscript, we should like to recap briefly some critical points of DBP and FVT, and then to compare them in the context of polymeric solid electrolytes. By so doing, we gain some insight into the microscopic meaning of some of the parameters of each theoretical scheme, and also appreciate more clearly sets of physical conditions under which FVT may work or may fail.

The nature of the ionic conductivity in polymeric solid electrolytes is complex, depending on such variables as degree of hydration [3,27], impurity ions from the polymerization process [3], ion pairing [28], inhomogeneities in the sample and possibly conduction by both ion types [7]. For reasons of simplicity, we couch our discussion in terms of a simple limiting case in which ion pairing and anion transport are unimportant.

II.   Brief Review of FVT as Applied to Solid Electrolytes

The first application of free-volume concepts to the viscosity of glass formers and the liquid-glass transition was given by Fox and Flory [29]; several subsequent workers elaborated upon their ideas [18,23]. Turnbull, Cohen and Grest [15,16,23-25] have recently extended the free-volume ideas to deal with thermodynamic and relaxation phenomena, as well as viscosity. For a substance comprised of small molecules, they derive the empirical Doolittle [30] equation for the fluidity ϕ (which is simply the reciprocal of the viscosity η). The equation is

$$\phi = \phi_0 \exp\{-b\bar{v}_0/v_f\} \ , \tag{1}$$

where b is a constant of order unity, v_f is the average free volume per molecule, defined by

$$v_f = \bar{v} - v_0 \ , \tag{2}$$

$\bar{v}$ being the average volume per molecule in the liquid and v_0 the van der Waals volume of the molecule. To derive (1) within FVT, four assumptions are made [18].

1.   It is possible to associate a local

volume v of molecular scale with each molecule (or motile segment of a flexible molecule).

2.   When v reaches some critical value v_c, the excess can be regarded as free.

3.   Molecular transport occurs only when voids having a volume greater than some critical value v^* approximately equal to the molecular volume v_m form by the redistribution of the free volume.

4.   No local free energy is required for free-volume redistribution.

It is the fourth of these assumptions, in particular, which can become problematic when considering ionic transport in polymers.

The free-volume form for the diffusion coefficient may be written [15]

$$D = gau e^{-\gamma v^*/v_f} \ , \tag{3}$$

where g is a geometric factor of order 0.2, u is the thermal velocity, a is roughly the diameter of the molecule and γ (related to b of (1)) is an overlap factor of the free volumes, and should be close to unity. The factor v^* is the minimum void volume that can contain the diffusing molecule. The form (3) is derived by Cohen and Turnbull [15], who point out that "in our view, diffusion occurs not as a result of activation in the ordinary sense but rather as a result of redistribuiton of the free volume within the liquid." More specifically, (3) is derived by maximizing the number of ways of distributing the free volume, without consideration of whether all such distributions are in fact reasonably accessible. It is this question of accessibility (or, alternatively, of the rate of free volume motion or interchange) which appears to us to limit the validity of FVT in situations involving ionic transport in polymeric electrolytes; it is equivalent to the failure of assumption (4) above.

For the situation of small ions (or molecules) in a polymeric host, one can, following (3), derive diffusion coefficients for polymer segments and for ions; these are

$$D_{seg} = u_{seg} a_{seg} g \exp\{-\gamma v^*_{seg}/v_f\} \tag{4}$$

$$D_{ion} = u_{ion} a_{ion} g \exp\{-\gamma v^*_{ion}/v_f\} \ , \tag{5}$$

where v^*_{ion}, the critical void size for ions, is considerably smaller than v^*_{seg}, the critical void size for polymer segments. The temperature behavior of the free volume can be approximated as [15,31]

$$v_f = \alpha \bar{v}_m (T-T_0) \ , \tag{6}$$

where T_0 is the temperature at which the free volume disappears (close to the equilibrium

glass transition temperature), α is the coefficient of thermal expansion, and v_m is the mean molecular volume of the species whose motions create free volume (in our case, polymer segments). Then for temperatures fairly close to T_0, v_f will, from (6), be considerably smaller than v_{seg}^*. Thus from (4), the polymer motion (and free volume reorganization rate) is small, while at the same time v_f is larger than v_{ion}^* and therefore (5) will predict facile ionic diffusion. It is just this conundrum (predicted rapid diffusion from a free-volume mechanism in a temperature range where the free volume is not mobile) which implies serious limits to free-volume explanations for diffusion in polymeric solid electrolytes.

III. Dynamic Bond Percolation (DBP) Theory

A microscopic interpretation of (3), as well as an understanding of some limits to its applicability, may be gleaned from considerations based on a model of ion hopping within a dynamically-disordered medium, which we have recently developed [26] and applied to polymeric solid electrolytes. This model, which we call dynamic bond percolation (DBP) theory, describes the motion of ions between sites in the dynamically disordered polymer. It is physically motivated by several key observations, including the response of both polymeric host and complex at microwave frequencies [8], the suggestion from vibrational spectra [3] that ion sites are well defined in these electrolytes, and the fact that the interesting regions for experimental study lie above T_0, where rearrangements are occurring on a characteristic slow timescale.

For any fixed polymer configuration, the motion of the ions is described by a percolation process; that is, by a hopping model with the hopping rates between any two sites chosen as finite or zero, depending on whether those sites are mutually accessible (an available, or open, bond) or not (an unavailable, closed bond). This is the static percolation aspect of the model. But since the polymer (for $T > T_0$) is in motion, the various stable sites for the ion will move with respect to one another, thus changing the complexion of closed or open bonds. The dynamic motion of the polymeric host is then modelled by allowing the hopping probabilities to readjust, or renew, their values on a timescale corresponding to polymer motion. The model then consists of a master equation

$$\dot{P}_i = \sum_{j \neq i}' \{P_j(t) w_{j \rightarrow i} - P_i(t) w_{i \rightarrow j}\} \qquad (7)$$

where P_i is the probability of occupying an ionic site j at time t, and the w are hopping transition probabilities per unit time. The percentage of available bonds is denoted f, and we choose, for a one-dimensional model,

$$w_{i \rightarrow j} = \begin{cases} 0 & i,j \text{ not neighbors} \\ 0 & \text{bond } (i,j) \text{ not available} \\ w & \text{bond } (i,j) \text{ available .} \end{cases} \qquad (8)$$

The assignment of (i,j) bonds as available or unavailable is changed at a rate $(\tau_{ren})^{-1}$, where τ_{ren} is the time of the renewal [32], or solvent motion, process. For simplicity, we have assumed that the reassignment of bonds is random, independent of their former assignment or that of their neighbors; this seems appropriate for a fully amorphous polymer, but other choices may be made [33].

The analysis of DBT has been given elsewhere [26]. Here we review a few of the salient points, which can then be contrasted to FVT. Within the DBP, one finds:

1. For hopping lifetime τ_h ($= \ln 2/2w$ for one dimension) such that $\tau_h \gg \tau_{ren}$, the motion process corresponds to hopping in a homogeneous (non-percolating) system, in which the effective hopping rate is wf.

2. For observation times t_{obs}, such that $\tau_h \ll t_{obs} < \tau_{ren}$, the mean-squared displacement will be fixed by the static percolation problem, becoming

$$\langle x^2 \rangle = \frac{f}{(1-f)^2} \cdot a^2 \qquad (9)$$

in one dimension ($a =$ distance between sites), and with well-defined values for higher dimension, so long as f is below the percolation threshold.

3. For $t_{obs} \gg \tau_{ren}$, the behavior is diffusive (that is, $\langle x^2 \rangle \propto t_{obs}$), independent of the behavior for times shorter than τ_{ren}; the diffusion coefficient in this regime increases monotonically with $1/\tau_{ren}$ (Fig. 2). An example of this is shown in Fig. 1, where $\langle x^2 \rangle$ is seen to be linear in t, once $t > \tau_{ren}$. This is to be contrasted with the static percolation problem defined by (7,8), (or the short-time behavior in Fig. 1), for which no diffusion occurs in one dimension.

4. A closed form expression (albeit involving many summations) may be given for $\langle x^2 \rangle$ [26].

The essential differences between the assumptions of FVT and of DBP are: (A) that the FVT assumption (4) is not made in the DBP model and (B) that FVT is not a lattice-hopping model, while DBP is. These differences become important when we consider the motion of ions in polymer hosts.

IV. Polymeric Solid Electrolytes: FVT and DBP Ideas

The first suggested mechanism for ion transport in solid polymer electrolytes was given by
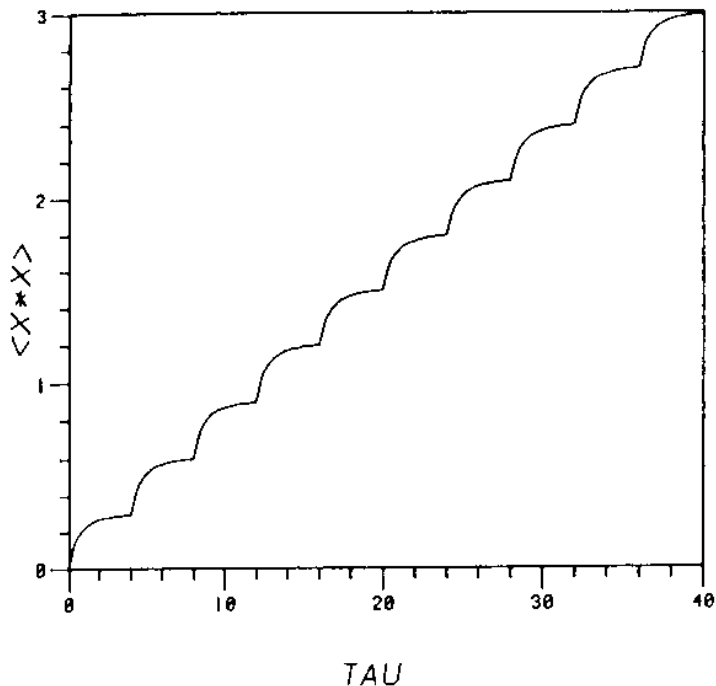
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Figure 1. Mean-squared displacement of an ion obeying the DBP model, for the case in which $\langle x^2 \rangle_1$ is limited by percolation. Note that the long-time behavior ($\tau > \tau_{ren}$) is diffusive. Parameters: f = 0.2, $w\tau_h$ = 0.2, renewal after twenty hops (from [26]).
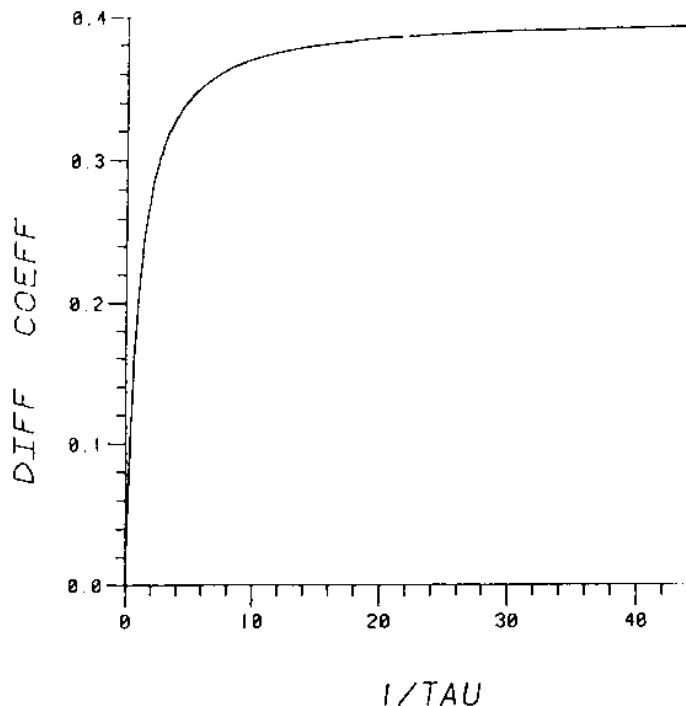

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Figure 2. Diffusion coefficient, calculated in DBP, as a function of inverse renewal time. Note that the shortest renewals give highest diffusion, since the blocking effect of unavailable bonds is minimal. Value of f is 0.2 (from [26]).

Armand et al. [2] who suggested that the helical channels in which cations were situated provided one-dimensional motion pathways. Later, Armand et al. [13] and Papke et al. [4] suggested that, while the cations were probably largely complexed in locally-helical regions, their transport was very probably dominated by motion through the disordered regions. The former group invoked the empirical VTF equation (1) and the qualitative notions of free volume transport to explain the curved Arrhenius plots for log (σT) vs T^{-1}, while the latter group instead gave an explanation in terms of the Adam, Gibbs, and Di Marzio configurational entropy model as extended by Angell [19-22]. Most commonly, discussions are couched in terms of the FVT [18] or configurational entropy [21,22] models. Both of these, however, are quasithermodynamic, and therefore do not include the dynamical modeling of DBP. Our aim here is to discuss the FVT in light of insights provided by the DBP model.

The typical parameters of FVT are the thermal velocities u, the sizes of the diffusing species, the free volume v_f and the critical volumes v_{seg}^* and v_{ion}^* (of 4,5); those of DBP are the fraction of available bonds f, the hopping rate w and the renewal time τ_{ren}. We wish to relate these to one another in order to understand FVT on the kinetic basis of DBP. A more complete treatment will be given elsewhere [33]; we wish here only to review some important points.

If for a moment the polymer strands are considered to follow a sort of hopping motion from one region to another with a hopping rate K, then we could write

$$D_{seg} = \lambda\ a^2_{seg}\ K\ f_{seg} \ . \tag{10}$$

Here λ is a factor of order unity and a^2_{seg} is a typical segment area. Eq. (10) is simply the generalization of the definition of the diffusion result for a simple random walker to take into account (through f_{seg}) of the fact that not all jumps are allowed; that is, the effective jump rate is Kf_{seg} rather than K, since only a fraction f_{seg} of bonds are available. By comparison of (10) with (4), we find

$$\lambda\ a^2_{seg}K\ f_{seg} = a_{seg}\ g\ u_{seg}\ \exp(-\gamma v^*_{seg}/v_0) \ .$$
$$\tag{11}$$

then identifying K as u_{seg}/a_{seg}, we find

$$f_{seg} = \frac{g}{\lambda}\ \exp(-\gamma v^*_{seg}/v_f\ ) \ . \tag{12}$$

In the limiting case of very large free volume, all sites should become available: $\lim_{v_f \to \infty} f = 1$. Thus g = λ, and we have

$$f_{seg} = \exp\{-\gamma v^*_{seg}/v_f\} \ . \tag{13}$$

An analogous argument for the hopping ions gives

$$f_{ion} \approx \exp\{-\gamma v^*_{ion}/v_f\} \qquad (14)$$

This behavior seems correct in both limits: when $v_f \to \infty$, $f \to 1$, since then the free volume is very large and all sorts of motion should be permitted. When $v^*/v_f \to \infty$, $f \to 0$, which is also reasonable, since no motions will be permitted when the free volume is too small to permit voids of the size of the critical volume of the diffuser.

The identifications (13,14), along with

$$w = u_{ion}/a_{ion} \qquad (15)$$

provide FVT equivalents of w and f. The renewal time τ_{ren} can be related via

$$(\tau_{ren}) \cdot (u_{seg}) = (a_{seg}) \cdot \left(\frac{\text{fraction of unavailable bonds}}{\text{fraction of available bonds}}\right) \qquad (16)$$

or

$$\tau_{ren} = \left(\frac{1-f_{seg}}{f_{seg}}\right)\left(\frac{a_{seg}}{u_{seg}}\right) = \frac{(\frac{1}{f} - 1)a_{seg}}{u_{seg}} \qquad (17)$$

Verbally, (16) says that the velocity times the time is the probable distance moved. Using (14), we can rewrite (17) as

$$\tau_{ren} = \left(\frac{a_{seg}}{u_{seg}}\right)\left(\exp[\gamma v^*_{seg}/v_f]-1\right) \qquad (18)$$

As the free volume becomes larger, the renewal time decreases, but for T not too much larger than T_0, v_f is small and τ_{ren} is long.

Having associated the parameters of the two approaches, we can make some comments on the nature of the FVT description. Firstly, if (5) is used, the actual polymer dynamics, which should enter via a_{seg}, u^*_{seg}, and v^*_{seg}, is lost. In particular, if $v^*_{seg} \gg v^*_{ion}$ (which is reasonable), the polymer may still be nearly frozen when (5) might predict high mobility. In the language of FVT, we have a breakdown of the assumption (4), that the free volume can freely distribute itself; equivalently, we have the situation, ignored in FVT, in which [23] solidlike and liquidlike cells exchange volume, or solidlike cells become liquidlike and vice versa. These processes, which correspond to low fluidity, are indeed relevant for polymer electrolytes. In fact, in this regime the percolation is almost static, and in one dimension we expect no diffusion.

If the FVT model (4) is accepted for the polymer motion, but DBP is taken for the ion motion, some other limits may be examined (this seems a physically reasonable arrangement, since

the ionic motions, as opposed to ionic potentials, should not influence polymer segment motion). If the polymer motion is rapid, w becomes $u \cdot f_{ion}$, and

$$D_{ion} \propto a_{ion} u_{ion} f = a_{ion} u_{ion} \exp(-\gamma v^*_{ion}/v_f). \qquad (19)$$

This is just the FVT result, which is indeed appropriate to this limit. The limit is not a very probable one, however, since it assumes $u^*_{ion}/u^*_{seg} \ll 1$; usually the opposite limit should hold, since the ions are lighter and smaller than the segments. Nevertheless, we see that the short τ_{ren} limit is the FVT situation.

Consider now the opposite case, in which $T-T_0$ is not too large, v_f is smaller than or near to v^*_{seg}, and, from (18), τ_{ren} is long. Then, from Eq. (65) of [26], we have

$$D_{ion} = \langle x^2 \rangle_1/\tau_{ren} , \qquad (20)$$

where $\langle x^2 \rangle_1$ is the average diffusion distance within one renewal cycle. Then using (17),

$$D_{ion} = \langle x^2 \rangle_1 u_{seg}/a_{seg}(\frac{1}{f_{seg}} - 1). \qquad (21)$$

for $\tau_{ren} >$ time to span average connected cluster, we have $\langle x^2 \rangle$ of order of cluster size. More exactly, using [26]

$$\langle x^2 \rangle_1 = a^2 f/(1-f)^2 \qquad (22)$$

appropriate for long τ_{ren}, we find

$$D_{ion} = \frac{u_{seg} a_{seg} \exp\{-2\gamma v^*_{seg}/v_f\}}{(1 - \exp(-\gamma v^*_{seg}/v_f)} \qquad (23)$$

In this limit, D_{ion} is controlled only by the properties of the polymer; this cannot arise from the FVT result (5). Here we use f_{seg}, which is appropriate, since polymer motion limits $\langle x^2 \rangle$.

One interesting experimental implication of the DBP which is not so clear in FVT involves the situation in which excess salt is added to a polymer host, with resulting decrease in fluidity and sharp decrease in ionic conductivity; such observations have in fact been made for polysuccinates [11,12]. The glass transition temperature T_g varied only slightly in these experiments. Thus, from (6) v_f changes only slightly, but enough (from the Doolittle equation) to change the fluidity. Using (3), however, with $v^*_{ion} > v_f$, the predicted ionic conduction is still high; its observed [12] decrease may be attributed to long τ_{ren} brought on by high viscosity of the polymer. This results in slow rearrangement of free volume,

and a breakdown of assumption (4) of FVT. This situation is easily dealt with in the DBP picture: the fluidity decreases, so τ_{ren} increases and D_{ion} drops.

The quasithermodynamic theories of free volume and configurational entropy have been very valuable for understanding thermodynamic and transport properties of polymers, liquids, and glasses. We feel that the DBP approach, by including solvent dynamics in a kinetic approach to the transport problem, offers both a useful interpretation of FVT and an attractive alternative approach to the discussion of transport in these materials.

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