FEATURE ARTICLE

Conduction in Polymers: Dynamic Disorder Transport

Abraham Nitzan

Department of Chemistry, Tel Aviv University, Tel Aviv, Israel

Mark A. Ratner*

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60208

Hopping and diffusion models are extremely useful for describing processes occurring in extended systems, on time scales far longer than some underlying molecular time, such as a characteristic solvent vibrational time or (for crystals) an inverse Debye frequency. Most applications of hopping models to problems in chemistry and materials science assume the presence of two time scales, a residence time and hopping time, and that the time of residence is far longer than the time involved in hopping from one site to another. We describe a generalization of this model to deal with systems in which the underlying structure exhibits dynamical disorder—that is, in which in addition to the species undergoing hopping motions, the lattice itself is reorganizing in time. An important example is glass-forming liquids above their glass transition temperature, especially polymeric materials. In its simplest realization, this multiple time scale hopping model involves only two times—a hopping time and a renewal time τ_R characterizing the average relaxation time of the underlying lattice motions. One then is faced with the analysis of a problem involving motion on these two time scales, and with the application of that model to a number of systems. Experimentally, a model was originally developed to deal with polymer electrolyte materials, in which ionic diffusion occurs in polymer hosts well above their glass transition temperatures. In this case, the renewal time can be roughly correlated with the glass transition relaxation in the neat polymer host. The dynamic disorder hopping model, or dynamic bond percolation model, is closely related to other models used in solid-state theory, such as the continuous time random walk of Scher and Lax, or the stirred percolation model used in the study of microemulsions. It has a very simple chemical interpretation, since only two times are defined. We describe the nature of the dynamic disorder models, their solutions in particular cases, and their application to a number of physical systems. Particularly important results include formal proofs that, when dynamic disorder is present, percolation thresholds disappear and the system is always diffusive over times long compared to the renewal time. One can also derive generalized analytic continuation results relating the frequency-dependent diffusion in the dynamically renewing lattice to the frequency-dependent diffusion in the static lattice. While the model was originally developed to deal with ionic transport in polymer media, a number of interesting applications in other areas, including polymer viscosity and polymer dynamics, are also briefly discussed.

Introduction

Studies of chemical reactions and processes in the condensed phase, like those in isolated molecule vapor-phase chemistry, often focus on the interrelationship of structure and properties. In the past two decades, a great deal of activity has been devoted to research in the electroactive polymers—that is, polymeric systems that exhibit interesting conductivity and charge transport properties. In the majority of these polymeric systems, the definition of structure is a complicated one. Even highly crystalline polymers exhibit substantial disorder, and in noncrystalline polymers, while short-range order and primary chemical structure are quite well-defined, typical radial distribution functions lose their structure after only a few repeat distances. Moreover, in polymers above the glass transition temperature, whatever average order there is evolves dynamically in time, due to structural relaxation processes in the polymer. In this sense, disorder in polymers above their glass transition temperatures is both static (only short-range order in the pair distribution functions) and dynamic (density at any point in the structure changes on characteristic relaxation time scales). The problem of charge transport in

polymers, then, involves systems that are characterized by either one or both kinds of structural disorder.

This article is devoted to the definition and application of a dynamic disorder model for characterizing transport in polymeric systems. The motivation for the model came originally from the field of polymer electrolytes, in which charge is transported by ions.[1,2] The obvious necessity for dealing with dynamic disorder is most clearly marked in these systems. At the same time, applications to other systems, such as diffusion of neutral species, conductivity by hopping electrons in polymeric systems, and impurity diffusion in a binary mixture or polymer physical properties, are conveniently discussed within the context of the dynamic disorder model, and the comparisons among the different transport processes illustrate the interplay between particle motion and host relaxation.

Polymer electrolytes are most simply pictured as ionic solutions in an essentially immobile solvent. They are generally prepared by dissolving a 1:1 electrolyte, such as NaSCN, in a polymeric host such as poly(ethylene oxide). If the lattice energy of the parent salt is sufficiently low, and the solvating power of the polymeric solvent sufficiently high (for example, by complexation of the alkali cation by oxygen lone pairs on ether subunits), then a homogeneous, stable, and thermodynamically well-defined
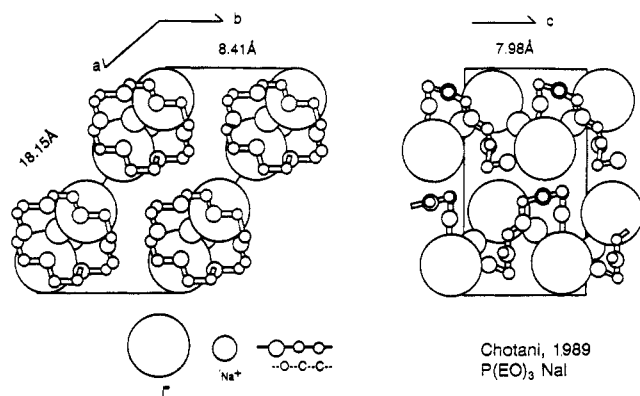
Figure 1. Structure, deduced from fiber X-ray diffraction, of poly(ethylene oxide)/NaI, at a relative O:I concentration of 3:1. Note the high relative atomic concentration, or density, corresponding to the space-filling fluid (from ref 31).

solution phase, an ionic solution in the polymer host, can be prepared and studied. The ionic conductivity associated with such materials is of the order 10^{-8}–10^{-4} S/cm at ambient temperatures. The materials are under very active study, partly because of promising applications as electrolytes in all-polymer, high energy density batteries.[3-6]

Intrinsically, the polymer electrolytes are substantially challenging because they are concentrated electrolytes (characteristic concentrations 0.1–4 M). Since the solvent is a polymer of large molecular weight, diffusion of the polymer itself can be neglected. In this latter sense, the polymer electrolytes differ substantially from solutions (like sea water) in which small molecules form the solvent. As concentrated electrolytes, that exhibit ion pairing, crystallization at elevated temperatures, and ion transport, the polymer electrolytes are representative of strong electrolyte solutions that have challenged physical chemists since the time of Nernst and van't Hoff.

Because conductivity is due solely to mobile charge carriers, the model which we focus on concentrates on such carriers. Moreover, it focuses on charge-carrier displacive motions, rather than local motions (vibrations or librations). Therefore, the characteristic time scales on which the model is valid are long compared to momentum relaxation times, and to characteristic vibration times. Therefore, the equations of motion assumed for the ions disregard local motions, including all inertial motions. In other words, charge carriers can be described in terms of diffusive motion in the host. Furthermore, the host is represented by a disordered lattice and the diffusion is analyzed in terms of a random walk process in this lattice.

The model, which we call dynamic bond percolation (DBP) theory,[7-30] is one of several possible models for dynamic disorder hopping (DDH). It is based on four important physical assumptions:

(1) The materials in which the transport is occurring are dense, and charge can move from site to site only if the path is open, or available. Polymer electrolytes are indeed dense materials, like liquid electrolytes—Figure 1 shows[31] a characteristic structure of a concentrated poly(ethylene oxide)-based electrolyte and demonstrates clearly that polymer strands completely fill the spaces around the ions (it also shows strong ion pairing).

(2) Within this dense material, local sites exist on which the charge carriers reside. In polymer electrolytes, such sites correspond to local energy minima for the ion carriers.

(3) Motion between sites involves at least two time scales. The first of these time scales is simply the hopping time for charge motion from one stable site to another and is characterized by hopping time τ_h. The second time scale is the characteristic structural relaxation time of the host, which we call the renewal time τ_R; in fact, relaxation in polymer systems occurs over many time scales, and therefore the renewal time is best thought of as

a mean time for structural change of the local polymer segment around an ionic site.

(4) The experimental time scale is at least as large as τ_h and long compared to time of local vibrational motion.

Because we are interested in charge transport, the hopping particles are charged. In polymer electrolytes, they are simply ions. In conductive polymers such as polythiophenes or redox polymers, the hoppers can be electrons or holes, so long as the band is narrow enough that motion occurs by activated hopping (or variable-range hopping or any other sort of hopping), rather than by band conduction.[32] Finally, while the model contains enough flexibility to allow interionic interactions, only short-range (nearest neighbor) interactions were included in the theory in the present stage of its development.

If the four assumptions above are made, then one can write[7] an equation of motion for the charged particle in the form of a master equation (generalized first-order chemical kinetics)

$$\frac{dP_i(t)}{dt} = \sum_j \{W_{j \to i}(t)P_j - W_{i \to j}(t)P_i\} \qquad (1)$$

Here P_i is the probability of finding a hopping particle on site i and is time-dependent. The $W_{j \to i}$ are simply the frequencies of ion jumping from site j to site i. We have formally denoted these rates as dependent upon time, and it is this time dependence that distinguishes DBP from standard static percolation models.[33] In both kinds of percolation theory, one assumes that intersite motion is characterized by only two possible values:[1]

$$W_{i \to j} =$$

$$\begin{cases} 0 & \text{when } i \text{ and } j \text{ are not neighbors} \\ 0 & \text{when } i \text{ and } j \text{ are neighbors with broken } (ij) \text{ bond} \\ w & \text{when } i \text{ and } j \text{ are neighbors with available bond} \\ 1 - \sum_{k \in \{i\}} W_{i \to k} & \text{when } i = j. \ \{i\} \text{ denotes the group of neighbors to } i. \end{cases}$$

$$(2)$$

(The word "bond" in this context means a pathway between two sites on which a hopper can be located; it is *not* a chemical bond.)

$$\langle W_{i \to j} \rangle = pw \qquad (3)$$

This states that the rate constant for motion between neighbor sites is either finite, with the probability p, or 0, with a probability of $1 - p$. The static percolation model corresponds to, for example, electronic conductance in a square lattice (such as screening wire) in which bonds are randomly cut. Static percolation theory has been widely applied to transport processes in disordered materials and has proven an effective predictive and correlative tool.[33] In polymers above their glass transition temperatures, however, because the structures are dynamically relaxing on a time scale τ_R that can be comparable to or shorter than experiment, the characteristic hopping rates W themselves evolve in time. It is this evolution that is taken into account in the dynamic disorder models and that makes them more general than, but closely related to, ordinary static percolation.

We just stated the fundamental ideas, and essential equation, characterizing dynamic disorder hopping pictures. The most important characteristic feature is the use of a hopping model, and the fact that the transition rates are time-dependent. In the next section, we will discuss the different approaches to the dynamic disorder that have been taken by different authors and some of the problems to which the model has been applied. Following that, we discuss the renewal time approach itself, both the simplest picture and a more general model in which the renewal times are distributed rather than being single-valued. After discussion of solutions to the dynamic disorder hopping model, based either on the use of effective medium (mean field type) approximations or on the use of simulations, we survey the applications of dynamic disorder hopping models to ionic

conductivity, electronic conductivity, diffusion, and viscosity. Finally, some comments are made on the general applicability of the methods and areas in which they may be useful.

Brief Review of Mathematical Approaches

The problem of carrier motion in a dynamically disordered lattice was first posed by Laguës[34] in connection with the electrical conductivity of microemulsions; Laguës termed this process "stirred percolation". Druger, Nitzan, and Ratner (DNR) have[7] presented the first exactly soluble problem of this kind as a model for ionic motion in polymer electrolytes above the glass transition temperature. In the DNR dynamic bond percolation theory (DBP), the random walk was described by eq 1, a master equation for the probability $P_i(t)$ for the walker to be in site i, with time-dependent transition probability $W_{j \to i}(t)$. The $W_{i \to j}$ are determined following eqs 2 and 3. The assignment of a bond (ij) as broken or available was taken to fluctuate in time $W_{i \to j} = W(t)$, where $W(t)$ is a two-state (0 and w) stochastic process such that $\langle W(t) \rangle = wp$. At random time intervals (characterized by an average renewal time τ_R) this assignment is "renewed" throughout the lattice. This model is thus characterized by *global dynamic disorder*. These model assumptions lead to the following simple expression for the dc ($\omega = 0$) diffusion coefficient (d = space dimensionality) where $\langle r^2 \rangle_{\tau_R}$ is the mean square distance traveled by the random walker during the average renewal time τ_R.

$$D = \frac{\langle r^2 \rangle_{\tau_R}}{2d\tau_R} \tag{4}$$

The same model[9] yields for the frequency-dependent diffusion

$$D(\omega) = -\frac{1}{2d} \lim_{\epsilon \to 0+} \omega^2 \int_0^\infty e^{-i\omega t - \epsilon t} \langle r^2 \rangle(t) \, dt \tag{5}$$

the following remarkably simple result

$$D(\omega, \tau_R) = D_0 \left(\omega - \frac{i}{\tau_R} \right) \tag{6}$$

where $D_0(\omega)$ is the frequency-dependent diffusion coefficient associated with motion on the corresponding (same average bond availability p) *static* random lattice. Equation 6 provides a simple way to obtain the diffusion coefficient on the dynamically random lattice as an analytical continuation of the corresponding quantity associated with the static lattice.

This approach has been extended and applied in several ways.[10-22] In particular it has been shown[13,16] that the original formulation of this theory corresponds to the case where the lattice renewal process is associated with a Poissonian waiting time distribution $\psi(t) = (\tau_R)^{-1} e^{-t/\tau_R}$ (where $\psi(t)$ is the probability to wait an interval t between renewals). More details of this approach and its generalizations are given in the next section.

A different approach to DBP was presented[35] by Harrison and Zwanzig (HZ). In the HZ model the dynamic disorder is *local*. Each bond (ij) is taken to fluctuate between two states, broken and available, in a stochastic process which is uncorrelated with the other bonds. The master equation (1) is then rewritten in the form

$$\frac{d}{dt} \mathbf{P} = -\mathbf{W} \cdot \mathbf{P} \equiv -\sum_\alpha \sigma_\alpha(t) V_\alpha \cdot \mathbf{P} \tag{7}$$

$$V_\alpha = (|i\rangle - |j\rangle)(\langle i| - \langle j|) \tag{8}$$

$$\mathbf{P} = \sum_i P_i |i\rangle \tag{9}$$

where α denotes the bond (ij) between nearest neighbor sites i and j, and where $|i\rangle$ denotes a column vector with the ith entry equal to 1 and all others zero. Each "state" $\mathbf{P}$ of this system specifies the probability distribution of the tracer over all the lattice sites. The time-dependent hopping rate $\sigma_\alpha(t)$ across the bond α is determined by the state $\sigma_\alpha = 0$ or $\sigma_\alpha = 1$ of this bond. The probability $\phi_\alpha(\sigma_\alpha t)$ to be in the bond state

σ_α evolves in time according to

$$\frac{d}{dt} \begin{bmatrix} \phi_\alpha(\sigma_\alpha = 0,t) \\ \phi_\alpha(\sigma_\alpha = 1,t) \end{bmatrix} = \frac{1}{\tau} \begin{pmatrix} -p & q \\ p & -q \end{pmatrix} \begin{bmatrix} \phi_\alpha(\sigma_\alpha = 0,t) \\ \phi_\alpha(\sigma_\alpha = 1,t) \end{bmatrix} \tag{10}$$

Equations 7-10 define the HZ model. This problem has been solved[35,36] in the single-bond effective medium approximation (EMA) in which a single bond is assumed to fluctuate according to eq 10 in a lattice where all other lattice bonds are characterized by a uniform constant effective transition rate. The latter is determined by the usual EMA requirement that the *averaged* transition rate in this medium is equal to the predesignated effective rate. HZ thus provide an EMA solution to their dynamic percolation model which is analogous to the well-known EMA solution of the corresponding static network.[37,38] It is remarkable that their EMA result is identical to eq 6, with τ_R replaced by τ of eq 10. It should be emphasized that this simple analytical continuation rule is obtained here and in the DNR global disorder model for the same reason: The dynamic disorder is associated with a single characteristic time. It has been shown[16] that a necessary and sufficient condition for the validity of the analytical continuation rule (6) is that the velocity autocorrelation function $\langle v(o)v(t) \rangle$ of the diffusing particle in the dynamic environment is related to that $(\langle v(o)v(t) \rangle_0)$ in the static environment by

$$\langle v(o)v(t) \rangle = e^{-t/\tau} \langle v(o)v(t) \rangle_0 \tag{11}$$

(see also ref 39). In the DNR model eq 11 is satisfied exactly, while in the HZ local disorder model the single-bond EMA approximation with the bond dynamics given by eq 10 appears to imply the same damping behavior for the velocity autocorrelation function.

The HZ model was generalized by Granek and Nitzan[21] to include the possibility of many bond states so that eq 10 is replaced by a larger set of kinetic equations for the bond states. The same extended formalism makes it possible to study clusters of bonds and therefore correlations among the states of several bonds. More details on the EMA approach and its application are given below in connection with actual computations.

An interesting extension of the EMA approach in another direction was given by Zwanzig,[40] who presented an EMA solution to a model for diffusion in a dynamically disordered continuous medium. In this model the environment is made of a uniform background characterized by diffusion coefficient D_1 and spherical regions embedded in this background in which the diffusion coefficient is D_2. These spheres appear and disappear at a characteristic rate subjected to a given average concentration (or volume fraction).

In addition to these general approaches, exact solutions to models of dynamic disorder in 1d systems (of both local and global nature) are available.[41] The starting point of this approach is the 1d analog of eq 1 with stochastic transition probabilities

$$\frac{\partial P(n, t)}{\partial t} = \mu(E^+ + E^- - 2) P(n, t) + \alpha \xi^-(t)(E^+ - 1) P(n,t) + \alpha \xi^+(t)(E^- - 1) P(n,t) \tag{12a}$$

$$E^\pm f(n) = f(n \pm 1) \tag{12b}$$

where $\xi^+(t) = \xi^-(t)$ in the special case of symmetric diffusion. These are random processes taken to be Poisson white noise functions with zero mean

$$\xi(t) = \sum_{i=1}^{n(t)} \omega_i \delta(t - t_i) - \lambda \bar{\omega} \tag{13}$$

where $\bar{\omega}$ is the average of $\{\omega_i\}$ and the value of λ ensures $\bar{\xi} = 0$.

These parameters satisfy $\mu \geq \alpha\lambda\bar{\omega}$ so the transition probabilities in (1) are always positive. When the noise $\xi(t)$ is site independent, eq 12 represents global dynamic disorder (note however that this global disorder is different from the DNR model where the transition probabilities are different for different bonds but the bond renewal process was implemented globally). If $\xi_n(t)$ is site dependent, this is a local disorder model, similar to of that used by Harrison and Zwanzig. Note however that in this one-dimensional model the dynamic disorder is *site, not bond, disorder*. Hernandez-Garcia et al. derive an effective generalized master equation (with constant transition probabilities) for the averaged diffusion in the model described by eqs 12 and 13. Interestingly, the averaged equation for the global disorder models includes long-range hopping steps. In the local disorder model a regular master equation with nearest neighbor hopping (as in the original equation) is obtained. For example, for symmetric dynamic disorder ($\xi^+ = \xi^-$), the effective master equations are

$$\frac{\partial P(n,t)}{\partial t} = [(\mu - 2\alpha\bar{\omega})(E^+ + E^- - 2) + \lambda(e^{\alpha\bar{\omega}(E^+ + E^- - 2)} - 1)] P(n,t) \quad (14)$$

for global disorder and

$$\frac{\partial P(n,t)}{\partial t} = \left[\mu - \frac{\lambda}{2}(e^{-2\alpha\bar{\omega}} - 1 + 2\alpha\bar{\omega})\right](E^+ + E^- - 2) P(n,t) \quad (15)$$

for local disorder. Clearly the propagator in eq 14 includes long-range hops. A solution for a global disorder model can be obtained using a multistate version of the continuous time random walk (CTRW) formalism.[42-45]

Dynamic disorder may be thought of as induced by some external noise source. In actual applications the noise is usually associated with some internal motion(s) in the system. Thus, in the application to polymer ionic conductors, τ_R is associated with motions of the host polymer. More generally, in a system of interacting particles, each particle experiences dynamic disorder arising from its interaction with the other moving particles. Therefore all transport phenomena in many-body systems can be formulated as problems of motion in dynamic disorder.[24-26,46-49] An important issue here is the need to make the characteristic time associated with the dynamic disorder consistent with the calculated dynamics of the diffusing particles. This provides an approximate means of solving such problems.

Another important issue is the behavior of the system near the percolation threshold of the corresponding static system. Consider eq 4 for a system with $p < p_c$ (p is the bond availability, and p_c is the percolation threshold). When τ_R is long relative to the time needed for the diffusive particle to explore the finite cluster, $\langle r^2 \rangle_{\tau_R}$ becomes the mean square cluster size so that[51]

$$D(p - p_c) \sim \frac{(p - p_c)^{-(2\nu - B)}}{\tau_R} \quad (16)$$

However, the actual dependence of D on $p - p_c$ near the static percolation threshold depends on whether or not τ_R itself shows a critical behavior near the threshold.[50] Although possible implications of criticality of τ_R have been studied,[52] experiments do not show this criticality and seem to support the scaling (16).[51]

In the following two sections we describe in greater detail the models used in actual applications: the DNR and the HZ models and their generalizations.

Dynamic Bond Percolation Theory[7-11]

A useful, exact solution of a simple DBP model was given by Druger, Nitzan, and Ratner.[7-11] This most primitive DBP model[7-11] involves the following 10 assumptions: (1) There exists a periodic array of sites, on which hoppers can be present. (2) The paths (called bonds, but to be distinguished from chemical bonds) among these sites exist in only two states, open (available) with probability p, and closed (unavailable) with probability $1 - p$. (3) The probability p averaged over the entire lattice is fixed in time. (4) After a certain time interval, called the renewal time, all bonds in the lattice randomly change their state between open and closed, such that p remains constant (global renewal). (5) The renewal process occurs in equal intervals of exactly τ_R, the renewal time. (6) There are no correlations in the renewal process—that is, there is no correlation between the renewal of one bond and another bond, either in space or in time. (7) Particles hop only to nearest neighbor sites, following the master equation (1). (8) The jump rate w (eq 2) is the inverse of the hopping time τ_h, which is a constant (that is, after each interval τ_h, an ion tries to hop to a nearest neighbor site). (9) There are no correlations of the hopping particles; that is, there are no potentials acting between them, and double occupancy of sites is permitted. (10) No correlations exist between the motions of the hopper and the reassignment processes for the host bonds, except that hoppers cannot hop over bonds that are closed. The first six assumptions describe the host lattice on which hoppers are moving, and the last four describe the motion of the hoppers themselves.

The model defined by these 10 assumptions is a generalization of ordinary percolation theory[33] that takes into account the dynamic disorder of the host by permitting global reassignment of particular bonds as being open or available ($W_{i \rightarrow j} = w$) or closed or unavailable ($W_{i \rightarrow j} = 0$). If the renewal time τ_R, that describes how often individual bonds are reassigned as open or closed, is allowed to become infinite, then the dynamic percolation model becomes the standard bond percolation model, often used to describe hopping in rigid materials.

The solution of the transport problem described by this model proceeds by writing a Markovian equation of motion for probability $P^{(N+1)}(r + i)$, which is the probability for occupation of the site $r + i$ at the end of the renewal period $N + 1$. Because of the sequential nature of hopping, this can depend only on $P^{(N)}(i)$. The actual evolution equation, or Chapman–Kolmogorov equation, for the motion is then

$$P^{(N+1)}(r) = \sum_i P^{(N)}(i)P^{(1)}(r - i) \quad (17)$$

Using this equation of motion, one can derive results for the mean square displacement and determine diffusion coefficients for hoppers on the dynamically renewing lattice.[7-11]

The most straightforward analysis proceeds by using the general linear response form for the diffusion coefficient as a function of frequency for any hopping model. This form, originally derived by Scher and Lax,[53] is given by eq 5. Several important results can be derived[9] by computing the $\langle r^2 \rangle$ using the evolution equation (17):

(A) As long as neither p nor w vanishes, the motion is always diffusive for time scales long compared to τ_R—that is, mean square displacement is always proportional to total elapsed time. No percolation threshold behavior occurs. This is in contrast to static percolation problems (τ_R becoming infinite), for which p must generally exceed some threshold value, p_c, for diffusion to occur. Static thresholds for one-dimensional diffusion occur at $p = 1$, for diffusion on a square net in two dimensions, $p_c = 0.5$, and other thresholds occur for different lattices in different dimensionalities.

Qualitatively, one can understand this result quite straightforwardly: if a hopper starts to move on a lattice and encounters a blocked (unavailable) bond, its motion stops with static percolation. With dynamic percolation, on the other hand, that bond will eventually open, due to the renewal (reassignment) process of the host lattice. Therefore, for times much longer than the characteristic renewal time, no bond is ever blocked, and
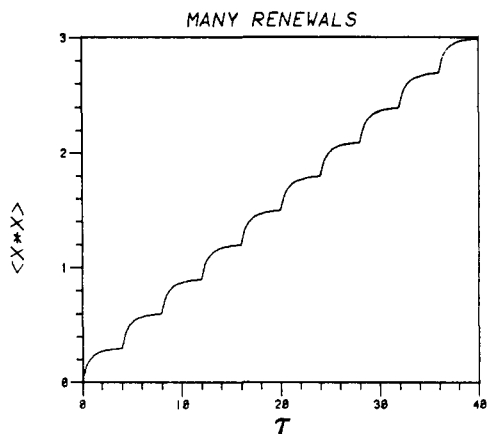
Figure 2. Mean square displacement as a function of time, for a one-dimensional dynamic bond percolation calculation, with $p = 0.2$ and $\tau_R = 20$. Note that although within each renewal period the mean square displacement becomes limited by finite boundaries, over many renewal periods the mean square displacement is linear in time, indicating diffusive behavior (from ref 7).

so the motion should be diffusive. Formally, this can be proved quite straightforwardly using the evolution equation (17).

There are then three physical limits that one might consider, relating the mean observation time t_{obs}, the renewal time τ_R, and the hopping time w^{-1}. These are

$$\text{(i)} \quad t_{obs} \gg \tau_R \gg w^{-1}$$

$$\text{(ii)} \quad \tau_R \gg t_{obs} \gg w^{-1} \qquad (18)$$

$$\text{(iii)} \quad t_{obs} \gg w^{-1} \gg \tau_R$$

Case (ii) is simply static percolation theory, since renewal occurs on a time scale longer than that of a characteristic observation. In case (iii), the assignment of any given bond as open or closed is averaged many times before a hopper attempts to move; under these conditions, the effective diffusion coefficient D_{eff} is simply $pwa^2/2d$, where a is a lattice spacing. This corresponds to simple diffusion with characteristic jumping rate pw. The most interesting regime is (i), in which renewal occurs after many jumps have been attempted but observations made only after many renewal sequences. For example, Figure 2 shows[7] the mean square displacement calculated for a one-dimensional dynamic bond percolation problem, for $p = 0.2$, substantially below the static threshold, with $\tau_{ren} = 20w^{-1}$. Note that over each small subinterval, of length 4, the hopper, while beginning with diffusive motion for short times, has reached a point at which its mean square displacement is effectively constant; that is, the hopper has essentially explored the connected network of local bonds, and its mean square displacement can no longer increase because it has saturated the connected network. After renewal occurs, however, a different network of connected bonds becomes available to the hopper, and it can move further. After each renewal, the same opening up of a new cluster occurs, and over long periods of time, the motion is clearly diffusive.

This result occurs in regime (i) for any values of p, w, and τ_R in any spatial dimension.

(B) The diffusion coefficient is related to the mean square displacement within a renewal time, denoted $\langle r^2 \rangle_{\tau_R}$, by eq 4. If the renewal time is sufficiently long that the particle's motion within that renewal epoch covers a connected cluster completely, so that the numerator of eq 4 becomes a constant related to the size of the local connected cluster, then the diffusion coefficient is inversely proportional to the renewal time. Under these conditions the diffusion, and therefore the conductivity, is determined largely by relaxation or renewal processes of the host.

(C) The analytic continuation result (eq 6) holds, relating the diffusion coefficient as a function of frequency for the problem with renewal to the diffusion coefficient on a static lattice. This
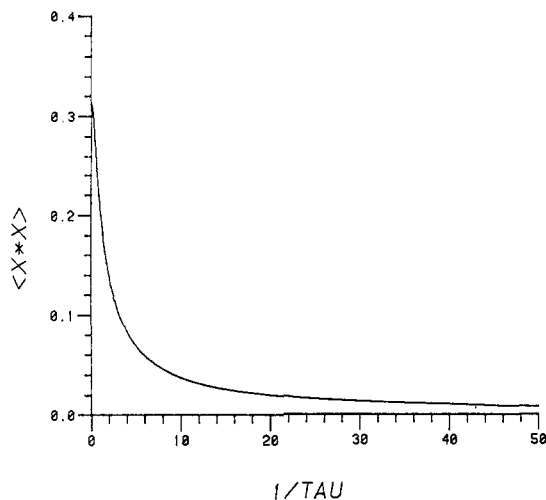

Figure 3. Mean square displacement as a function of inverse renewal time, for the same conditions as for Figure 2. For longest renewal times, mean sqare displacements become asymptotically fixed by the average connected domain size (from ref 7).
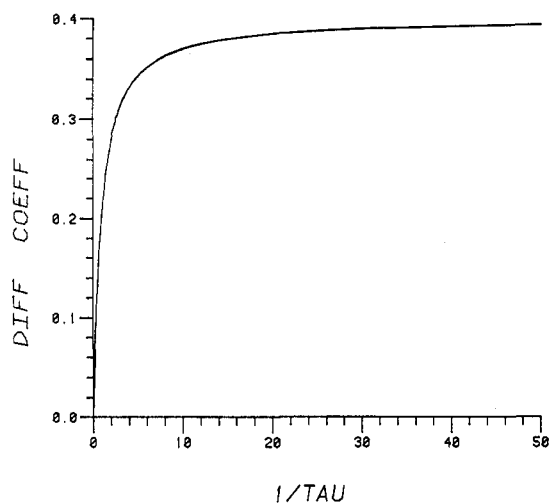

Figure 4. Diffusion coefficient as a function of inverse renewal time, for the same conditions as for Figure 2. Notice that the diffusion coefficient increases as renewal time gets shorter, finally becoming asymptotically flat in the limit of short renewal times (from ref 7).

very useful formal result permits information gained (from simulation, experiment, or theory) for static percolation to be used to describe dynamic percolation.

(D) Using eq 6 and the fact that mean square displacement at very short time is independent of renewal, one can derive a general result for the mean square displacement $\langle \vec{r}^2 \rangle$ in terms of $\langle \vec{r}^2 \rangle_0$, the displacement without renewal, as[15]

$$\langle \vec{r}^2 \rangle(t) = \langle \vec{r}^2 \rangle_0(t) e^{-\lambda t} + \lambda \int_0^t d\xi \, (2 + \lambda t - \lambda \xi) e^{-\lambda \xi} \langle \vec{r}^2 \rangle_0(\xi)$$

$$(19)$$

This result permits direct computation of a mean square displacement, knowing only the results for the static lattice and the renewal time, $\lambda^{-1} = \tau_R$.

As an illustration of the renewal time dependence for values of p below the percolation threshold, Figures 3 and 4 show the mean square displacement and the diffusion coefficient as a function of inverse renewal time, for $p = 0.05$. Note that, in Figure 3, the actual mean square displacement within a renewal epoch, the numerator of eq 4, is maximal at the longest renewal time, since the particle has time to explore a larger region of the lattice. Nevertheless, when the diffusion coefficient D is computed (essentially by multiplying the two axes of Figure 3), Figure 4 shows that D increases monotonically with increase in renewal rate (decrease in renewal time).
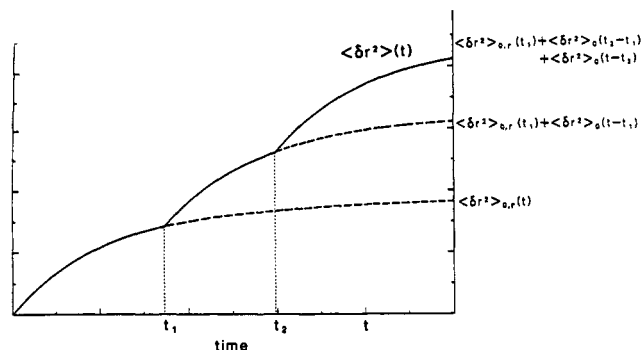
Figure 5. Mean square carrier displacement for a specified number of renewal events; this general continuous increase with renewal characterizes a growth law, whose mathematical description generalizes the simple dynamic percolation model (from ref 16).

Generalized Dynamic Disorder Hopping Models[15,16]

Many of the results just demonstrated for the simplest DBP model hold more generally. In particular, consider transport characterized by the behavior of Figure 5, that shows general growth in an observable, here written as a mean square displacement, as a function of time. Mathematically, the behavior in Figure 5 can be written as[15,16]

$$F(T) = g(\tau_0) + \sum_{i=1}^{N} f(\tau_i) \qquad (20)$$

Here $F(T)$ is an unspecified observable, and the times T_1, T_2, T_3, and so forth are times during the period $(0,T)$. Defining, then, $\tau_i = T_{i+1} - T_i$, the growth law given by eq 20 corresponds to that in Figure 5. Here the τ_i are the times between successive renewal events, and $g(0) = f(0) = 0$; $f(T)$ is the growth in $F(T)$ that would be observed without further renewal starting from a previous renewal at time $T = 0$, and $g(T)$ is the corresponding growth that would be observed without further renewal from the arbitrary time $T_0 = 0$ for which random renewal had been an ongoing process. With this specification of a generalized growth law process, the important results just stated continue to hold. In particular, some of the assumptions stated above can be relaxed as follows:[15,16]

(1) Periodic array of sites is not necessary. The important results in eqs 4, 6, and 19 hold off the lattice as well as on the lattice. Consequently, the condition that hoppers jump to nearest neighbor sites can also be relaxed without significant change.

(2) A generalized distribution of renewal times, subject to characteristic statistics, will not change the results significantly. In particular, and most importantly, the numerator and denominator of eq 4 must be averaged over the distribution of renewal times, as must the renewal frequency λ.

(3) Temporal correlations between the renewal events can be handled.

(4) The renewal concept can be used to characterize motion in dynamically disordered media, whether that motion occurs by hopping, by a ballistic motion, or by band conductivity. In particular, quantum mechanical behavior can be straightforwardly included in the generalization of the model.[15,16,22]

One way to understand the results of this section is in terms of a transport process involving two characteristic times: one time corresponds to local motion, and the second corresponds to motion, on a longer time scale, that yields reinitialization of the distribution of transporting particles. A number of other similar two-time models for transport are current in the literature.[54] The generality and precision of the dynamic disorder hopping models, such as the ones discussed here, make them attractive both for understanding and for analysis of real situations.

To demonstrate the general scope, consider the linear response expression for the k,l spatial component of the frequency-
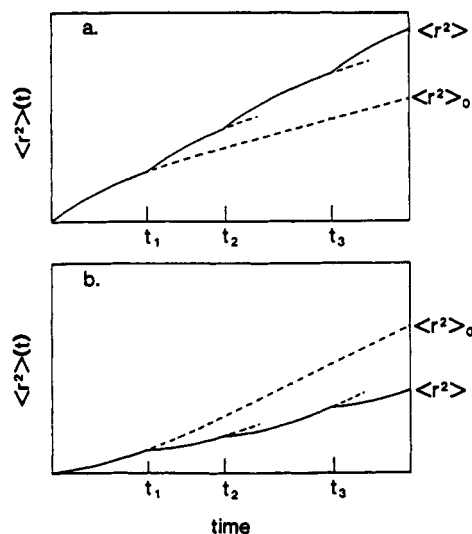

Figure 6. (a) Schematic renewal process, showing mean square displacement as a function of time following the general growth law of Figure 5 for diffusionlike situations, in which the mean square displacement is increased by the renewal process. Part b shows precisely the opposite behavior, corresponding to (for example) ballistic transport within each renewal time; here the renewal process reduces the mean square displacement. General analytic continuation results discussed in the text hold for both sorts of growth law dynamics (from ref 15).

dependent conductivity tensor[55]

$$\sigma_{kl}(\omega) = \lim_{\epsilon \to 0} \int_{-\infty}^{0} \exp\{(\epsilon + i\omega)\tau\} K_{kl}(\tau) \, d\tau \qquad (21)$$

where the temperature-dependent kernel K_{kl} is, in turn,

$$K_{kl}(\tau) = \int_{0}^{\beta} d\nu \langle J_k(0) J_l(\tau - i\hbar\nu) \rangle \qquad (22)$$

Here $\beta = k_B T$ and J_k is the kth component of the current density operator. Form 21 follows from the linearization of the equation of motion for the density operator; the convergence parameter ϵ arises, formally, from the inclusion of a relaxation term $-\epsilon(\rho - \rho_{eq})$ in the equation for the time derivative of the density matrix. This term describes linear relaxation toward equilibrium, with ϵ a rate constant.

If the thermally averaged velocity correlation function obeys eq 11, then the analytic continuation formula (eq 6) follows directly from the formal linear response results, eqs 21 and 22, in both the quantum mechanical and the classical regime.[15,16] This yields a formal understanding of the relationship of the renewal process and the time evolution of the system density matrix. The renewal process is an extra relaxation pathway, and the renewal rate λ, just like ϵ, combines additively to the decay rate of the system toward equilibrium. Within the original DBP model involving global renewal at all places in the ensemble, the relaxation is uniform throughout the system, and the analytic continuation form follows exactly from eq 11. For spatially local renewal models such as the HZ model, the analytic continuation formula is valid only in the lowest order effective medium approximation.

Similarly, when the renewals are temporally correlated, deviations from simple exponential decay of the correlation function can be observed, and therefore the analytic continuation formula does not hold exactly.[16]

The analytic continuation formula (eq 6), and from it the relationship between mean renewal time and diffusion coefficient (eq 4), can therefore be used to describe diffusion of quantum and classical particles, since they can be derived from the general linear response (eq 21) if the correlation function decays following eq 11. It is useful to discuss the implications of this for several sorts of motion. For example, Figure 6 shows two sorts of behavior characterized by renewal, or reinitialization. In Figure 6a, the motion between renewal times is that characteristic of diffusion

below the percolation threshold, with the mean square displacement behaving concave downward, and tending toward a limit $\langle r^2 \rangle_0 = $ constant. When renewals occur, the reinitialization results in a higher local curvature and a higher initial slope, such that the mean square displacement over times long compared to the renewal time is *increased* by renewal. Conversely, if the process is ballistic, or coherent, for short times, as shown in Figure 6b, reinitialization results in a smaller local slope and therefore reduction of $\langle r^2 \rangle$ compared to $\langle r^2 \rangle_0$. This characteristic shape defines bandlike motion, with the renewal process here corresponding to a scattering.

Formally, one can begin from the Scher–Lax expression

$$D_0(\omega) = \frac{1}{2d}(i\omega)^2 \int_0^\infty \exp(-i\omega t)\langle r^2\rangle_0 \, dt \qquad (23)$$

that relates the diffusion coefficient in the absence of renewal to the mean square displacement in the absence of renewal. If this equation is integrated by parts, and then the analytic continuation form of eq 6 is inserted, one obtains

$$\frac{d}{d\lambda}\text{Re}[D(\omega)] = -\frac{1}{2d}\int_0^\infty te^{-\lambda t}\cos\omega t \frac{d^2}{dt^2}\langle r^2\rangle_0 \, dt \qquad (24)$$

for the dependence of diffusion coefficient, in the renewing system, on renewal time. Then if the short time behavior of $\langle r^2\rangle(t)$ is concave downward for short times, corresponding to hopping-like transport, the right-hand side will be positive, and renewal will increase the diffusion coefficient. This is precisely what is seen in Figure 6a. Conversely, in coherent-like transport, $\langle r^2\rangle(t)$ is concave upward, and the derivative is negative; under these conditions, scattering impedes transport for low frequencies (Figure 6b).

The form of eq 4, relating mean square displacement, renewal time, and diffusion coefficient, can then be used to characterize diffusive behavior in three regimes, denoted by eq 25:

$$\text{(i)} \qquad \langle r^2 \rangle_{\tau_R} \sim \tau^2$$
$$\text{(ii)} \qquad \langle r^2 \rangle_{\tau_R} \sim \tau$$
$$\text{(iii)} \qquad \langle r^2 \rangle_{\tau_R} \sim A^2 \qquad (25)$$

Case (i) corresponds to ballistic or coherent motion, such as that of electrons in good conductors. Under these conditions, renewal impedes conduction, and from eq 4 the diffusion coefficient (and therefore the conductivity) is proportional to the renewal time. This is the Drude-like limit of conductivity, in which increased scattering time leads to increase in conduction and represents a characteristic quantum behavior. For hopping-like motion (of ions, electrons, or neutrals), the mean square displacement as a function of time within a renewal epoch will have different forms, depending on whether one is above or below the percolation threshold. Above the percolation threshold, the behavior is diffusive and characterized by (ii); it then follows from eq 4 that the diffusion coefficient is independent of renewal time and is in fact essentially the diffusion coefficient that holds within a renewal epoch. The existence of renewal does not change the effective motion in any substantive way. Below the percolation threshold, on the other hand, a mean square displacement within a renewal epoch is characterized by (iii), with A a characteristic dimension of a region connected by permitted bonds. Under these conditions, it follows from eq 4 that the diffusion coefficient is inversely proportional to the renewal time. This is exactly the limit that holds in most polymer electrolytes, in which the conductivity is directly proportional to the rate of renewal.

Therefore the renewal concept is a powerful way to deal with diffusion and conductivity of noninteracting particles, be they quantum or classical, charged or uncharged, ballistic or diffusive, above or below the percolation threshold. The generality of the model makes it potentially useful in many applications. A recent example is the study of evaluation of reaction patterns in condensed media.[55a] The characteristic two-time behavior of the dynamic disorder hopping model then manifests itself in terms of diffusivity within the cluster, and a rate of renewal of the cluster. While these results are only slightly modified by temporal correlation of the renewal process,[16] interactions among the particles being transported result in substantive change in the transport process.

Effective Medium Theory

A very useful approach to motion in dynamically disordered systems is the dynamic effective medium theory DEMA.[35] In what follows we outline a generalization of this approach due to Granek and Nitzan.[21]

The starting points of this approach are eqs 7–10. In the Granek–Nitzan generalization eq 10 is replaced by its many-bond state analog

$$\frac{\partial}{\partial t}\phi_\alpha(\sigma,t) = \sum_\sigma \Omega_\alpha(\sigma,\sigma')\phi_\alpha(\sigma',t) \qquad (26)$$

Here $\phi_\alpha(\sigma,t)$ is the probability that the bond $\alpha \equiv (ij)$ between nearest neighbor sites i and j is in state σ (which characterizes the instantaneous transition rate through this bond (cf. eq 7).

The joint probability distribution $f(\mathbf{P},\sigma,t)$ to find the walker distributed according to $\mathbf{P}$ and the bonds in state $\sigma = (\sigma_1, \sigma_2, ...\sigma_\alpha, ...)$ at time t satisfies the Liouville master equation

$$\frac{\partial f}{\partial t} = \frac{\partial}{\partial \mathbf{P}}(\mathbf{W}\cdot Pf) + \Omega f \qquad (27)$$

where, since all the bonds fluctuate independently,

$$\Omega = \sum_\alpha \Omega_\alpha \qquad (28)$$

Here Ω_α is the *matrix* of bond transition rates defined in eq 26. The partial average

$$P(\sigma,t) = \int dP' \, Pf(P',\sigma,t) \qquad (29)$$

satisfies the equation

$$\frac{\partial P(\sigma,t)}{\partial t} = -W\cdot P(\sigma,t) + \Omega P(\sigma,t) \qquad (30)$$

Note that $P(\sigma,t)$ is a vector in site space which also depends on the collective state σ of the bonds. Equation 30 gives the time evolution of P in terms of two contributions, one arising from the evolution of the walker state, the other from that of the bond states. The initial condition for $f(P,\sigma,t)$ is taken to be

$$f(P,\sigma,t = 0) = \delta(P - P_0)\rho(\sigma) \qquad (31)$$

whence

$$P(\sigma,t = 0) = P_0\rho(\sigma)$$

where $\rho(\sigma)$ is the equilibrium distribution of bond states, i.e.

$$\rho(\sigma) = \prod_\alpha \rho_\alpha(\sigma_\alpha) \qquad (32a)$$

$$\sum_{\sigma'} \Omega_\alpha(\sigma\sigma')\rho_\alpha(\sigma') = 0 \qquad (32b)$$

To solve eq 30, we first write the solution in terms of its Laplace transform $(t \rightarrow z)$:

$$P(\sigma,z) = g(\sigma,z)\cdot P_0 \qquad (33)$$

with

$$g(\sigma,z) = [z1 + W(\sigma) - \Omega1]^{-1}\rho(\sigma) \qquad (34)$$

($\Omega 1$ is a direct product of a unit operator in the site space and the operator Ω which operates in the space of the bonds.)

Averaging now over bond states leads to

$$\langle P(z) \rangle = \sum_\sigma P(\sigma, z) = g(z) \cdot P_0 \qquad (35)$$

$$g(z) = \sum_\sigma g(\sigma, z) \qquad (36)$$

We now assume that $g(z)$ can be written in the form

$$g(z) = (z1 + W_m(z))^{-1} \qquad (37)$$

where

$$W_m(z) = \psi(z) \sum_\alpha V_\alpha \qquad (38)$$

Equations 37 and 38 describe the averaged propagator for the random walk in terms of a constant, uniform transition probability $\psi(z)$ which is yet to be determined. In the (single bond) EMA we introduce a medium consisting of one fluctuating bond imbedded in this effective medium, so that the transition operator W becomes

$$W = \psi(z) \sum_{\alpha \neq 1} V_\alpha + \sigma_1 V_1 = W_m + (\sigma_1 - \psi(z)) V_1 \qquad (39)$$

and bond fluctuations occur only for bond 1

$$\Omega = \Omega_1 \qquad (40)$$

The effective rate is then determined self-consistently by using eqs 39 and 40 in eq 34 and then performing the summation (36). If some technical details that may be found in ref 15 are skipped, this procedure leads to the requirement that the determinant of the following matrix M of order n, the number of bond states, vanish

$$M_{1j} = \sigma_j - \psi \qquad j = 1, ..., n \qquad (41)$$

$$M_{nj} = 1 + (\sigma_j - \psi) h_j \qquad n > 1, j = 1, ..., n \qquad (42)$$

where h_j are scalars defined from

$$V \cdot H^{(j)} \cdot V = h_j V \qquad (43)$$

$$H^{(j)} = [(z + \lambda_j)1 + W_m]^{-1} \qquad (44)$$

and where λ_j are the eigenvalues of the bond transition matrix $\Omega_\alpha(\sigma', \sigma)$ (with $\lambda_l = 0$ corresponding to the equilibrium distribution ρ_α).

The equation

$$\det|M| = 0 \qquad (45)$$

now yields the desired effective medium rate ψ. Before describing how these formal results may be applied to actual systems, we note that the z dependence of the resulting solution $\psi(z)$ on the bond dynamics enters via the combination $z + \lambda_j$, or $(\omega - i\lambda_j; \omega = -iz), j = 2, ..., n$. For the case $n = 2$ (eq 10) there is only one characteristic time for the bond dynamics and eq 6 is regained.

This approach may be generalized further by considering a cluster of bonds rather than a single bond. "Bond states" σ_α are now replaced by "cluster states", each cluster state is associated with a set of transition probabilities through the bonds associated with this cluster. The procedure continues in much the same way as before, and the final result is again expressed in terms of combinations of the form $\omega - i\lambda_j$ where λ_j are now eigenvalues of the matrix Ω which determine the transitions between different *cluster states*.

As an example of this method, consider a dynamically disordered $2d$ square lattice where two different dynamical processes control the bond state. These two processes are depicted in Figure 7. Clearly the process shown in Figure 7a is that described by eq 10. The process shown in Figure 7b is a bond
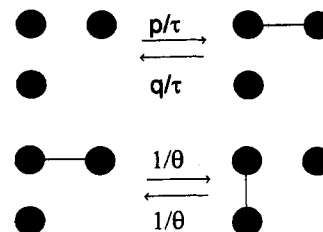

Figure 7. Two different bond dynamical processes: the renewal bond from open to closed, following the generalized behavior of eq 10, and the "flip" of a bond, changing the particular geometry of available bonds but leaving the total number unchanged.
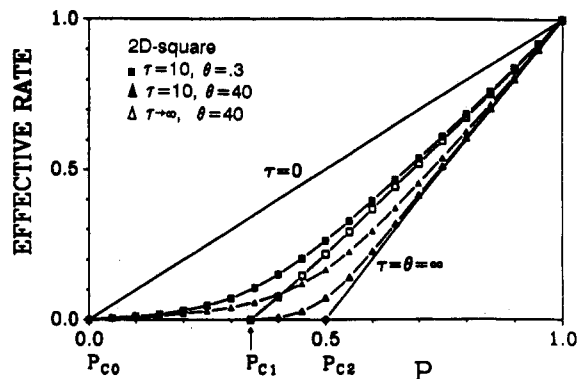

Figure 8. DC effective medium rate for combined processes of renewal and exchange. The rates are calculated for different values of the renewal and exchange processes of Figure 7. The straight line with no markings is for very fast renewal. The open squares have $\theta = 0.33$, the hollow triangles have $\theta = 40$, and both of these have $1/\tau = 0$. The filled squares have $1/\tau = 0.1$, $\theta = 0.33$; the filled triangles $1/\tau = 0.1$, $\theta = 40$. Note the three different percolation thresholds that are observed (from ref 21).

flip that does not change the overall number of available bonds. The bond dynamics are described by considering the cluster of two bonds shown in Figure 7b. This cluster can be in four states, 00, 10, 01, and 11, when 0 denotes a broken bond and 1 an available one. Equation 26 for the present case is

$$\frac{\partial}{\partial t} \begin{pmatrix} \phi(0,0) \\ \phi(1,0) \\ \phi(0,1) \\ \phi(1,1) \end{pmatrix} =$$

$$\begin{pmatrix} -\dfrac{2p}{\tau} & \dfrac{q}{\tau} & \dfrac{q}{\tau} & 0 \\ \dfrac{p}{\tau} & -\left(\dfrac{1}{\tau}+\dfrac{1}{\theta}\right) & \dfrac{1}{\theta} & \dfrac{q}{\tau} \\ \dfrac{p}{\tau} & \dfrac{1}{\theta} & -\left(\dfrac{1}{\tau}+\dfrac{1}{\theta}\right) & \dfrac{q}{\tau} \\ 0 & \dfrac{p}{\tau} & \dfrac{p}{\tau} & -\dfrac{2q}{\tau} \end{pmatrix} \begin{pmatrix} \phi(0,0) \\ \phi(1,0) \\ \theta(0,1) \\ \theta(1,1) \end{pmatrix} \quad (46)$$

The effective transition rate obtained for this model is shown in Figure 8 as a function of the fraction p of available bonds. If both processes shown in Figure 7 were frozen ($\tau, \theta \to \infty$), we get the EMA result for a square random bond lattice with a percolation threshold at $p_c = p_{c2} = 0.5$. When τ is infinite and $\theta \to 0$, we get a new percolation threshold at $p_c = p_{c1} \simeq 0.34$. When τ is finite, the macroscopic diffusion rate is of course non-zero for all $p > 0$.

Another application of this formalism is for random walk of interacting particles.[24-26,46,47] This is an example of internal noise where the dynamic disorder experienced by a tracer particle arises from its interaction with other moving particles. DEMA provides a way to treat this problem with the effective medium approximation provided that a proper closure relation can be found which associates the characteristic time, τ, of the dynamic disorder with the motion under consideration (namely τ in, e.g., eq 10
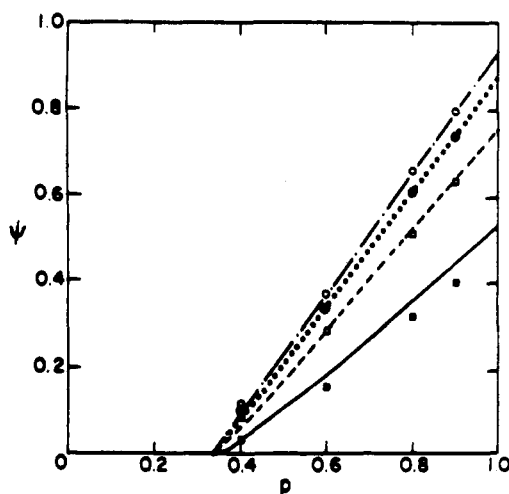
Figure 9. Effective medium hopping rate with differing assumed models for diffusion of particles with blocking interactions on the 3d cubic lattice with static bond disorder. The different curves show results for different coverages: the full line was coverage 0.4, the dashed line coverage 0.2, the dotted line coverage 0.1, and the dash–dotted line coverage 0.05. The points show results of Monte Carlo simulation, and the lines result in the approximation of eq 47 (from ref 26).

should be expressed in terms of the effective medium hopping rate ψ). While no explicit general relations are available, several approximations are possible as discussed by Granek and Nitzan.[24] In Figure 9 we show a comparison of the result from such a calculation[26] for the diffusion of particles with blocking interactions only (double-site occupancy forbidden) on a 3d cubic lattice with static bond disorder. Shown is the calculated effective hopping rate as a function of p, for different concentrations of hopping, self-avoiding particles. The postulated relation between τ and the dynamics of the hopping particles was

$$\tau^{-1} = (Z - 1)\frac{p - p_c}{1 - p_c} \tag{47}$$

where Z is the lattice coordination number. The rationale for this choice is[24] that the dynamic disorder for the present example is associated with density fluctuations of background particles on the sites neighboring the tracer. These density fluctuations are associated with the *chemical* diffusion coefficient, which for self-avoiding but otherwise noninteracting particles is equal to that in a system of completely noninteracting particles, and therefore is associated with the effective hopping rate $\psi = (p - p_c)/(1 - p_c)$ for a single particle moving on a statically disordered lattice. The factor $Z - 1$ in (47) results from the fact that the lifetime of a blocking particle on a nearest neighbor to the tracer particle is associated with jumps into and out of its $Z - 1$ nearest neighbors (not including the occupied tracer site). As seen in Figure 9, this formalism with this choice of dynamic disorder time gives a good approximation (within EMA) to the coverage-dependent diffusion on the disordered lattice. An alternative choice, $\tau^{-1} = (Z - 1)p$, based on the mean field approximation, was also shown[26] to give a reasonable approximation.

Application of DEMA to polymer dynamics was recently presented by Loring and co-workers.[48,49,56] They focus on a single flexible linear polymer molecule which undergoes slithering along its contour (to mimic reptation) together with stochastic independent bead jumps (the Stockmayer "kink-jump" algorithm).[57] The effect of the surrounding molecules is represented by the fact that a fixed fraction of the beads are immobilized by obstacles (presumably associated with entanglements) which appear and disappear with a characteristic rate. The calculation of the dynamical properties of this model was shown to be equivalent to the calculation of the propagator for a random walk on a dynamically disordered lattice similar to that introduced by Harrison and Zwanzig. The model can be made self-consistent[50]by

taking the obstacle relaxation time to be the relaxation time associated with the slowest internal modes of the system. However, caution needs to be exercised in carrying out such a closure (as in the Granek and Nitzan application to diffusion of interacting particles) because of the inherent non-Markovian nature of this motion.[58,59]

Applications to Elastic Properties

In the original introduction of DBPT, the model was designed to account for the fact that the charge carrier's motion in a disordered host polymer environment is (as observed experimentally) strongly dependent on the dynamics of the host, represented in the model by the renewal time τ_R. On a somewhat more fundamental level one would like to associate this characteristic time for local segmental motion of the polymer host with its elastic properties.

A simple model which makes it possible to associate τ_R with the viscosity η was proposed[27] by Nitzan, Granek, and Ratner. In this model τ_R is associated with the relaxation of local distortions in the dynamic random network representing the polymer host, and a simple argument leads to the following relation between τ_R and the shear viscosity

$$\eta = \frac{mc^2 p}{a^3}\tau_R \tag{48}$$

Here m is a typical segment mass, c the speed of sound in the polymer, p the fraction of intact bonds (so $1 - p$ is related to the free volume), and a is the typical linear segment size. Together with eq 4 for the ion diffusion coefficient D and with the Stokes–Einstein relation between D and the conductivity σ

$$\sigma = \frac{ne^2 D}{kT} \tag{49}$$

(where n is the density of *mobile* charge carriers), this leads to a simple Walden-type relation between σ or D and n. (Note that deviations from the Walden behavior are expected because the number of mobile charge carriers (e.g. unpaired ions) may change with temperature.)[60]

A more sophisticated approach to obtaining viscoelastic properties from DBPT was recently described by Granek.[61] He considers a random spring network of the kind studied before by Alexander, Orbach, and their co-workers[62] and introduces dynamic randomness by allowing each spring frequency to fluctuate between zero and a finite value ω. This model is solved within the DEMA and yields a generalization of the phonon–fracton theory of Alexander and Orbach to the case of dynamic disorder.

Granek and Cates[63] have examined the problem of stress relaxation in living polymers using a Poisson renewal model; they deal with polymers that can break and recombine on the time scale of their reptation, or even Rouse-like regimes. This work demonstrates quite clearly the ability of renewal models to deal with relaxation, as well as transport, properties in complex polymeric systems.

Dynamic Percolation Models in Polymer Ionics

The application of the dynamic percolation model to the understanding of polymeric ionic conductors has been discussed extensively elsewhere[1,8,10,18–22] and alluded to several times in the early sections of this paper. Polymer electrolytes conduct ions only above their glass transition temperature, T_g. A number of early experimental investigations[1,64] showed direct correlations between the conductivity and the physical properties of the polymer electrolyte. If interionic correlations are ignored, so that the diffusion coefficient is proportional to the conductivity, then the

Walden-like or Stokes–Einstein relationship

$$D\eta = \text{constant} \tag{50}$$

quantifies the relationship between the viscosity η and the diffusion coefficient. By and large, polymer electrolytes fit eq 50 rather well, though it is important to use the microviscosity, which is a measure of the local physical relaxation, rather than the shear viscosity which, for a polymer, can be determined by entanglements.[65]

Empirically, the viscosity of glass-forming materials, including glass-forming polymers, in the range above the glass transition temperature fits the Doolittle result

$$\eta = \eta_0 \exp(B/T - T_0) \tag{51}$$

where B is a pseudoactivation energy and T_0 is a temperature, called the equilibrium glass transition temperature, that is substantially below the kinetically observed glass transition temperature (normally by about 50 K). By combining eqs 50 and 51, we obtain

$$D = D_0 \exp(-B/T - T_0) \tag{52}$$

relating the diffusion coefficient and the temperature. All these results follow from empirical observations, quite apart from any modeling.

The Walden relationship of eq 51, however, is highly reminiscent of the DBP result, especially in limit (i) of eq 18. That is, the viscosity is proportional to the renewal time, and the diffusion coefficient is proportional to the inverse of the viscosity. This relationship between the microscopic relaxation processes of the material and its macroscopic transport processes provides an important link between the observed conductivity of polymer electrolytes and their microscopic relaxation properties. It is on this basis, in fact, that applications of the DBP model to polymer electrolytes were originally based.

The DBP model has been used to discuss the frequency-dependent conductivity, the dielectric response, and the temperature dependence of polymer electrolytes.[7–22] Perhaps more importantly, it has been used to suggest design criteria for preparing better electrolytes: increased renewal rates, corresponding to decreased glass transition temperatures, should result in higher diffusion coefficients and therefore in higher conductivities. On the basis of these ideas, Shriver, Allcock, and co-workers[66] prepared phosphazene-based polymer electrolytes, which exhibited both the lowest T_g (and therefore the fastest renewal rates) and the highest room-temperature conductivities of any polymer electrolyte materials then known. Very recent work from the Northwestern group[67] has used microwave conductivity measurements on both polymer electrolyte materials and the parent polymers to obtain information both on the renewal time itself and on the relationship between the glass transition relaxation in the parent polymer and the conductivity of the electrolyte. Figure 10 shows conductivity plotted in reduced coordinates (the temperature axis scaled by the glass transition temperature, and the conductivity and glass transition relaxation both plotted against this reduced scale). It is clear from this graph that there is a very close correlation between diffusivity on the one hand and the glass transition relaxation on the other. The glass transition relaxation is thought to describe the local segmental relaxation of the polymer host; it is precisely this that correlates with the renewal time.

The renewal time is best thought of as describing the local structural relaxation of the polymer. One would expect the renewal time to increase substantially with salt concentration (due to transient cross-linking of the polymer), to decrease with increase in temperature, to scale essentially like the local viscosity, and to be largely independent of polymer chain length after sufficient length to achieve local entanglement. The dynamic
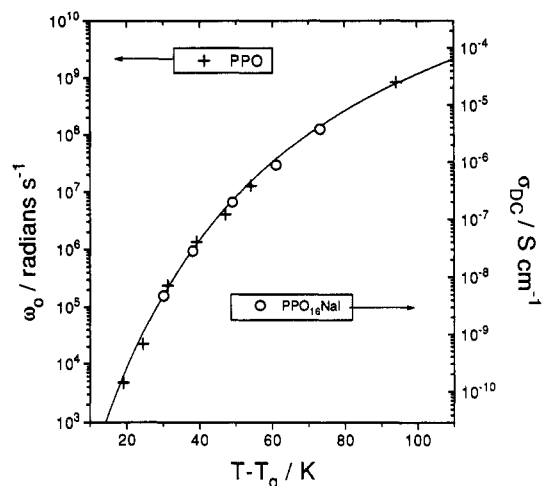

Figure 10. DC conductivity of the polymer electrolyte poly(propylene oxide)$_{16}$·NaI plotted against reduced temperature (T_g is the measured glass transition temperature). Also plotted is the maximum frequency ω_0 for the so-called α-relaxation (glass transition relaxation) for the parent PPO host. The very similar temperature dependences of the physical relaxation and the conductivity indicate the dependence of ionic diffusion on polymer relaxation time, as suggested by the result of eq 4 (from ref 67).

percolation model then provides a theoretical understanding of the mobility, or diffusivity, of ions in the polymer electrolyte materials.

Several simulations, and interpretations, have suggested that a number of transport processes in both static and dynamic disordered materials depend on two time scales, the first corresponding to hopping, the second to reinitialization or reorganization. The DBP model, by including this two time scale idea, provides a convenient language to interpret diffusion in a number of solid electrolyte materials.

It is important to remember that the dynamic percolation model describes mobility, or diffusivity, rather than conduction. The conductivity is a collective property of all the ions, and in concentrated electrolytes (polymeric or small-molecule solvents), the interionic correlations result in substantial changes from an independent particle conduction picture. Indeed, correlation effects manifest themselves in two ways: the tracer diffusion coefficient is substantially modified by ionic correlations from the value it would have in the absence of such correlations, and the conductivity diffusion coefficient can differ substantially from the tracer, again due to correlations (in this case, multiparticle correlations). The understanding of conduction in polymer electrolytes on a quantitative basis, then, requires going beyond the simple dynamic percolation model and including the effects of interionic correlations. Recent calculations utilizing both molecular dynamics[68a] and Monte Carlo simulations,[68b,c] in addition to experimental work based on Raman spectroscopy demonstrating temperature dependencies of ion pairing and clustering,[68d,e] illustrate the importance of these correlation effects in determining the conductivity of real polymer electrolyte materials.

Polymeric materials, and other disordered media, including separation membranes and mixed membranes, can exhibit electronic charge-transfer phenomena that can be "gated", or controlled, by the motion of the ionic countercharges. As part of their extensive and important analysis of coupled charge and diffusion processes in electrochemical systems, Saveant and his collaborators[70] have completed simulations on electron hopping coupled to the physical motion of charge carriers. This is a generalization of the Dahms–Ruff treatment and is relevant for considerations of electronic motion in redox polymers.[71] They find that the mean field limit for bounded diffusion is reached when the rate of physical motion exceeds that of electron hopping,

and the range of this physical motion is sufficiently great to overcome interactions among neighboring redox molecules.

Remarks

Percolation processes involve transport in heterogeneous materials and structures. The dynamic percolation model deals with situations in which the structure is not only statically but also dynamically disordered. Under these conditions, the rate of transport can depend on both the average structure of the material and the dynamical evolution of that structure. In glass-forming materials above their glass transition temperature, for example, the excursion from the glass transition temperature changes the nature of the structural disorder, and therefore the transport.

The dynamic percolation model is the simplest approach for understanding how transport, including diffusion and conductivity, occurs in these systems. As chemists focus more attention on polymeric, glassy, molecular, and heterogeneous materials, the concepts involved in this model will become even more relevant. The notion of transport determined by at least two characteristic times (one involving local motion, the other involving structural relaxation) seems to be an important one in a very large number of condensed-phase transport processes, including structure and diffusion in microemulsions,[73] coupled electron/ion motion and physical displacement/charge hopping in redox polymers,[69] and ionic conductivity in polymer electrolytes.

Acknowledgements

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