Dynamic bond percolation theory: A microscopic model for diffusion in dynamically disordered systems. I. Definition and one-dimensional case

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A dynamic bond percolation model is defined and studied. The model is intended to describe diffusion of small particles (ions, electrons) in a medium which is statistically disordered (as in ordinary bond percolation), but which is also undergoing dynamic rearrangement processes on a timescale short compared to the observation time. The model should be applicable to polymeric solid electrolytes, where the orientational motions of the polymer (which are responsible for configurational entropy) cause the dynamic motion of the medium (polymer) in which the small particles (alkali ions) diffuse. The model is characterized by three parameters: an average hopping rate w which appears in the master equation for hopping, a percentage of available bonds f, and a mean renewal time $\bar{\tau}_{\text{ren}}$ for dynamic motion of the medium to rearrange the assignments of closed and open bonds. We show that the behavior is *always* diffusive for observation times long compared to $\bar{\tau}_{\text{ren}}$, in agreement with experiment on polymeric solid electrolytes. We also derive a closed-form expression for the diffusion coefficient. For observation times smaller than the renewal time there is no diffusion, again in accord with the behavior of polymeric solid electrolytes below the glass transition temperature. The diffusion coefficient is a monotonically increasing function of the inverse renewal time and hence of the free volume, the configurational entropy, and the temperature.

I. INTRODUCTION

Percolation theory is extremely useful in understanding transport processes in disordered media, and has been recently used in the interpretation of the free-volume behavior of transport properties of several disordered materials (polymers, molten salts).[1] Both bond percolation and site percolation models are usually used to discuss transport in a rigid, but disordered, material.[2] There are many experimental systems, however, in which the structure of the host material is itself undergoing change at the same time that transport is occurring. A simple case is afforded by a micelle in which one might be concerned with ionic or electronic motion between the center and the periphery, while the micellar structure itself is changing, both through wagging of the molecular chains about the center and (possibly) through molecular addition and separation.[3] Another example might be diffusion of solvent particles in an emulsion. An especially important example is that of ionic diffusion in soft polymeric solid electrolytes. In poly-(ethylene oxide)·NaSCN, for instance (called PEO·NaSCN henceforth), the Na^+ are largely tetrahedrally coordinated by polyether oxygens, but at the same time that Na^+ are hopping from one fourfold coordination site to another, the oxygens themselves, along with the polymeric backbone, are undergoing large-amplitude wagging and even diffusive motions.[4–9]

In contrast to the case, for instance, of ion-conducting or electron-conducting glasses, in which the diffusion process occurs by hopping in a *rigid* disordered medi-um,[10] the three cases cited above involve transport in a *dynamically* disordered structure. From the viewpoint of an individual hopper this means that, if the local environment at any given time does not permit a hop, that environment will evolve such that, after a certain average waiting time, the hop will no longer be prohibited. As far as we are aware, there has not been adequate theoretical consideration of this latter situation, which occurs for several experimentally well-studied cases. The present paper is devoted to the definition and preliminary study of a dynamic bond percolation model (DBP) to describe precisely such transport situations. The particular case which will be referred to is that of polymeric ionic conductors, but many other systems seem susceptible to a similar analysis (see Sec. V). We show that such a model is the natural extension of the static bond percolation model to systems in which the host structure is evolving.

Static percolation theory describes transport in systems in which hops between sites are either forbidden or allowed with specific fixed probabilities.[2] In the DBP model, these probabilities change with time because of the structural evolution of the host. A more careful definition of DBP is given Sec. II, in which the (master) evolution equation for the diffusive particles in DBP is also given. Some formal properties of DBP are given in Sec. III. In particular, we show that the two characteristic times of the model, the average particle hopping time $\bar{\tau}_{\text{hop}}$ and the average system evolution renewal time $\bar{\tau}_{\text{ren}}$ have quite different roles in the dynamics. For observation times t much greater than $\bar{\tau}_{\text{ren}}$, the process is diffusive, even if it is not diffusive for $t < \bar{\tau}_{\text{ren}}$. On the other hand, when the average time $\bar{\tau}_{\text{hop}}$ is much less than $\bar{\tau}_{\text{ren}}$, the hopper (in one dimension) will be equally distributed along connected sites, so that a fixed mean-square distance, depending only on the fraction of filled

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bonds, is found. We also derive closed-form expressions for the mean-square displacement at arbitrary times, and for the diffusion coefficient. Section IV presents some numerical results which confirm by simulation, for a one-dimensional model, the formal results of Sec. III. It also includes data concerning the diffusion coefficient dependence on bond hopping probabilities, on τ_{ren}, and on the percentage of available bonds. Finally, Sec. V contains a brief discussion of the model and its possible applications, especially to polymeric solid electrolytes.

One issue of nomenclature will be necessary in our discussion: we will call a "bond" between sites (i, j) *available* or *open* or *filled* if an ion can hop between the ends of that bond, and call it *unavailable* or *closed* if the hop cannot occur.

II. THE DYNAMIC BOND PERCOLATION MODEL: MOTIVATION AND DEFINITION

We consider the problem of classical particles moving in a dynamically disordered medium. For the particular application to polymeric solid electrolytes, the medium is the polymeric solvent (or host), but in general it can be any rearranging material. Because the actual amorphous polymer is of complicated geometry, we adopt a dynamic lattice model. A space lattice is imposed on the system, such that the stable positions for the moving particles (which we call ions) are at the lattice sites. Then for any given fixed configuration of the medium, the dynamics of the ions are characterized by a (kinetic) master equation. If $P_i(t)$ is defined as the probability of observing a particle at site i at time t, the master equation for the time derivative $\dot{P}_i$ reads, in one dimension,

$$\dot{P}_i(t) = \sum_{j \neq i}{}' \{P_j(t)w_{j \to i} - P_i(t)w_{i \to j}\} . \tag{1}$$

Here $w_{i \to j}$ is the probability per unit time of hopping from site i to site j; it is related to $\overline{\tau}_{hop}$, the average waiting time for a hop to occur, by

$$n_c w \overline{\tau}_{hop} = 1 , \tag{2}$$

where n_c is the coordination number, equal to 2 in the one-dimensional case. Then for a bond percolation situation, with only nearest-neighbor hops and with some bonds unfilled, $w_{i \to j}$ is given by

$$w_{i \to j} = \begin{cases} w \text{ or } 0, & \text{when } (i, j) \text{ are neighbors} & (3) \\ 0, & \text{when } (i, j) \text{ are not neighbors} & (4) \\ 1 - (w_{i \to i+1} + w_{i \to i-1}), & \text{for } i = j . & (5) \end{cases}$$

For neighboring sites, we take

$$w_{i \to j} = \begin{cases} 0, & \text{bond } (i, j) \text{ not available} \\ w, & \text{bond } (i, j) \text{ available} . \end{cases} \tag{6}$$

We denote by f the fraction of available bonds, so that

$$0 \leq f \leq 1 . \tag{7}$$

The master equation (1) describes a continuous-time hopping model with the time that the particle actually takes to hop off site i distributed according to some probability distribution that is continuous in time. For some of the formal developments that follow, it will be convenient to assume instead a discrete distribution. That is, in place of the differential equation (1), there would be a difference equation that physically describes a hopper on a given site trying jumps at instants of time each separated by exactly $\Delta\tau$. For observation times $t \gg \Delta\tau$, the difference between the continuous and discrete distribution of hopping times should be of little consequence. The discrete distribution is sometimes more useful for mathematical manipulation (Sec. III); although it is physically unreasonable, we suspect it is adequate for the short $\Delta\tau$ limit in which it is used.

Equations (1)–(7) define a static bond percolation model, which has been exhaustively studied and fruitfully applied to a number of experimental and theoretical problems in the dynamics of statistically disordered systems.[2] We wish to generalize it to consider dynamic disorder.

For ionic conductors, the static model corresponds to a hopping model, such as has been extremely useful in characterizing framework rigid-lattice species.[11-13] The probability w is determined by the energy barrier for hopping from one stable solvation position to another; this is in turn determined by solvation energies and ultimately by the strength of the ion-medium bonding. It is reasonable to assume an activated form for w:

$$w = w_0 \exp(-E_a/k_B T) . \tag{8}$$

For media such as noncrystalline polymers in which the solvation sites each have a different environment, there will in fact be a distribution of activation energies E_a, but we can to a first approximation neglect the width of this distribution, and assume a single activation barrier.

The percolation aspect of the problem results from the static disorder in the medium. For rigid glasses, for instance, or for any fixed geometry of a polymer, the hopping route between i and j may be blocked by a local structural defect or an adventitious impurity. The simple choices (3)–(6) imply that all hops are either allowed or fully blocked. The master equation (1) with probabilities given by Eqs. (3)–(6) defines a static percolation problem. In one dimension, it cannot result in diffusion, since the first jump that is blocked ($w = 0$) will stop the ion.

The important aspect of the DBP model is the inclusion of the dynamic structure changes in the host material in which the hoppers are located. For a solid electrolyte of polymeric type, for instance, the polymer chains will themselves move. From the viewpoint of ion motion, this means that the solvation geometry in the neighborhood of any given ion will evolve in time, as the motions of the polymer bring other regions of the chain near the ion. [There are also higher-frequency vibrations, whose role, for our purposes, is either unimportant or is involved in providing the activation energy of Eq. (8).] As these chain reorientations change (or renew) the solvation environment of the ion, the hopping probability changes; some channels become opened and some become closed. If we assume, as in Eq. (6), that the hopping rate $w_{i \to j}$ for an available bond is a single value, then

the renewal process resulting from the polymer motion simply reassigns the values of w and 0 to different bonds during a characteristic average polymer motion time, or renewal time $\bar{\tau}_{ren}$. To model this mathematically, we assume each renewal to occur abruptly at some time τ_{ren} after the previous renewal. It is convenient to make two assumptions: (a) The renewal times occur, as do the hopping times, with a given distribution. Again, it is reasonable to take this time either as a continuous or as a discrete random variable; (b) There is no local correlation of jumping probabilities; i.e., the w_{i-j} are recalculated randomly for each site pair, subject only to the overall constraint that a fraction f has value w, a fraction $(1-f)$ has value zero.

While (a) is generally reasonable, (b) is often not, since structural changes in the host material might well be closely correlated when sites are close together. However, (b) should remain valid for times long enough so that the average distance which an available bond moves is larger than the average separation of such bonds. More importantly, the model contains the combination of local hops and dynamic renewal processes which characterize the ionic polymers and several other systems (see Sec. V).

Some limiting results of the present DBP model are clear:

(i) For $\bar{\tau}_{ren}/\bar{\tau}_{hop} \ll 1$, the physical process should correspond to hopping in a homogeneous (nonpercolative) system, whose dynamics are described by (1, 2) but where

$$w_{i,k} \to fw , \quad \text{for neighboring sites .} \tag{9}$$

This is because the local hopper will be able to sample several values (each one w or 0) within the hopping time;

(ii) When $\bar{\tau}_{ren}$ is very large compared to a typical time for a jump to occur, the behavior for time $t < \bar{\tau}_{ren}$ will be fixed by the *static* percolation problem. For one dimension, this means that the mean-squared displacement $\langle x^2 \rangle$ within this time will attain an asymptotic maximum; for higher dimensions, the behavior depends on how f compares to the value of f at the percolation threshold.[2]

The DBP model in one dimension is described by the static percolation model master equations (1)–(6), with the extra feature that, after a renewal time τ_{ren}, the choice of which bonds are available and which are not is randomly reassigned. When the renewal time $\bar{\tau}_{ren}$ is much greater than the observation time t, the DBP model reduces to the ordinary bond percolation picture, but for $t \gg \bar{\tau}_{ren}$, we believe that it contains important experimentally realized behavior absent in static percolation theory.

III. THE DBP MODEL: SOME FORMAL RESULTS

We derive here some formal results for the DBP model of hopping motion on a dynamically rearranging lattice. For simplicity, we first assume the time axis divided into intervals of equal length $\Delta\tau$, with a hop attempted at each endpoint, and we assume a single fixed renewal time τ_{ren}; these restrictions will later be relaxed. We seek the averages of observable quantities

taken over an ensemble of systems with various possible bond assignments and hopping sequences.

(i) First, we will show that, for time $t < \tau_{ren}$, the mean-square displacement is given by the simple expression

$$\langle x^2 \rangle \to d^2 \frac{f}{(1-f)^2} \tag{10}$$

as $t \to \infty$, where d is the lattice spacing. To prove Eq. (10), consider a chain of bonds which are all filled (open channels), with k bonds to the left and l bonds to the right of the site of interest. Then if f is the probability for a bond to be open (available), the probability for this arrangement of open bonds is

$$\text{prob}(k+l) = (1-f)^2 f^{k+l} , \tag{11}$$

where the first factor accounts for the closed (unavailable) bonds to the left and right of the $(k+l)$ consecutive ones. Now within this configuration, for the limit $t \to \infty$, all sites will be visited equally, independent of w. Then averaging both over configurations and over sites within each configuration, we find

$$\langle x^2 \rangle = (1-f)^2 \sum_k \sum_l f^{k+l} \left\{ \frac{1}{k+l+1} \sum_{m=-k}^{l} (md)^2 \right\} , \tag{12}$$

where the quantity in brackets is merely $\langle x^2 \rangle$ for the $(k+l)$ consecutive sites. Equation (12) can be rewritten as

$$\langle x^2 \rangle = (1-f)^2 d^2 \sum_k \sum_l \frac{f^{k+l}}{k+l+1} \left(\sum_{n=0}^{k} n^2 + \sum_{n=0}^{l} n^2 \right) \tag{13}$$

which, after several rearrangements, becomes

$$\langle x^2 \rangle = \frac{d^2(1-f)^2}{6} \sum_{m=0}^{\infty} f^m(m^3 + 3m^2 + 2m) . \tag{14}$$

Using differentiation identities, such as

$$\sum_{m=0}^{\infty} mf^m = f \frac{\partial}{\partial f} \sum_{m=0}^{\infty} f^m = f \frac{\partial}{\partial f} \frac{1}{1-f} , \tag{15}$$

we can replace the sums in Eq. (14), whence Eq. (10) follows directly. Note that, as expected for the broken chain in one dimension, $\langle x^2 \rangle$ [Eq. (10)] is finite for infinite time unless $f = 1$ (all bonds available). Thus, any break in the one-dimensional chain blocks diffusion.

(ii) Our second formal result is that, for many renewal processes (i.e., $t/\tau_{ren} \equiv N > 2$), the behavior will be diffusive (with $\langle x^2 \rangle \propto t$), independent of its behavior for $t < \tau_{ren}$. At the end of a given renewal cycle, we assume that the bonds are randomly reassigned, independently of the location of the particle. The process is then fully Markovian, and $P^{(N+1)}(r+i)$, the probability for occupation of site $r+i$ at the end of cycle $N+1$, depends only on $P^{(N)}(i)$. The difference equation for evolution of the system is then

$$P^{(N+1)}(l) = \sum_i P^{(N)}(i)P^{(1)}(l-i) . \tag{16}$$

This is the version of the Smoluchowski–Chapman–Kolmogorov equation[14] appropriate for renewal processes.

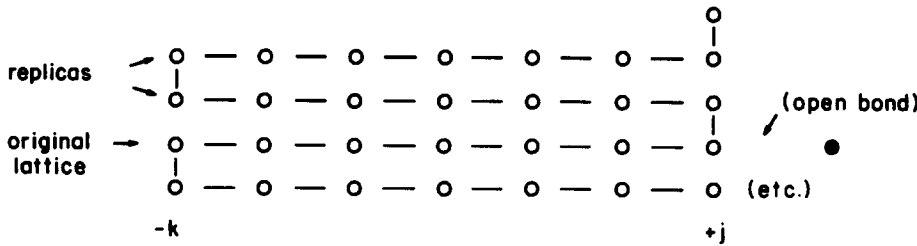We can use Eq. (16) to find $\langle x^2 \rangle$, the mean-square

FIG. 1. Replica lattice construction for the calculation of $\langle x^2 \rangle$ for a one-dimensional static percolation problem. The original chain has available bonds from site $-k$ to site j, as do all replica lattices.

displacement. Formally, for one dimension,

$$\langle x^2 \rangle_{N+1} = d^2 \sum_l l^2 P^{(N+1)}(l) \tag{17}$$

$$= d^2 \sum_l \sum_i l^2 P^{(N)}(i) P^{(1)}(l-i) \tag{18}$$

$$= d^2 \sum_l \sum_i \{(l-i)^2 + i^2 + 2(l-i)i\} P^{(N)}(i) P^{(1)}(l-i) \tag{19}$$

$$= d^2 \left[\sum_i P^{(N)}(i) \right] \left[\sum_{l-i} (l-i)^2 P^{(1)}(l-i) \right] \tag{20}$$

$$+ d^2 \left[\sum_i i^2 P^{(N)}(i) \right] \left[\sum_{l-i} P^{(1)}(l-i) \right]$$

$$+ 2d^2 \left[\sum_i \sum_{l-i} (l-i) i P^{(N)}(i) P^{(1)}(l-i) \right] \tag{21}$$

$$= \langle x^2 \rangle_1 + \langle x^2 \rangle_N + 2 \langle x \rangle_1 \langle x \rangle_N . \tag{22}$$

Here $\langle \ \rangle_k$ denotes the ensemble average at the end of the kth renewal cycle and $\langle x \rangle_1 = \langle x \rangle_N = 0$ by symmetry. Thus, Eq. (22) is simply

$$\langle x^2 \rangle_{N+1} = \langle x^2 \rangle_1 + \langle x^2 \rangle_N \tag{23}$$

or, more generally,

$$\langle x^2 \rangle_N = N \cdot \langle x^2 \rangle_1 . \tag{24}$$

Thus, the mean-squared displacement after a number N of renewals is proportional to the time; this behavior is diffusive for $t \gg \tau_{\rm ren}$, as was to be shown.

The result (24) holds in any number of dimensions (the proof is similar to that given here for one dimension). It holds whether or not $\langle x^2 \rangle_1$ itself obeys a diffusion equation. A result similar in structure to Eq. (23) holds also for any specific sequence $\{\tau_i\}$ of unequal renewal times

$$\langle x^2 \rangle_N = \sum_i \langle x^2 \rangle_1(\tau_i) . \tag{25}$$

(iii) The third formal result is a closed-form summation expression for $p_n^{(1)}(i)$, the probability to be at site i after n hopping intervals (each of length $\Delta\tau$) with no renewals. When used with Eq. (24), this result determines the diffusion coefficient for the process with given f and w, without requiring a numerical simulation. The actual formula is given by Eq. (42) and its derivation proceeds as follows: We consider one-dimensional hopping on a chain of open and closed bonds, as defined by Eq. (24). We consider a bond configuration $S(k,j)$, defined to have available bonds from site k to site j, with closed bonds from site $(-k-1)$ to $-k$ and from j to $(j+1)$. The relative probability for the occurrence of this configuration is $(1-f)^2 f^{k+j}$. Then we can construct a replica lattice with which to calculate directly

$p_n^{(1)}(i)$. As shown in Fig. 1, this replica lattice consists of the original $(-k,j)$ chain and a series of replicas of $(-k,j)$; the hopping probability w is the same between all sites on the enlarged lattice, and the sites are labeled from $(-k)$ to (j) on the original chain and all replicas. Instead of regarding the chain as terminating at $-k$, we now allow a hop from $-k$ (on the original chain) to $-k$ (on the first replica). Then $p_n^{(1)}(i)$, the total probability of being at either site i or any one of its replicas after n hops, is required, since the mean-squared displacement $\langle x_n^2 \rangle$ after n hops will be just

$$\langle x_n^2 \rangle = \sum_i i^2 d^2 p_n^{(1)}(i) , \tag{26}$$

in terms of this total $p_n^{(1)}(i)$.

To obtain $p_n^{(1)}(i)$, we consider the situation after n hopping intervals. The actual number of hops will vary from zero to n. Define m_r as the number of hops taken to the right, m_l as the number to the left, and $m_0 = n - (m_l + m_r)$ as the number of null hops (those in which the particle remains in the same place). Then the number of ways to construct the sequence of hops such that m_l, m_r, and m_0 are unchanged is

$$\frac{n!}{(n - m_l - m_r)! \, m_r! \, m_l!} .$$

Now we have taken η as the probability of a left or right hop and $(1-2\eta)$ for that of a null hop, where $\eta = w\Delta\tau$. Thus the total probability for the situation (m_l, m_r, m_0) is

$$\frac{n!}{(n - m_l - m_r)! \, m_r! \, m_l!} \eta^{m_r + m_l} (1 - 2\eta)^{n - m_r - m_l} . \tag{27}$$

We want to find the probability to be at site l. The hopper will be at site $l \geq 0$ if $m_r - m_l = l$. We need, then, to sum Eq. (27) over all possible values of m_0 (between 0 and l). Since we require both

$$n = m_l + m_r + m_0 \tag{28a}$$

and

$$l = m_r - m_l , \tag{28b}$$

the sum over m_0 can be replaced by one over m_l, with Eq. (28b) used to replace m_r and m_0. We find the range of m_l to be

$$0 \leq m_l \leq \tfrac{1}{2}(n - l) . \tag{29}$$

The desired probability (to be at any site l on any of the chains in Fig. 1) is found to be

$$\sum_{m_l} \frac{n!}{(l + m_l)! \, m_l! \, (n - l - 2m_l)!} \eta^{l + 2m_l} (1 - 2\eta)^{n - l - 2m_l} , \tag{30}$$

with the range of m_l specified by Eq. (29).

We now need to sum the expression (30) over all the replica sites of any given site on the original chain, in order to obtain the correct probability of being at a given site on the original chain. Then the probability of being at site l on a chain of bond configuration $S(k,j)$ after n hops is

$$\sum_{\{l\}}\sum_{m_l}\frac{n!}{(l+m_l)!\,m_l!\,(n-l-2m_l)!}\,\eta^{l+2m_l}(1-2\eta)^{n-l-2m_l}\,,$$

(31)

where $\{l\}$ denotes site l and all of its replica sites; the sums in Eq. (31) have a finite number of terms for finite n. Examination (if careful!) of Fig. 1 shows that the following replicas of site l have to be considered:

$$l\pm 2\nu(j+k+1)\,,\qquad\text{(all }l)\,,\tag{32}$$

$$2j+1-l+2\nu(j+k+1)\,,\quad\text{for }l>0\,,\tag{33}$$

$$-(2k+1)-l-2\nu(j+k+1)\,,\quad\text{for }l<0\,,\tag{34}$$

where $\nu=0,\,1,\,2,\dots$.

With these results, we can find the overall $p_n^{(1)}(l)$ by summing Eq. (31) over the relative probability $f^{k+j}(1-f)^2$ of finding $S(k,j)$. Thus,

$$p_n^{(1)}(l)=\sum_{k=0}^{\infty}\sum_{j=1}^{\infty}\left\{\sum_{\{l'\}}\sum_{m_l}\frac{n!}{(l'+m_l)!\,m_l!\,(n-l'-2m_l)!}\right.$$
$$\left.\times\eta^{2m_l+l'}(1-2\eta)^{n-l'-2m_l}\right\}f^{k+j}(1-f)^2\,,\tag{35}$$

where $l\geq 0$, and $\{l'\}$ denotes summation over l and its replicas (in Fig. 1) for fixed $S(k,j)$. The symmetry relation

$$p_n^{(1)}(l)=p_n^{(1)}(-l)\,,\tag{36}$$

when used with Eq. (35), permits calculation for all possible sites.

The result (35) can be put into a more useful form by removing infinite summations, which can be accomplished by separating the contribution of the original chain from that of the replica chains (in Fig. 1). That is, we separate the terms with $l'=l$ in Eq. (35). We then find that $p_n^{(1),0}(l)$, the contribution from the original chain, is given by

$$p_n^{(1),0}(l)=\sum_{k=0}^{\infty}\sum_{j=1}^{\infty}\left((1-f)^2f^{k+j}\right)\sum_{m_l}\frac{n!}{(l+m_l)!\,(n-l-2m_l)!\,m_l!}$$
$$\times\eta^{l+2m_l}(1-2\eta)^{n-l-2m_l}\,.\tag{37}$$

Simplifying, we obtain

$$(1-f)^2\sum_{k=0}^{\infty}\sum_{j=1}^{\infty}f^k f^j=(1-f)^2(1-f)^{-1}\sum_{j=1}^{\infty}f^j\tag{38}$$

$$=(1-f)(1-f)^{-1}f^l$$

$$=f^l\,.\tag{39}$$

Therefore,

$$p_n^{(1),0}(l)=f^l\sum_{m_l}\frac{n!}{(l+m_l)!\,(n-l-2m_l)!\,m_l!}\,\eta^{l+2m_l}$$
$$\times(1-2\eta)^{n-2m_l-l}\tag{40}$$

$$\equiv f^l p_n^{(C)}(l)\,,\tag{41}$$

where $p_n^{(C)}(l)$, defined as the probability of being on site

l after n jumps along a linear chain with all sites connected, is given by comparing Eqs. (40) and (41).

Then finally we rewrite Eq. (35) as

$$p_n^{(1)}(l)=f^l p_n^{(C)}(l)+[\text{summation in Eq. (35) but with only}$$
$$\text{replicas, not original chain, included}$$
$$\text{in sum over }\{l'\}]\,.\tag{42}$$

For any finite number of hops n, the sum in $p_n^{(C)}(l)$ contains a finite number of terms. In addition, the number of terms in Eq. (42) over m_l and $\{l'\}$ is also finite, since when k and j become large enough, no nontrivial replicas of $S(k,j)$ exist for fixed n. One condition for this to hold, that is for

$$p_n^{(1)}(l)=f^l p_n^{(C)}(l)\,,\quad\text{is}\quad|2(j+k+1)\pm l|>n\,.\tag{43}$$

Two comments might be made about Eq. (42). The first is that as $f\to 1$, the $(1-f)^2$ factor in the sum of Eq. (35) results in $p_n^{(1)}(l)\to p_n^{(C)}(l)$, with replicas becoming unimportant, as expected, since $f=1$ corresponds to the simple linear chain. The second is that the f^{k+j} factor in Eq. (35) makes the sum over k, j converge fairly rapidly for f small compared to unity. The advantage of Eq. (42) is that it permits the calculation of $\langle x^2\rangle_1$ in Eq. (24) by means of a closed-form summation. This summation not only is more rapidly calculated than is a straightforward simulation, but is also more useful for examining limiting behaviors.

The formal result (35) has been derived assuming that the hops occur evenly spaced by a fixed hopping interval $\Delta\tau$. For times much greater than $\Delta\tau$, this assumption is not a serious one, but as pointed out above, a more realistic assumption is that the hops occur over a continuous range of times. This is particularly important when either the renewal time τ_{ren} or the observation time t is of the same order as the average hopping time. We must then consider the limit of a continuous time random walk.[15] To this end, we take

$$\eta\to 0\,,\tag{44}$$

$$\Delta\tau=0\,,\tag{45}$$

$$n\to\infty\,,\tag{46}$$

keeping

$$w=\eta/\Delta\tau\tag{47}$$

and

$$t=n\Delta\tau\tag{48}$$

constant. We also define a dimensionless time θ by

$$\theta=wt\,.\tag{49}$$

The generalization of the formal results above to the case of continuous time is now straightforward. First we must obtain $p_\theta^{(C)}(l)$, the probability for the linked chain $(f=1)$. Then we can use Eq. (42) to obtain $p_\theta^{(1)}(l)$ as a function of time. Combined with Eq. (24) this will yield the diffusion coefficient. The last generalization, to the case of a Poisson distribution of renewal times, is considered at the end of this section.

To obtain $p_\theta^{(C)}(l)$, the probability to be at site l after time θ, we start with Eq. (41), the result for n hops.

In the continuous-time limit, n will far exceed any l or m_l which contribute significantly to Eq. (41). Now consider the factor

$$(1 - 2\eta)^{n-l-2m_l} = \left(1 - \frac{2[n\eta]}{n}\right)^n (1 - 2\eta)^{-l-2m_l} \qquad (50)$$

$$\rightarrow e^{-2\theta} \qquad (51)$$

in the limit $\eta \rightarrow 0$, $\theta = $ constant, $n \rightarrow \infty$. Then with Stirling's approximation used for the n-containing factorials, the second factor (41) is just

$$\frac{n!}{(n-l-2m_l)!} \cong (n)^{l+2m_l} \, , \qquad (52)$$

and thus

$$p_\theta^{(C)}(l) \cong \sum_{m_l=0}^{\infty} \frac{(n\eta)^{l+2m_l} \exp(-2n\eta)}{(l+m_l)! \, m_l!} \qquad (53)$$

$$= e^{-2\theta} \sum_{m_l=0}^{\infty} \frac{\theta^{l+2m_l}}{m_l! \, (l+m_l)!} \, . \qquad (54)$$

The continuous-time result (54) is simpler in form than the equal-hop-interval result (41). In fact, rewriting Eq. (54) as

$$p_\theta^{(C)}(l) = e^{-2\theta} \left(\frac{2\theta}{2}\right)^l \sum_{m_l=0}^{\infty} \frac{(2\theta/2)^{l+m_l}}{l! \, (m_l+l)!} \qquad (55)$$

leads, by comparison with standard forms, to simply

$$p_\theta^{(C)}(l) = e^{-2\theta} I_l(2\theta) \, , \qquad (56)$$

where I_l is the modified Bessel function. Bessel functions appear as the solutions to several random walk problems, as well as in the problem of Brownian diffusion in a sinusoidal potential.[16] Note that

$$\sum_l p_\theta^{(C)}(l) = 1 \qquad (57)$$

as implied by the identity

$$e^z = I_0(z) + 2I_1(z) + 2I_2(z) + \cdots \, . \qquad (58)$$

We also note that the present continuous-time result is equivalent to a Poisson distribution in the limit of small times θ, since then only the $m_l = 0$ term is a significant contributor to Eq. (54), leading to

$$p_\theta^{(C)}(l) = \frac{\theta^l}{l!} e^{-2\theta} \, , \qquad (59)$$

which is a Poisson distribution, normalized to consider the fact that l can be negative, in which case l is replaced by $|l|$.

The use of the replica lattice to go from $p_\theta^{(C)}(l)$ to $p_\theta^{(1)}(l)$, the probability to be at site l after (dimensionless) time θ, follows just as $p_n^{(1)}(l)$ followed from $p_n^{(C)}(l)$ [Eqs. (26)–(42)]. Thus, the result for a random percolation problem ($f \neq 1$) in the continuous-time limit is

$$p_\theta^{(1)}(l) = \sum_{k=0}^{\infty} \sum_{j=1}^{\infty} \sum_{\{l'\}} p^{(C)}(l')(1-f)^2 f^{k+j} \, , \qquad (60)$$

where the innermost summation is over the original chain and all replicas, or

$$p_\theta^{(1)}(l) = f^l p_\theta^{(C)}(l) + \sum_{k=0}^{\infty} \sum_{j=1}^{\infty} \sum_{\{l'\}}' p_\theta^{(C)}(l')(1-f)^2 f^{k+l} \, , \qquad (61)$$

where the sum is only over replica chains. For $l > 0$,

Eq. (61) applies as written; for $l < 0$, $|l|$ replaces l in the summations. The result (60) permits evaluation of the average squared distance of particle motion evaluated over an ensemble of different configurations of open and closed bonds. Observe that unless $f = 1$ in Eq. (61), $P^{(1)}(l)$ for $l \rightarrow \infty$ is zero; i.e., diffusion cannot occur in a one-dimensional chain with some empty sites, in the absence of a renewal process.

The last generalization required is to relax the artificial constraint that the renewal times all be equal. There exists for renewal times, just as for the hopping times, some distribution. If we assume that the distribution of renewal times is Poisson-like and controlled by a renewal rate λ, then

$$P_{ren}(\tau) = \lambda e^{-\lambda t} \, , \qquad (62)$$

here $P_{ren}(\tau)$ is the probability density for renewal times, and

$$\bar{\tau}_{ren} = \lambda^{-1} \, , \qquad (63)$$

where the bar denotes average over the distribution (62). We can now distinguish between two limiting cases. When the observation time $t_{obs} \ll \lambda^{-1}$, we have a static percolation problem, since no renewals occur. When $t_{obs} \gg \lambda^{-1}$, there are many renewal cycles occurring during the observation time and it is reasonable to expect that the diffusion coefficient is determined by the average over the distribution of renewal times of $\langle x^2 \rangle$ and of τ_{ren}:

$$\overline{\langle x^2 \rangle_1} = \int_0^\infty d\tau \langle x^2 \rangle_1(\tau) P_{ren}(\tau) \qquad (64)$$

so that

$$D = \overline{\langle x^2 \rangle_1} / \bar{\tau}_{ren} = \lambda \overline{\langle x^2 \rangle_1} \, . \qquad (65)$$

This is a simple extension of Eq. (24) to the case of distributed τ_{ren}. In the limit $P_{ren}(\tau) = \delta(\tau - \tau_{ren})$ it becomes

$$D = \langle x^2 \rangle_1 / \tau_{ren} \qquad (66)$$

which is equivalent to Eq. (24). A rigorous derivation of Eq. (65) is provided below.

In the intermediate case $\lambda^{-1} \sim t_{obs}$, the problem of computing D becomes quite complex, since it is necessary to compute the mean-square displacement subject to the constraint that the observation time is the sum of the renewal times; this situation becomes of importance in the study of $\sigma(\omega)$, the frequency-dependent conductivity, where the observation time is in a sense fixed by the frequency. For dc conduction, with which we are concerned here, the observation time can generally be chosen such that $t_{obs} \gg \lambda^{-1} = \bar{\tau}_{ren}$ provided any renewals occur at all. We therefore investigate this limit, deferring consideration of the intermediate case.

To prove Eq. (65) for $t_{obs} \gg \bar{\tau}_{ren}$, we first consider the average total time elapsed after N renewals. This is simply

$$\bar{t} = \int_0^\infty \cdots \int_0^\infty \left(\sum_I \tau_I\right) P_{ren}(\tau_1) P_{ren}(\tau_2) \cdots P_{ren}(\tau_N) d\tau_1 \cdots d\tau_N$$

$$= N \left[\int_0^\infty \tau_1 P_{ren}(\tau_1) d\tau_1\right] \left[\int_0^\infty P_{ren}(s) ds\right]^{N-1} \qquad (67)$$

$$= N\bar{\tau}_1 \, , \qquad (68)$$

where $P_{ren}(\tau)$ is the probability density for a cycle of length τ and where $\bar{T}_1$ is the mean renewal time

$$\bar{T}_1 \equiv \bar{T}_{ren} \ . \tag{69}$$

We compute $\bar{t^2}$ as

$$\bar{t^2} = \int_0^\infty d\tau_1 \cdots \int_0^\infty d\tau_N \left(\sum_I \tau_I\right)^2 P_{ren}(\tau_1) P_{ren}(\tau_2) \cdots P_{ren}(\tau_N) \tag{70}$$

$$= \int_0^\infty d\tau_1 \cdots \int_0^\infty d\tau_N \sum_I \tau_I^2 P_{ren}(\tau_1) \cdots P_{ren}(\tau_n)$$

$$+ \sum_I \sum_{J \neq I} \int_0^\infty d\tau_1 \cdots \int_0^\infty d\tau_N \, \tau_I \, \tau_J \, P_{ren}(\tau_1) \cdots P_{ren}(\tau_N)$$

$$= N \overline{\tau_{ren}^2} + N(N-1)(\bar{\tau}_{ren})^2 \ . \tag{71}$$

Thus we obtain the fluctuation as

$$\frac{\overline{(t^2)} - (\bar{t})^2}{(\bar{t})^2} = \frac{1}{N}\left[\frac{\overline{(\tau_1^2)} - (\bar{\tau}_1)^2}{(\bar{\tau}_1)^2}\right] \ . \tag{72}$$

This is the usual result: the fluctuation in the macroscopic observable scales as the inverse square root of the number of repetitions. By repeating the manipulations of Eqs. (67)–(72) with τ replaced by x^2, we show that the fluctuations in the mean-square displacement also go to zero for large N, varying like N^{-1}. Therefore for large N, neither $\overline{\langle x^2 \rangle}_1$ nor $\bar{\tau}_{ren}$ will fluctuate significantly.

We know from Eqs. (68) and (72) that because of the lack of fluxion, the constraint $\sum_I \tau_I = t$ is not necessary. We then write [using Eq. (25)]

$$\overline{\langle x^2 \rangle}_N = \frac{\int_0^\infty \cdots \int_0^\infty \sum_{I=1}^N \langle x^2(\tau_1) \rangle_1 P_{ren}(\tau_1) \cdots P_{ren}(\tau_N) d\tau_1 \cdots d\tau_N}{\int_0^\infty \cdots \int_0^\infty P_{ren}(\tau_1) \cdots P_{ren}(\tau_N) d\tau_1 \cdots d\tau_N} \ . \tag{73}$$

This is just

$$\overline{\langle x^2 \rangle}_N = N\overline{\langle x^2 \rangle}_1 \ , \tag{74}$$

while the observation time for N renewals is (for large N)

$$\bar{T} = N\bar{T}_1 \ . \tag{75}$$

Therefore,

$$D = \frac{\overline{\langle x^2 \rangle}_N}{\bar{t}} = \frac{\overline{\langle x^2 \rangle}_1}{\bar{\tau}_1} \ , \tag{76}$$

which was to be shown. Thus, for macroscopic observation times, the diffusion coefficient is the ensemble average of the mean-square displacement within one renewal time, divided by the ensemble average of the renewal time.

The results (76) and (42), taken together, permit computation of D for any choice of renewal time distribution, hopping time distribution, and fraction f of filled bonds. Thus, they provide a general solution to the DBP model for one dimension, assuming only that the observation time is long compared either to the mean hop and mean renewal times.

IV. CALCULATIONAL RESULTS: DIFFUSION COEFFICIENTS FOR A ONE-DIMENSIONAL CASE

For concreteness, we present here calculated diffusion coefficients and mean-square displacements for

a one-dimensional model obtained using our ensemble-averaged solution to the master equation (1) with f, the fraction of filled bonds, chosen arbitrarily. Renewal was taken as a random process following a Poisson distribution; i.e., the renewal process was taken as a simple first-order rate process. The computations then were performed in several ways.

(a) Numerical simulation. The bonds in a finite chain were randomly assigned as open or closed, and a particle was allowed to hop, starting from the origin, following the equation of motion (1). The bond renewals occurred every n hopping intervals, each of length $\Delta\tau$ (fixed renewal time). Averages of $\langle x^2 \rangle$ for each value τ were evaluated over many trials.

(b) Closed-form evaluation. The expressions (42), (61), and (26) were evaluated, leading both to mean-square displacements and to diffusion coefficients.

These computations were performed for a series of f and w and, in all cases, for both fixed-time and continuous-time motion, the results of (a) and (b) agreed to arbitrary tolerance. Therefore, we report here only the results of (b). There are clearly three limiting cases of interest, specifically,

(i) $t_{obs} \gg \bar{\tau}_{ren} > w^{-1}$,

(ii) $\bar{\tau}_{ren} \gg t_{obs} \gg w^{-1}$,

(iii) $t_{obs} \gg w^{-1} > \bar{\tau}_{ren}$.

Case (ii) is just ordinary percolation theory, since the observations are made before renewal can occur. For $f \neq 1$ (some broken bonds), limit (ii) will not show diffusive behavior but, rather, a fixed maximum value of $\langle x^2 \rangle$, as given by Eq. (10). Physically, such systems simply will not conduct. For case (iii), the particle in the short time Δt will have a probability of hopping left or right given by

$$\text{prob} = fw\Delta t \tag{77}$$

[no second hop will occur, since its probability is proportional to $(\Delta t)^2$]. Then in time Δt, the average mean-square displacement is

$$\overline{\langle x^2 \rangle} = 2fw\Delta t d^2 \tag{78}$$

so that

$$\frac{\langle x^2 \rangle}{\Delta t} = 2fd^2 w = \text{const.} \tag{79}$$

This is the case, as physically expected, of "gray" diffusion, which is ordinary diffusion, but with the hopping probability reduced from w to fw. For all cases, calculated values based on numerical simulation fit those based on closed-form evaluation extremely well (Fig. 2).

The most interesting limit is case (i). Here, depending on how large the (renewal time)/(hop time) ratio becomes, the observed diffusion coefficient will exhibit differing f dependencies. For very long renewal times, we have from Eq. (10) that

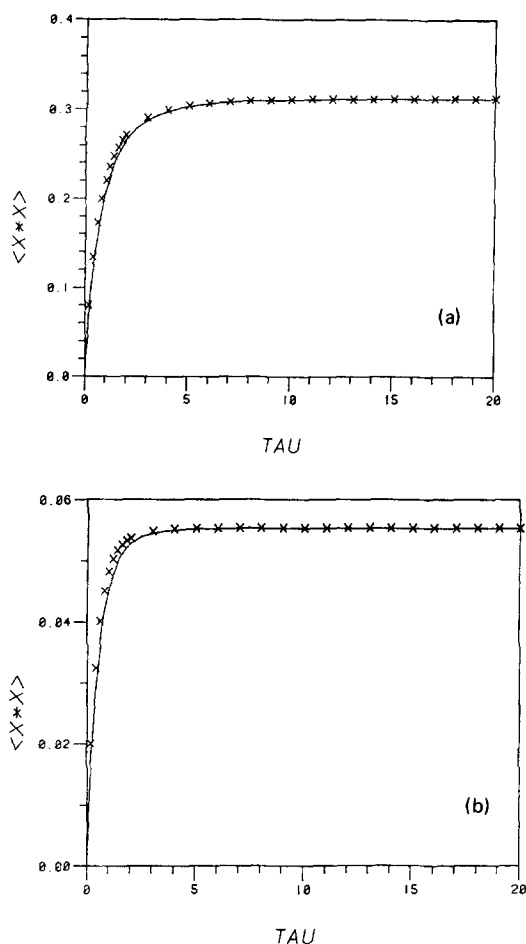$$D \to \frac{fd^2}{(1-f)^2 \bar{\tau}_{ren}} \ . \tag{80}$$

FIG. 2. (a) Computed mean-square displacement $\langle x^2 \rangle$ as a function of time θ [Eq. (49)] for the one-dimensional walk within one renewal time. The x's are for the hop discrete-time hopping process with hopping interval 0.2, while the continuous curve is calculated for the continuous-time walk. Values chosen for the parameters are $f = 0.2$, $\eta = 0.2$. Note that, as expected, slight differences occur until $\theta \gg 1$. The flat asymptotic behavior is as expected [Eq. (13)] for $f \neq 1.0$. (b) The same as in Fig. 2(a), but for $f = 0.05$, $\eta = 0.2$.

TABLE I. Calculated mean-square displacements and fits to diffusive behavior; $f = 0.2$, $\eta = 0.2$.

t_{obs}	τ_{ren}	$\langle x^2 \rangle$	D	Normalized[a] variance
1000	4	74.76	0.0150	0.2×10^{-5}
200	4	14.95	0.0151	0.6×10^{-4}
1000	20	15.62	0.0032	0.1×10^{-3}
200	20	3.12	0.0033	0.003
10	10	0.31	0.009	0.16
100	0.2	40	0.08	0.2×10^{-14}

[a]Defined as $(\sum_i \{\langle x^2 \rangle_i - Dt_i\}^2 / \sum_i \langle x^2 \rangle_i^2)$, where D is the calculated diffusion coefficient. It measures the accuracy of the fit to $\langle x^2 \rangle \propto Dt$.

finite conductivity, even in one-dimensional systems with a large preponderance of empty bonds (blocked jumps).

V. DISCUSSION

We have defined a time-dependent bond percolation model for the process of particle hopping in a system undergoing dynamic motions. The fundamental notion
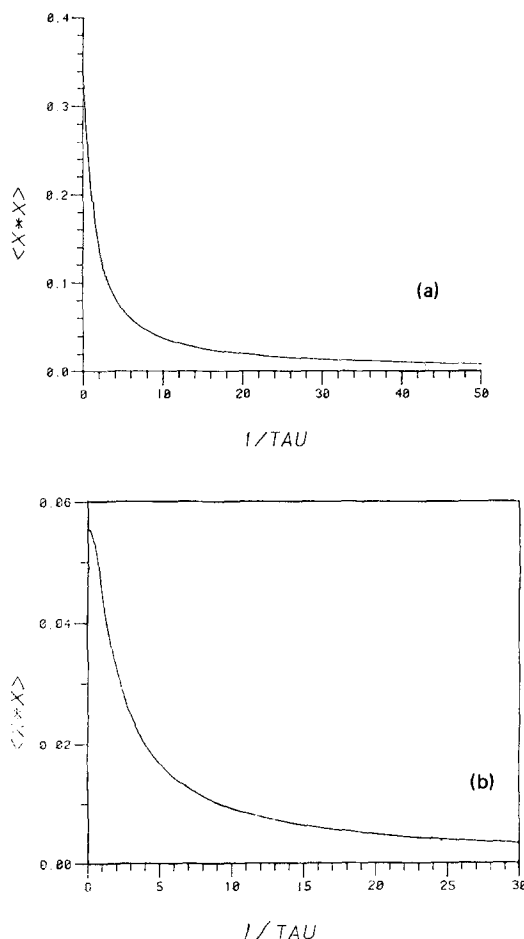
Thus, a plot of diffusion coefficient vs inverse mean renewal time will be linear with slope of $fd^2/(1-f)^2$ near the origin, and bend over to become constant [Eq. (79)] asymptotically. This behavior is illustrated in Figs. 3 and 4 which show the mean-square displacement and the diffusion coefficient as functions of the inverse mean renewal time; while the former monotonically decreases for increasing τ_{ren} (or decreasing $1/\tau_{ren}$), the latter goes smoothly to the limit of Eq. (80).

Some typical numerical values are given in Table I, along with the accuracy of a fit to the diffusive relationship $\langle x^2 \rangle \propto t_{obs}$. For case (iii) above, the fit to diffusive behavior is perfect. For case (ii) it fails utterly, and for case (i), diffusion is observed over the time scale of many renewal events.

The numerical results thus confirm all of the formal arguments made in Sec. III. In particular, they show that the occurrence of renewal processes can produce well-characterized diffusive behavior, and therefore

FIG. 3. (a) Mean-squared distance calculated as a function of inverse renewal time τ_{ren}, for $f = 0.2$. The distance is largest for longest renewal time. (b) The same as in Fig. 3(a), but for $f = 0.05$.
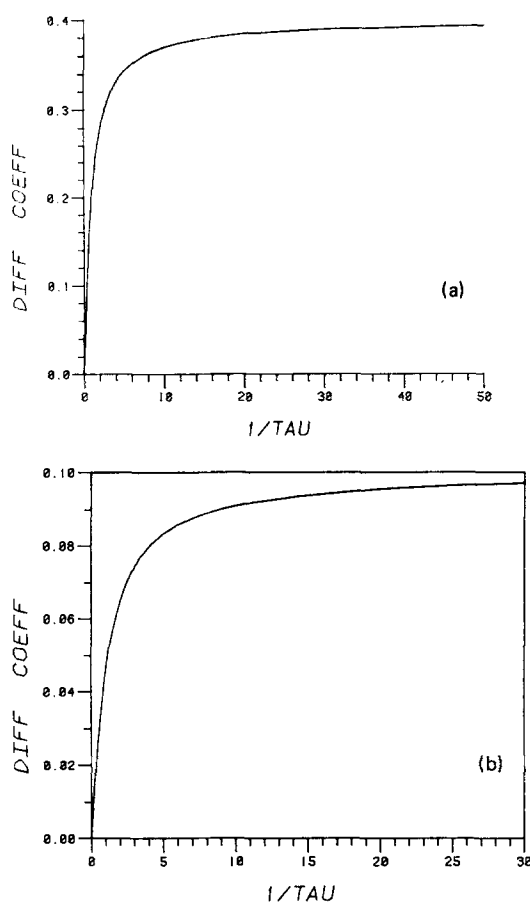
FIG. 4. (a) Diffusion coefficient, calculated from Eq. (76), as a function of inverse renewal time τ_{ren}, for $f = 0.2$ and for a delta-function renewal time distribution. For τ_{ren} less than an average hopping time, the curve is flat, as expected from the arguments surrounding Eq. (10), while for longer τ_{ren}, the diffusion coefficient drops off; in a sense, time is wasted, since for long renewal times, the particle reaches the ends of the corrected chain and Eqs. (10) and (65) become relevant. (b) The same as in Fig. 4(a), but for $f = 0.05$. Note that the ratio of asymptotic values for D of Figs. 4(a) and 4(b) is 4.0, as expected from Eqs. (10) and (65).

involves the existence of two characteristic times, one corresponding to the average hopping of a particle from one site to another, and denoted $\bar{\tau}_{hop}$, the other describing the mean time for the host material to undergo substantial structural change. This latter time is characteristic for changing, or renewing, the complexion of available and unavailable bonds between sites, and is called $\bar{\tau}_{ren}$. We find that for observation times $t \gg \bar{\tau}_{ren}$, the process is diffusive, independent of the percentage of available bonds, and of whether or not diffusive behavior is found within a single renewal time. An example is shown in Fig. 5 for the case in which diffusion is *not* observed within a single renewal. We derive closed-form summation expressions for the diffusion coefficient.

When $t \ll \bar{\tau}_{ren}$, the problem reduces to the usual static percolation case; for one dimension, there is no diffusion. There are a large number of physical systems for which static and/or dynamic disorder occur. Static dis-

order corresponds to the $\bar{\tau}_{ren} \to \infty$ case, for which ordinary percolation theory is applicable. Cases for which this is true involve, e.g., rigid glasses, highly disordered framework solids, and random metallic alloys. For softer materials such as polymer above the glass transition temperature, or micelles, or hydrogen-bonded aggregates, or electrode coatings of swelled polymer, or lipid bilayers or colloidal particles the structure of the (disordered) host material is itself evolving with a characteristic time, which is associated in the model with $\bar{\tau}_{ren}$. We have described, for a one-dimensional model, the situation with fixed, discrete times $\Delta \tau$ and τ_{ren}, and the physically more realistic continuous-time problem which corresponds to a master-equation situation (first order kinetics) for each assignment of closed and of open bonds. The distribution in $\bar{\tau}_{ren}$ becomes unimportant for large differences between the observation time t and the average $\bar{\tau}_{ren}$. For $t \gg \bar{\tau}_{ren} > \bar{\tau}_{hop}$ or $\bar{\tau}_{ren} \ll \bar{\tau}_{hop}$, simple diffusion occurs, through expressions for the diffusion coefficients in terms of f and w will differ.

Three parameters occur in the theory: f (fraction of filled bonds) and the average hopping and average renewal times. For application to any real physical situation, these need to be related to the system under study. For instance, in polymeric solids for which the free-volume theory description of conductivity is found valid,[1,5–7] the fraction f should be related to the free volume. Standard free-volume theories may be understood by comparison with a static percolation model,[1] in which local cells are either liquidlike or solidlike; the possibility of a cell changing from liquidlike to solidlike, which corresponds to our renewal process, is explicitly neglected. For temperatures near the glass transition temperature, in which the free volume is small, the renewal process (in a sense, motion of the free volume) may be the only realistic way to achieve transport. In this sense, our dynamic bond percolation model is an extension of free-volume theories.

We have found some results for a very special case of the dynamic bond percolation model: a one-dimen-
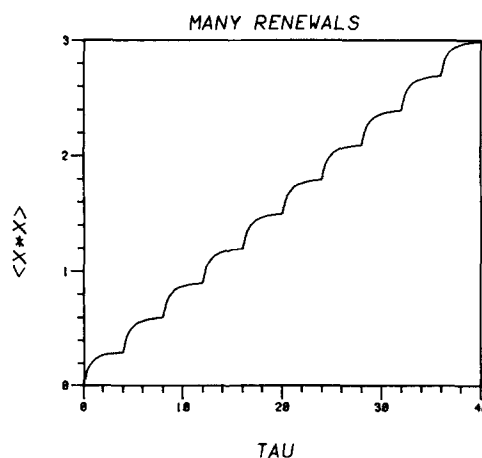

FIG. 5. Demonstration of diffusive behavior for many renewal times, even when behavior is percolation-length limited within one renewal time: $f = 0.2$, $\eta = 0.2$, renewal after every 20 hopping intervals.

sional case with completely random renewals. For this special situation we presented both formal and numerical results on the diffusive behavior. Several extensions of the present work are clearly called for: experimentally most relevant would be extension of our results to include the frequency-dependent conductivity, so that comparisons with microwave conductivity could be made (in the particular case of ionic conduction, the microwave results of Brodwin et al.[18] indicate that the response of the polymer chains follows that of the mobile ions for frequency above 10 GHz, which may fix the size of the renewal time). The artificiality of random renewals should also be improved upon: in polymeric systems, for instance, one expects substantial segments of the polymer to move in concert (e.g., reptation), so that several neighboring sites are renewed together. This "correlated renewal" might give substantially different behavior and, in particular, it might lead to lower diffusion rates for the same number of overall bond renewals, since bottlenecks would be less efficiently bypassed. Finally, the study of higher-dimensional systems is important both because they are more realistic, and because the threshold behavior exhibited by static percolation in two or three dimensions might be far less important when renewal occurs on a time scale which is not too much greater than the hopping time (in particular, which is less than the time for uniform filling of a local cluster).

Despite these shortcomings we feel that the present model is of potential utility, in that it generalizes both the (microscopic) percolation model and the (macroscopic) free-volume theory to include dynamic disorder of the host material. It may help to explain experimental systems for which neither of the previous pictures is fully adequate. Application to one particularly vexatious and important system, Na^+ diffusion in $PEO \cdot NaX$, is just beginning in our laboratory. This species is currently of wide experimental interest for battery applications,[4-7] but although an adequate qualitative picture of complex formation is available,[8] there are serious difficulties in description of the transport (failure of the Vogel–Tammann–Fulcher equation,[9,19] failure of substantial ion-pair blocks to impede conductivity,[9] the microwave behavior[18]) which have not yet been explained. We feel that the important physical process of renewal may help understand this behavior.

The actual application of the DBP model to polymeric electrolytes is discussed elsewhere.[20] There is an interesting relationship between DBP and free-volume theory[1]; in particular, the renewal time describes, in a way, the kinetic rearrangement of free volume which is normally ignored in free-volume theories. When small particles are diffusing in a medium of large solvent species or polymer segments, the mobility can be much smaller than that predicted by free-volume theory, essentially because of the kinetic restriction (large τ_{ren}). This can be of real qualitative importance, especially fairly near the glass transition temperature.

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