Generalized hopping model for frequency-dependent transport in a dynamically disordered medium, with applications to polymer solid electrolytes

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(Received 10 May 1984)

Protonic diffusion in hydrogen-bonded networks, ionic conduction in polymeric solid electrolytes, and other processes in which the carrier transport mechanism involves motion of the host medium on a time scale comparable to that of the carrier motion itself require generalization of the usual models based on carrier hopping in a static medium. Under the assumption that this concurrent motion of the host can be modeled by a random reassignment (or "renewal") of hopping probabilities, with a constant probability λ per unit time for renewal to occur, the effects of host motion on the frequency-dependent diffusion coefficient $D(\omega)$ are now considered. We consider both the dynamic bond-percolation model (in which the site-to-site hopping probability is randomly assigned either the value w or the value 0) and the more general model based on a possibly continuous distribution of hopping rates randomly assigned between different pairs of sites. Under these assumptions, the diffusion coefficient $D(\omega)$ with renewal is shown to be obtainable from $D(\omega)$ without renewal through the formal substitution $i\omega \rightarrow \lambda + i\omega$. For the $\omega = 0$ limit, an expression is obtained for the time-dependent mean-square displacement with renewal in terms of the mean-square displacement without renewal. These general formal results are applied to the one-dimensional dynamic percolation model, for which specific exact analytic results are thereby obtained, and $D(\omega)$ is calculated and studied for this case.

I. INTRODUCTION

Hopping models have proved extremely useful in studying and understanding diffusion or conduction in a variety of systems, including some involving charge transport by carriers of small mass (such as electrons in a narrow conduction band[1]) and many in which the carriers are massive (e.g., ionic conduction in framework lattices,[2] and in polymeric[3] and glassy ceramic[4] solid electrolytes). One limitation of most hopping models is the assumption that the hops between sites (on some assumed lattice structure) are instantaneous; a second is that the probability function describing the likelihood of a new hop at a time t after the previous hop is assigned permanently to each pair of sites (corresponding to static disorder if different probability functions are assigned randomly to different pairs of sites for each system in some ensemble).[5] Relaxation of the instantaneous-hop assumption alone leads to kinetic equations with memory effects.[6] The systems of physical interest to us[7,8] however are those, such as the polymeric solid electrolytes,[9–11] in which ongoing dynamical changes alter the preferred pathways through the host medium on a time scale often comparable to that of the carrier motion itself, thereby corresponding to dynamic, rather than static, disorder. In a polymer complexed nonstoichiometrically with an ionic salt, such as polyethylene-oxide·NaSCN (PEO·NaSCN) for example, the PEO backbone (at temperatures greater than the glass transition temperature T_g) undergoes large-amplitude motion as the Na^+ ions diffuse through it.[12–14] Other systems that appear to be characterized by the kind of dynamic disorder considered here include electrons or polarons moving within a liquid medium, and protons moving by means of a Grotthus mechanism.[15,16] All of these cases involve two characteristic time scales, the first describing a typical waiting time between the (instantaneous) hops, and the second describing a typical time for the host medium to reorganize (or renew) and thereby to provide a new set of preferred pathways for hopping. We denote the representative rates determined by these two times as w for the mean hopping rate and λ for the mean renewal rate, respectively.

It appears reasonable to model the charge transport dynamics in such systems by assuming the carrier diffusion to be described by random-walk hopping between available sites, with the hopping probabilities randomly assigned according to some (possibly continuous) distribution and reassigned (or renewed) according to the same distribution as time passes; it is also useful to assume in this model that the carrier resides between hops on points of a periodic lattice. This general picture based on a random walk with renewal might be called a dynamic disorder hopping (DDH) model. A somewhat more restrictive version of the DDH model is based on considering hops only between nearest-neighbor sites with the hopping probability per unit time having either the value w (for a fraction f of bonds, or pathways, between nearest-neighbor sites) or else 0 (for a fraction $1-f$ of bonds)—

the same as in the ordinary static bond percolation theory except for the added feature once again that at certain instants the hopping probabilities are randomly reassigned, corresponding therefore to a *dynamic* bond percolation (DBP) theory.

We have already examined[7] some of the implications of this DBP model. Among the results we have obtained are the following.

(1) Exact expressions for the mean-square displacement $\langle r^2\rangle_0(t)$ in one dimension without renewal.

(2a) An equation for the occupation probability of any site at any time during the Nth renewal epoch (after precisely N renewals of a specific sequence of renewal times have already occurred) in terms of the occupation probabilities calculated for all times without renewal, applicable for any number of dimensions. (2b) A corresponding expression for $\langle r^2\rangle(t)$ in terms of $\langle r^2\rangle_0(t)$ (i.e., obtained without renewal) for any sequence of renewals in any number of dimensions.

(3) A general proof of diffusive motion over times which are long compared with the average renewal time, and a general expression for the corresponding diffusion coefficient.

Results (2)—(3) can be seen not to require the specific bond-percolation assumptions, and actually apply also for the continuous distribution of possible hopping probabilities involved in the dynamic disorder hopping model provided merely that the bond reassignments are still instantaneous and are each uncorrelated to the previous assignment. Nevertheless, limiting the hopping probabilities to the values w and 0 allows result (1) to be obtained in analytic form in one dimension, so that it can be combined with results (2)—(3) to study the behavior of $\langle r^2\rangle(t)$ and the static diffusion coefficient D as a function of renewal rate, hopping rate, and available bond fraction. The analysis published thus far suggests the importance of bond renewal in controlling the behavior of the static diffusion coefficient (and therefore, by virtue of the Nernst-Einstein relation, the behavior of the conductivity σ) under many conditions.

Much of the experimental data whose theoretical analysis could shed light on the conduction dynamics of polymer electrolytes is,[9–14,17–19] however, obtained at nonzero frequency of the applied field; this situation has yet to be considered for either dynamic bond-percolation or the more general dynamic hopping model. In extending our theory to this case, it becomes essential to make reasonable assumptions about the distribution of random renewal times rather than, for example, assuming a fixed sequence of renewal times, since the range over which $D(\omega)$ is to be studied includes values of ω^{-1} comparable to the average renewal time itself, and $D(\omega)$ is sensitive to the distribution of renewal times near this average value (as can be seen from the results derived in Sec. II). This is in contrast to the static diffusion coefficient, for which we have already obtained[7] a general expression [applicable to both the dynamic disorder hopping (DDH) and DBP models] in terms of only the average renewal time and the average $\langle r^2\rangle$ attained from one renewal to the next. The measurement[20–22] and theoretical study[23–25] of $\sigma(\omega)$, in the case of systems best modeled by a static lattice, has been of great value in correlating conductivity with phase-transition behavior, in determining attempt frequencies[26,27] for hopping, and in characterizing the effective damping of the carriers.[28] Extending theoretical study of $\sigma(\omega)$ to the case of dynamic disorder should allow important conclusions to be drawn concerning the mechanism of ionic conduction in systems such as polymer electrolytes for which experimental data are now becoming available.

Linear-response theory provides a relation between the frequency-dependent conductivity and the mean-square displacement $\langle r^2\rangle(t)$ of the carrier.[29] We show in the next section how, for a specific random distribution of possible diffusion times, the linear response result can be converted into an expression for $\sigma(\omega)$ in terms of the renewal rate λ and $\langle r^2\rangle_0(t)$, the mean-square displacement attained by the carrier over time t in the absence of renewal. The equivalence of these two expressions leads to a prescription for determining $\langle r^2\rangle(t)$ *with* renewal from $\langle r^2\rangle_0(t)$ *without* renewal; it also leads to a simple method for obtaining $D(\omega)$ with renewal from any $D(\omega)$ expression for the corresponding system without renewal merely by the replacement of $i\omega$ by $\lambda+i\omega$. Limiting cases for the results of Sec. II are considered in Sec. III, leading mostly to conclusions consistent with intuition but also to some limits on the range of applicability of our model assumptions. Section IV applies our results to the special case of the one-dimensional (1D) dynamic bond-percolation model,[7] leading to exact solutions for $\langle r^2\rangle$ and $D(\omega)$ obtained from our previously published expressions for $\langle r^2\rangle_0(t)$, and illustrating how the results of Sec. III can be used to generalize the static percolation results of Odagaki and Lax[30] to a dynamic percolation model. The application to the 1D DBP case concludes with the presentation and discussion of numerical calculations based on the analytic results of this section. Finally, Sec. V contains a brief discussion of our results, with some comments on their applicability to polymeric and protonic electrolytes.

II. THEORY OF THE FREQUENCY-DEPENDENT RESPONSE

We consider the average behavior evaluated over an ensemble of systems in which a carrier moving on a periodic lattice undergoes various possible sequences of hops, with various intervals between renewals, and with each renewal producing a random reassignment of hopping probabilities.[7] The hops are assumed instantaneous in the sense that at any given time the carrier is located on one of the lattice sites. Each renewal is also assumed to occur instantaneously, and to produce new hopping probability assignments uncorrelated with the previous assignment and unaffected by the location of the carrier at the instant of renewal.[31] Finally, we assume that the probability for a renewal to occur in any small time interval dt is $\lambda\,dt$ (for constant renewal rate λ) regardless of when the previous renewal occurred, thereby restricting the present results to a specific (exponential) renewal-time distribution.

Beyond the assumption of instantaneous hops, we make no specific assumptions about the hopping process, nor is

it necessary to assume that the hopping probabilities are limited to the values w and 0. Furthermore, the results presented here apply equally in any number of dimensions.

For notational convenience, the origin for each system is defined as whatever lattice site the carrier is on at time $t=0$. The general linear-response theory expression[29] for the conductivity $\sigma(\omega)$ in terms of the mean-square displacement from the origin $\langle r^2\rangle(t)$ is

$$\sigma(\omega)=\frac{ne^2}{kT}D(\omega) \tag{1}$$

where

$$\frac{1}{n_d}D(\omega)=\lim_{\epsilon\to 0^+}\left[(i\omega)^2\int_0^\infty e^{-i\omega t}e^{-\epsilon t}\langle r^2\rangle(t)dt\right] \tag{2}$$

with n_d a constant depending on the dimensionality of the lattice and n and e the density and charge of the carriers, respectively. We first examine some properties of the assumed renewal distribution, then derive an equation of motion governing the ensemble probability to be used in calculating $\langle r^2\rangle_0(t)$, which is $\langle r^2\rangle$ evaluated over an ensemble of systems that do not renew.

Suppose that the time scale has been discretized, so that any hop or renewal occurring in the interval $(t_{n-1},t_n]$ of length Δt is regarded as having occurred at the end point t_n. (Eventually, we assume $\Delta t\to 0$, thereby attaining a continuous-time limit in which the assignment described in the previous sentence has no effect on the final results obtained). Within the large but finite time interval $T=M\,\Delta t$, the probability of a renewal at any one given t_i is then

$$\lambda\,\Delta t=\frac{\lambda T}{M}\ . \tag{3}$$

The number of different ways to distribute N ($\ll M$) renewals among the M different times in this interval is

$$\frac{M!}{N!(M-N)!}\ . \tag{4}$$

The probability for N renewals to occur before time T is therefore

$$P(N,T)=\frac{M!}{(M-N)!N!}\xi^N(1-\xi)^{M-N}\ . \tag{5}$$

But as Δt is allowed to approach zero, M becomes large compared with 1, and use of Stirling's expansion and the appropriate limiting values of the ξ-dependent factors in (5) leads to a Poisson probability function[32]

$$P(N,T)=\frac{\xi^N}{N!}e^{-\xi}\ , \tag{6}$$

with

$$\xi\equiv\lambda T \tag{7}$$

for the probability of exactly N renewals between time 0 and T. In particular, the result actually used in the derivation that follows is the probability for zero renewals to have occurred in time T after an *arbitrary* time 0, and is given by

$$P(0,T)=e^{-\lambda T}\ . \tag{8}$$

For the exponential waiting-time function [Eq. (8)], this is also the probability for no renewal during a time T starting from the *previous renewal,* so that the present theory is not subject to the difficulty pointed out by Tunaley[33,34] which, in our case, might otherwise arise from the distinction between the waiting-time distribution starting from a random time and that starting from the last previous renewal.

Now consider the hopping motion together with renewal by defining $W_N(\mathbf{s},t)$ as the joint probability that there are N renewals between 0 and t *and* that the hopper occupies site $\mathbf{s}$ at time t. Note that W_N is defined without regard for when each of the renewals prior to t has occurred. For the discretized-time case, $W_{N+1}(\mathbf{s},t)$ is the sum (over all sites $\mathbf{m}$ and discrete intermediate times t_i prior to t) of the joint probability for all of the following:

(1) The hopper is on site $\mathbf{m}$ at t_i with N renewals having already occurred [probability $W_N(\mathbf{m},t_i)$].

(2) The $(N+1)$th renewal then occurs at exactly t_i {i.e., renewal in the interval $(t_{i-1},t_i]$, with probability $\lambda\,\Delta t$}.

(3) The hopper then moves from $\mathbf{m}$ to $\mathbf{s}$ without renewal [probability $W_0(\mathbf{s}-\mathbf{m},t-t_i)$].

Under our assumptions these three events are independent, and so the required joint probability is a product of their individual probabilities. This then implies

$$W_{N+1}(\mathbf{s},t)=\sum_{\mathbf{m}}\sum_{t_i\le t}W_N(\mathbf{m},t_i)(\lambda\Delta t)W_0(\mathbf{s}-\mathbf{m},t-t_i)\ . \tag{9}$$

In the continuous-time limit, (9) becomes

$$W_{N+1}(\mathbf{s},t)=\lambda\sum_{\mathbf{m}}\int_0^t W_N(\mathbf{m},t')W_0(\mathbf{s}-\mathbf{m},t-t')dt'\ . \tag{10}$$

The evolution equation (10) for the joint probability W_N is analogous to the evolution equation (16) derived in Ref. 7 for a specific sequence of renewals rather than the present random distribution of renewals. In particular, the relation of the joint probability $W_0(\mathbf{s},t)$ (for occupation of $\mathbf{s}$ at t and with no renewal having yet occurred) to the conditional probability $p_0(\mathbf{s},t)$ (for occupation of s at time t *given* that a renewal has not occurred) is simply

$$W_0(\mathbf{s},t)=e^{-\lambda t}p_0(\mathbf{s},t)\ . \tag{11}$$

A generating function method similar to that employed by Scher and Lax[29] can now be combined with these results to yield the desired expression for $D(\omega)$ in terms of $\langle r^2\rangle_0(t)$, where now

$$\langle r^2\rangle_0(t)\equiv\sum_{\mathbf{s}}s^2p_0(\mathbf{s},t)\ . \tag{12}$$

Readers uninterested in the detailed derivation of the $D(\omega)$ expression can skip to (31), where this final result is obtained.

Define the generating function,

$$G(\mathbf{s},t;z)=\sum_{N=0}^{\infty}z^NW_N(\mathbf{s},t)\ , \tag{13}$$

so that

$$G(\mathbf{s},t;1)=\sum_{N=0}^{\infty} W_N(\mathbf{s},t)\equiv W(\mathbf{s},t) \tag{14}$$

is the probability for the carrier to be on site $\mathbf{s}$ at time t. Next, multiply the evolution equation (10) by z^{N+1} and sum over N to obtain, using (13),

$$G(\mathbf{s},t;z)-\lambda z\sum_{\mathbf{m}}\int_0^t W_0(\mathbf{s}-\mathbf{m},t-t')G(\mathbf{m},t';z)dt' = W_0(\mathbf{s},t) . \tag{15}$$

The Laplace transform of (15) (in terms of the Laplace variable u) is then

$$\tilde{G}(\mathbf{s},u;z)-\lambda z\sum_{\mathbf{m}}\tilde{W}_0(\mathbf{s}-\mathbf{m};u)\tilde{G}(\mathbf{m},u;z)=\tilde{W}_0(\mathbf{s},u) . \tag{16}$$

To obtain a formal solution to this equation, multiply by $e^{-i\mathbf{k}\cdot\mathbf{s}}$ and sum over $\mathbf{s}$, where $\mathbf{k}$ has any value consistent with the imposition of periodic boundary conditions on the lattice. Then with

$$U(\mathbf{k},u;z)=\sum_{\mathbf{s}} e^{-i\mathbf{k}\cdot\mathbf{s}}\tilde{G}(\mathbf{s},u;z) ,$$

and

$$V(\mathbf{k},u)=\sum_{\mathbf{s}} e^{-i\mathbf{k}\cdot\mathbf{s}}\tilde{W}_0(\mathbf{s},u) , \tag{17}$$

Eq. (16) becomes

$$U(\mathbf{k},u;z)-\lambda z V(\mathbf{k},u)U(\mathbf{k},u;z)=V(\mathbf{k},u) ,$$

so that $U(\mathbf{k},u;z)$ is given by

$$U(\mathbf{k},n;z)=\frac{V(\mathbf{k},u)}{1-\lambda z V(\mathbf{k},u)} , \tag{18}$$

and, by inverse Fourier summation over the N sites on which the periodic boundary conditions are imposed,

$$\tilde{G}(\mathbf{s},u;z)=\frac{1}{N}\sum_{\mathbf{k}}\frac{V(\mathbf{k},u)}{1-\lambda z V(\mathbf{k},u)}e^{i\mathbf{k}\cdot\mathbf{s}} . \tag{19}$$

Now the linear-response result for $D(\omega)$, Eq. (2), can be written as

$$n_d^{-1}D(\omega)=(i\omega)^2\lim_{\epsilon\to 0^+}\left[\sum_{\mathbf{s}}\mathbf{s}^2\int_0^\infty e^{-\epsilon t}e^{-i\omega t}W(\mathbf{s},t)dt\right] \tag{20}$$

$$=(i\omega)^2\sum_{\mathbf{s}} s^2\tilde{W}(\mathbf{s},i\omega) , \tag{21}$$

where W is the sum over W_N [Eq. (14)], and has as its Laplace transform $\tilde{W}(\mathbf{s},i\omega)=\tilde{G}(\mathbf{s},i\omega,1)$. Therefore, we have

$$n_d^{-1}D(\omega)=(i\omega)^2\sum_{\mathbf{s}}\mathbf{s}^2\tilde{G}(\mathbf{s},i\omega;1) . \tag{22}$$

To evaluate (22), use

$$\sum_{\mathbf{s}}\mathbf{s}^2\tilde{G}(\mathbf{s},i\omega;1)=-\nabla_k^2\left[\sum_{\mathbf{s}}\tilde{G}(\mathbf{s},i\omega,1)e^{-i\mathbf{k}\cdot\mathbf{s}}\right]\Bigg|_{\mathbf{k}=0} \tag{23}$$

$$=-\nabla_k^2\left[\frac{1}{N}\sum_{\mathbf{k}'}\sum_{\mathbf{s}}\frac{V(\mathbf{k}',i\omega)}{1-\lambda(\mathbf{k}',i\omega)}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{s}}\right]\Bigg|_{\mathbf{k}=0} . \tag{24}$$

The $\mathbf{s}$ summation gives a $\delta_{\mathbf{k},\mathbf{k}'}$, and Eq. (17) for $V(\mathbf{k},u)$ leads to

$$\nabla_k V(\mathbf{k},u)\Big|_{\mathbf{k}=0}=L\left[-i\sum_{\mathbf{s}}\mathbf{s}W_0(\mathbf{s},t)\right]=0 \tag{25}$$

by inversion symmetry, where L denotes the Laplace transform operation. We then obtain from (22)–(25)

$$D(\omega)=n_d\left[\frac{i\omega}{1-\lambda V(0,i\omega)}\right]\left[\sum_{\mathbf{s}}\mathbf{s}^2\tilde{W}_0(\mathbf{s},i\omega)\right] . \tag{26}$$

But we also have

$$V(0,i\omega)=\lim_{\epsilon\to 0^+}\int_0^\infty e^{-\epsilon t}e^{-i\omega t}\sum_{\mathbf{s}}W_0(\mathbf{s},t)dt , \tag{27}$$

with

$$W_0(\mathbf{s},t)=e^{-\lambda t}p_0(\mathbf{s},t) . \tag{11}$$

So with the normalization condition

$$\sum_{\mathbf{s}}p_0(\mathbf{s},t)=1 , \tag{28}$$

Eq. (27) reduces to $(\lambda+i\omega)^{-1}$, and $D(\omega)$ reduces to

$$n_d^{-1}D(\omega)=(\lambda+i\omega)^2\sum_{\mathbf{s}} s^2\tilde{W}_0(\mathbf{s},i\omega) \tag{29}$$

$$=(\lambda+i\omega)^2\int_0^\infty e^{-i\omega t}\sum_{\mathbf{s}}s^2e^{-\lambda t}p_0(\mathbf{s},t)dt , \tag{30}$$

or

$$\frac{1}{n_d}D(\omega)=(\lambda+i\omega)^2\int_0^\infty e^{-(\lambda+i\omega)t}\langle r^2\rangle_0(t)dt , \tag{31}$$

where we have used the definition (12) of $\langle r^2\rangle_0(t)$ in terms of the conditional probability $p_0(\mathbf{s},t)$ defined by the corresponding ensemble of systems that suffer no renewal.

Equation (31) is the desired expression for $D(\omega)$ in terms of the renewal rate λ and the mean-square displacement $\langle r^2\rangle_0(t)$ calculated without renewal, and is the central result of this paper. It should be compared with the

formally similar Eq. (2) expressing $D(\omega)$ in terms of the $\langle r^2\rangle(t)$ that results from all dynamical processes involved in the carrier motion and which includes a (then unspecified and unevaluated) average over renewal sequences. It is also seen that $D(\omega)$ without renewal is given by (2) with $\langle r^2\rangle_0(t)$ appearing instead of $\langle r^2\rangle(t)$, and differs from Eq. (31) for $D(\omega)$ with renewal only in that $i\omega$ replaces $\lambda+i\omega$. Therefore, existing expressions for $D(\omega)$ evaluated without renewal can be converted to expressions for the corresponding system with a Poisson distribution of renewal events simply through the $i\omega\rightarrow\lambda+i\omega$ replacement or, equivalently,

$$D(\omega,\lambda)=D_0(\omega-i\lambda)\ , \tag{32}$$

where $D(\omega,\lambda)$ denotes the diffusion coefficient with renewal, and $D_0(\omega)$ denotes the diffusion coefficient in the absence of renewal. Because of the widespread intensive efforts in studying diffusion on a static (nonrenewing) percolation lattice[35] as well as in studying continuous-time random walk problems,[5,29] this simple formula for obtaining formal results with renewal from available results without renewal should be of considerable value.

The formal results of this section are now completed by showing how Eq. (31) leads to the determination of $\langle r^2\rangle(t)$ from $\langle r^2\rangle_0(t)$. Note first that at $t=0$,

$$\langle r^2\rangle(0)=\langle r^2\rangle_0(0)=0\ . \tag{33}$$

Furthermore, at sufficiently short times the overwhelming majority of systems in the ensemble used to calculate $\langle r^2\rangle(t)$ have not undergone renewal, and the rates of increase of $\langle r^2\rangle(t)$ and of $\langle r^2\rangle_0(t)$ are the same. [For the DBP model, in particular, with a fraction f of the bonds having hopping probability w and $(1-f)$ having hopping probability 0, the rates of increase of $\langle r^2\rangle$ and $\langle r^2\rangle_0$ would initially be $n_c f w d^2$, with d the lattice spacing and n_c the coordination number.] In general, therefore,

$$\left.\frac{d\langle r^2\rangle}{dt}\right|_{t=0}=\left.\frac{d\langle r^2\rangle_0}{dt}\right|_{t=0}\ . \tag{34}$$

When the two expressions (2) and (31) are equated for all ω, and the initial conditions (32) and (33) are employed in integrating by parts twice, the result

$$\int_0^\infty e^{-i\omega t}\frac{d^2}{dt^2}\langle r^2\rangle(t)dt=\int_0^\infty e^{-i\omega t}e^{-\lambda t}\frac{d^2}{dt^2}\langle r^2\rangle_0(t)dt$$

is obtained for all ω. Therefore, in the absence of any pathological functional behavior, $\langle r^2\rangle(t)$ satisfies the second order differential equation

$$\frac{d^2}{dt^2}\langle r^2\rangle(t)=e^{-\lambda t}\frac{d^2}{dt^2}\langle r^2\rangle_0(t)\quad(\text{for } t>0)\ , \tag{35}$$

which, together with the two initial conditions (33) and (34), fully determines $\langle r^2\rangle(t)$ (for $\omega=0$ diffusion with renewal) once $\langle r^2\rangle_0(t)$ is known. It is then easily verified that

$$\langle r^2\rangle(t)=\langle r^2\rangle_0(t)e^{-\lambda t}+\lambda\int_0^t(2+\lambda t-\lambda\xi)e^{-\lambda\xi}\langle r^2\rangle_0(\xi)d\xi \tag{36}$$

is the unique solution to (35) that also satisfies the initial conditions (33) and (34).

III. LIMITING CASES

In certain limits the $(\lambda+i\omega)$ formula (31) leads to explicit conclusions about the functional form of $D(\omega,\lambda)$. Examination of these limits provides information about the range of applicability of our model assumptions. We consider first the limits of either λ or ω as being large compared with a typical hopping rate $\overline{w}$, and second of λ and ω both small compared with $\overline{w}$. Third, we show that our expression for $D(\omega,\lambda)$ in the limit $\omega\rightarrow 0$ (for any finite λ) reduces to the same expression for the static diffusion coefficient previously derived[7] for a general sequence or distribution of renewal times.

A. Limit of large λ or of large ω

For large λ, the $\exp(-\lambda t)$ factor allows $\langle r^2\rangle_0(t)$ to contribute significantly only for small values Δt of t. During this very brief time period, only single hops to a nearest neighbor contribute, and do so with probability $\hat{w}\Delta t$. The probability of two hops is of order $(\Delta t)^2$. Hence,

$$\langle r^2\rangle_0(t)\approx n_c\hat{w}td^2\ ,$$

with $\hat{w}$ now defined as the average rate for such hops, n_c the coordination number, and d the lattice spacing. This leads to

$$D(\omega,\lambda)=n_d n_c\hat{w}d^2\ , \tag{37}$$

which is then independent of λ and ω (for sufficiently large λ). For the dynamic bond-percolation model,

$$\hat{w}=fw\ , \tag{38}$$

with f the probability for a bond to be available (hopping probability w rather than 0).

This result appears physically acceptable in the limit $\lambda\rightarrow\infty$ at finite ω. It is intuitively fully expected for $\omega\rightarrow 0$ because, for rapid-enough renewal, the hop occurs after many renewals, and the hopper in each system of the ensemble gets to choose an averaged hopping probability from the entire hopping-probability distribution. But the limiting behavior (37) is physically inconsistent with the expectation that, for carriers of nonzero mass, the dynamic response [proportional to $D(\omega)$] ultimately must go to zero as the frequency of the applied field becomes infinite. Furthermore, the present model predicts the unacceptable limiting behavior (37) for sufficiently large ω at all values of λ, because the rapid oscillations of $\exp(i\omega t)$ in this limit also restrict the contributions of $\langle r^2\rangle_0(t)$ to small values of t in Eq. (31).

This unsatisfactory behavior apparently results from the assumption of instantaneous hops,[33,36] which ignores the microscopic inertial dynamics of the particle motion and leads to $\langle r^2\rangle_0(t)$ increasing linearly with t even for very short times (corresponding to large ω). It might be expected on physical grounds, however, that as the time interval decreases sufficiently the carrier suffers fewer collisions able to destroy the coherence of its motion, so that classically $\langle[r(t)-r(0)]^2\rangle$ should ultimately increase approximately as t^2 for very short time. A t^ν dependence of

$\langle r^2\rangle_0(t)$ at sufficiently small times gives a $D(\omega)$ for $\nu>1$ that ultimately approaches zero with increasing ω (once ω^{-1} is sufficiently small to be comparable to the time over which the t^ν behavior occurs).

B. Limit of small λ and ω [$\max(\lambda,\omega)\ll\bar{w}$]

Our consideration of this limit will be restricted to the dynamic bond-percolation case (nearest-neighbor hopping probabilities restricted to the values 0 and w) well below the percolation threshold, i.e., for $f<f_c$ (with $f_c=1$ in one dimension). The main contribution to the integral for sufficiently small λ and ω then comes from the saturation value of $\langle r^2\rangle_0(t)$, which we take to be some value C/n_d. We then obtain from Eq. (31)

$$D(\omega,\lambda)=(\lambda+i\omega)C\ .$$

As expected intuitively, the $\omega=0$ static diffusion is completely renewal controlled, each carrier moving about and sampling each site within a cluster, and allowed to move out of the cluster only when one of the infrequent renewals occurs.

C. General limiting case of $\omega=0$

For zero ω and any nonzero λ, Eq. (37) gives, for the static diffusion coefficient,

$$D(0,\lambda)=n_d\lambda^2\int_0^\infty e^{-\lambda t}\langle r^2\rangle_0(t)dt\ , \tag{39}$$

which can be rewritten as

$$D(0,\lambda)=n_d\frac{[\langle r^2\rangle_0]_{\rm av}}{\bar{\tau}_{\rm ren}}\ , \tag{40}$$

where $\bar{\tau}_{\rm ren}=\lambda^{-1}$ for the exponential renewal-time distribution considered here, and where

$$[\langle r^2\rangle_0]_{\rm av}=\lambda\int_0^\infty e^{-\lambda t}\langle r^2\rangle_0 dt \tag{41}$$

is the average value attained by $\langle r^2\rangle_0(t)$ at the instant when renewal occurs in each ensemble system, $e^{-\lambda t}(\lambda\,dt)$ being the joint probability that time t elapses without renewal followed by renewal in the subsequent interval dt.

Equations (39)—(41) are in exact agreement with our previously derived[7] general expression for the static diffusion coefficient characterizing the average carrier motion after many renewals have occurred. It is less general, however, than the earlier result, having been derived here for a specific renewal-time distribution.

Similar conclusions follow also from Eq. (36), which describes the behavior of $\langle r^2\rangle(t)$ in terms of $\langle r^2\rangle_0(t)$. Both above and below the percolation threshold, the only unbounded contribution to (36) as $t\to\infty$ is the part of the integrand linear in t. The factor multiplying t in this contribution which, for $t\to\infty$, gives the static diffusion coefficient, reduces in that limit to precisely Eq. (39).

A significant conclusion follows, for the present model, by considering $\partial D(0,\lambda)/\partial\lambda$, given by

$$\frac{\partial D}{\partial\lambda}=2\lambda\int_0^\infty e^{-\lambda t}\langle r^2\rangle_0(t)dt-\lambda^2\int_0^\infty te^{-\lambda t}\langle r^2\rangle_0(t)dt\ . \tag{42}$$

For large λ, only the short-time behavior of $\langle r^2\rangle_0$ given by Ct (with C some positive constant) contributes, and evaluation of (42) in the large-λ limit leads to

$$\frac{\partial D(0,\lambda)}{\partial\lambda}\approx\frac{C}{\lambda}>0\ .$$

Therefore, under the present assumptions, $D(0)$ increases monotonically with λ for sufficiently large λ, all other parameters being held fixed, but eventually approaches some constant saturation value, in agreement with the behavior discussed in subsection A. We assume, of course, λ not to be so large that the assumption of $\langle r^2\rangle_0(t)$ linear in t breaks down.

IV. APPLICATION TO THE ONE-DIMENSIONAL DYNAMIC BOND-PERCOLATION MODEL

The dynamic bond-percolation model, in which a fraction f of bonds are available with hopping probability w and a fraction $1-f$ unavailable, is a useful special case to which the formal results of the previous sections apply. Furthermore, in the one-dimensional DBP model we have already reported an exact analytic solution for $\langle r^2\rangle_0(t)$, while Odagaki and Lax[30] have obtained solutions for $D_0(\omega)$ for the corresponding 1D static percolation model (without renewal). We show here how the results of Sec. II can be combined with the two sets of solutions for the static percolation problem in order to study $D(\omega,\lambda)$ and $\langle r^2\rangle(t)$ for the corresponding DBP problem.

A. $D(\omega,\lambda)$ in terms of the solution for $\langle r^2\rangle_0(t)$

In the one-dimensional continuous-time limit, the expression we have obtained[7] for $\langle r^2\rangle_0(t)$ is

$$\langle r^2\rangle_0(t)=2d^2(1-f)^2\sum_{l=0}^\infty l^2\sum_{k=0}^\infty\sum_{j=l}^\infty f^{k+j}\sum_{\{l'\}}e^{-2wt}I_{l'}(2wt)\ , \tag{43}$$

where d is the lattice spacing, I_l is the modified Bessel function of order l, l' denotes the various replicas[7] of lattice site l given, for a given k and j, by

$$l'=\begin{cases} l\pm 2\nu M, \\ (2j+1)-l+2\nu M, \\ -(2k+1)-l-2\nu M, \end{cases}$$

with $M=(j+k+1)$ and ν any non-negative integer. When (43) and (31) are combined, the resulting expression for $D(\omega,\lambda)$ involves the integral

$$\int_0^\infty e^{-(\lambda+2w+i\omega)t}I_{l'}(2wt)dt\ . \tag{44}$$

An analytic expression for (44) given by Gradshteyn and Ryzhik[37] leads to

$$D(\omega,\lambda)=\frac{2d^2(\lambda+i\omega)^2(1-f)^2}{A(\lambda,\omega,w)}\times\sum_{l=0}^\infty l^2\sum_{k=0}^\infty\sum_{j=l}^\infty f^{k+j}\sum_{\{l'\}}\left[\frac{2w}{B}\right]^{l'}\ , \tag{45}$$

where

$$A=[(\lambda+2w+i\omega)^2-(2w)^2]^{1/2} \tag{46a}$$

and

$$B=(\lambda+2w+i\omega)+A\ . \tag{46b}$$

Equations (45)—(46) are easily evaluated numerically.

B. $\langle r^2\rangle(t)$ in terms of the solution for $\langle r^2\rangle_0(t)$

Equation (43) expresses $\langle r^2\rangle_0(t)$ as a linear combination of $e^{-2wt}I_l(wt)$ terms. Precisely because of this linearity and the relation (36) between $\langle r^2\rangle(t)$ and $\langle r^2\rangle_0(t)$, it is seen immediately that $\langle r^2\rangle(t)$ is given by precisely the summation in (43) but with each $e^{-2wt}I_l(2wt)$ replaced by the corresponding

$$F_l=e^{-(\lambda+2w)t}I_l(2wt) +\lambda\int_0^t(2+\lambda t-\lambda\xi)e^{-(\lambda+2w)\xi}I_l(2w\xi)d\xi\ . \tag{47}$$

It should be noted, however, that although $e^{-2wt}I_l(2wt)$ is an occupation probability for site l in the 1D connected-chain random-walk problem, F_l often has values far larger than 1, and cannot be interpreted as a probability.

C. $D(\omega,\lambda)$ from the static percolation $D_0(\omega)$

The one-dimensional site percolation problem treated by Odagaki and Lax,[30] in which a fraction f of sites are occupied by acceptors whose possible excess electron can hop only to an occupied nearest neighbor (with hopping probability w) is formally equivalent to the *static* one-dimensional bond-percolation model of the preceding subsection (except for an extra factor of f which arises at certain points from the probability that the origin might be unavailable as an initial site). Although Odagaki and Lax evaluate $D_0(\omega)$ for the static percolation problem, extraction of an expression for $\langle r^2\rangle_0(t)$ from their results requires some effort, and so the two sets of solutions are somewhat complementary. By using our result (32) (replacing $i\omega$ by $\lambda+i\omega$) we can, however, now transform most of their conclusions about $D_0(\omega)$ for the static percolation problem directly into conclusions about our dynamic percolation model.

For example, we thereby obtain the following results.

1. Substitution of $\lambda+i\omega$ for $i\omega$ in $D^{(M)}(\omega)$

For a cluster of $M=(k+j+1)$ sites connected to each other and not connected to other sites, the formal result of substituting $\lambda+i\omega$ for $i\omega$ in the corresponding $D^{(M)}(\omega)$ is

$$D^{(M)}=wd^2\left[1+\frac{1}{M}\left[1+\frac{4w}{\lambda+i\omega}\right]\times\left[\frac{1}{Z_{(+)}^{2M}+1}-\frac{1}{Z_{(-)}^{2M}+1}\right]\right], \tag{48}$$

where

$$Z_{\pm}=\frac{1}{2}\left[\left[\frac{\lambda+i\omega}{w}\right]^{1/2}\pm\left[4+\frac{\lambda+i\omega}{w}\right]\right]. \tag{49}$$

This can be used to evaluate the ensemble-averaged diffusion coefficient for various possible M for the DBP model,

$$D(\omega,\lambda)=\sum_{M=1}^{\infty}(1-f)^2f^{M-1}MD^{(M)}(\omega,\lambda)\ . \tag{50}$$

2. Behavior of D in the $|\lambda+i\omega|\gg\omega$ limit

The behavior of D in the $|\lambda+i\omega|\gg\omega$ limit is given by

$$D(\omega,\lambda)\propto f-(2f)(1-f)\left[\frac{w^2}{(\omega-i\lambda)^2}-\frac{iw}{(\omega-i\lambda)}\right]. \tag{51}$$

The $i\omega\rightarrow\lambda+i\omega$ replacement used here can also be similarly applied to available analytic results for the static percolation problem in two or three dimensions.

3. Illustrative numerical results

Figure 1 shows the calculated behavior of $\langle r^2\rangle(t)$ calculated using (47) for the one-dimensional DBP model for various choices of λ/w. For $\lambda\gg w$, the motion is diffusive at all times, and the slope of $\langle r^2\rangle_0(t)$ versus wt [given by $D(\omega,0)$] is equal to its initial value $2fd^2$. Intermediate values of λ/w lead to curves with the same initial slope, but with a slope depending on λ in the long-time regime, and proportional to λ for long times in the small λ/w case (for which static diffusion is renewal controlled).

Figure 2 shows a typical $D(\omega)$ dependence on ω in one dimension. The curve approaches a saturation value with increasing ω. Although Fig. 2 bears a strong qualitative resemblance to some of the available ionic conduction frequency response data,[17] it must be kept in mind that certain important details (such as the frequency-dependent response of the polymer host) remain to be included, and that the present calculations are based on 1D solutions;

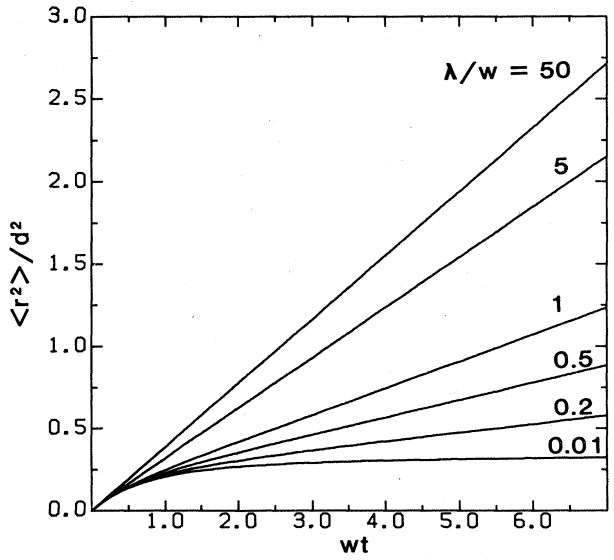

FIG. 1. Mean-square displacement in one dimension as a function of time for various renewal rates, calculated for $f=0.2$.

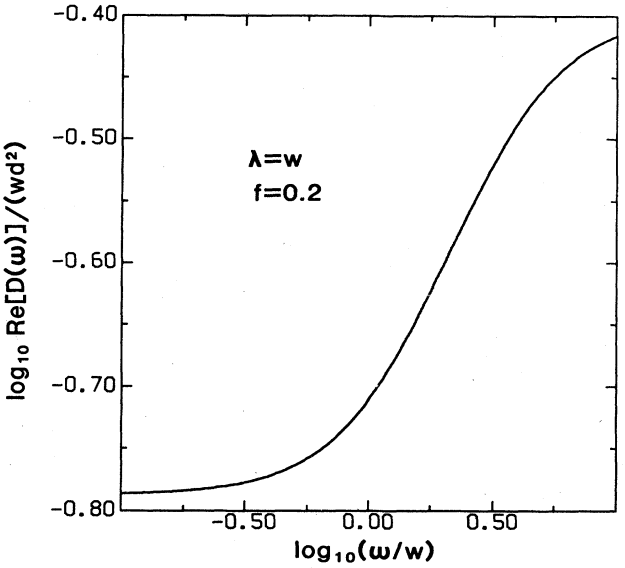

FIG. 2. Real part of $D(\omega)$ in one dimension [proportional to the conductivity $\sigma(\omega)$].

nevertheless, a more applied analysis[36] leads us to believe that the resemblance is not accidental. Also, as stressed above, the asymptotic behavior [$D(\omega)$ asymptotically constant for very large ω] is an artifact of the instantaneous hopping assumption, and certainly is unjustified for $\omega \gg w$.

V. CONCLUDING REMARKS

The great current interest in amorphous systems has led to extensive work on the theory and applications of generalized hopping and percolationlike models.[35] When, however, the matrix in which the hopping of the carrier of interest is itself moving and changing its configuration with an average rate λ, the observed transport behavior for observation times such that $t_{\rm obs} \gtrsim \lambda^{-1}$ will be affected both by the hopping and by the matrix renewal rate λ. This latter case of dynamic disorder appears to apply to many physical systems of interest, especially to transport in liquids, to membrane channel transport in biophysical situations,[38] and in polymers above T_g, but also to diffusion mechanisms such as the Grotthus scheme[15,16] for hydrogen-bonded materials, in which two different events, each occurring on a different time scale, are both required for diffusion to occur (in protonic materials, the two steps are a hydrogen-bond reorientation and a protonic jump). This case of motion in a dynamically disordered medium may be described by a modification of standard hopping models in which the hopping rate $w_{k\to j}$ from site k to site j changes its value on the time scale λ^{-1} (physically, this is caused by the changed relative geometry or energy of sites k and j as a result of the reorganization, or renewal, of the host material). A special case of such a dynamic disorder hopping model is the dynamic bond-percolation (DBP) model, in which the hopping rates $w_{k\to j}$ are restricted to the percolation-theory values 0 (for unavailable bonds with fraction $1-f$) and w (for available bonds with fraction f), and this assignment is changed (on the average) after time λ^{-1}. The DBP model has been discussed[7,8] previously, and some applications of it to ionic mobility in polymeric electrolytes have been given. As pointed out here (Sec. I), many of these results previously derived[7] for the DBP model apply also to a more general dynamic disorder model in which the distribution of hopping rates might be continuous. In the present paper, we have examined the frequency-dependent behavior for these more general dynamic hopping models. We have found a simple and general result, expressed by Eq. (31), which allows $D(\omega,\lambda)$ for the dynamic disorder hopping models to be found from $D(\omega,\lambda)$ for static disorder hopping models merely by the replacement $i\omega \to i\omega+\lambda$. We have also examined some limiting cases, and have calculated $D(\omega,\lambda)$ for one-dimensional DBP cases (Fig. 2).

The frequency dependence of the conductivity has been examined for polymeric electrolytes using microwave techniques;[17] the present results allow interpretation of those experiments in terms of the renewal process (Fig. 2 and Ref. 36). More importantly and more generally, the observed frequency-dependent conductivity may be interpreted, with the aid of these dynamic hopping models, in order to better understand the transport mechanisms in the physical systems to which the models are applicable. By starting with a microscopic model for these materials, we can therefore extend the considerations of the quasi-thermodynamic theories (free-volume,[39] configurational entropy[40]), in which kinetic effects are not easily included.

Kimball and Adams[25] have shown very generally that the conductivity $\sigma(\omega)$ must initially increase with ω for any hopping process.[41] The present analysis supports an analogous conclusion that $\sigma(\omega=0)$ must ultimately increase with λ in a dynamic-disorder hopping model (in accordance with intuition and with the case discussed in Sec. IV). This simple deduction is one example of the utility of (31); it also implies that maximization of λ should maximize $\sigma(0)$ so that maximum conduction results for maximum renewal rate. In the particular case of polymeric electrolytes, the best conductivity should then occur for the most liquidlike (lowest T_g) solid polymeric electrolyte; this conclusion has been tentatively reached previously.[42] Angell[4] has recently discussed a separation of disordered solid electrolytes on the basis of a decoupling ratio R_τ defined as the ratio of the structural relaxation time to the electric relaxation time. In the language of these dynamical hopping models, the glass case (such as glassy β-eucryptite[43] or NASIGLASS[44]) is characterized by very slow renewals and high elastic modulus $\lambda^{-1} \ggg t_{\rm obs}$, whereas the liquidlike regime applicable to polymeric solid electrolytes is defined by $\lambda^{-1} < t_{\rm obs}$. For the understanding of this latter case, we feel that standard hopping models must be generalized to consider the role of dynamic disorder, as in the work presented here.

ACKNOWLEDGMENTS

We are grateful for support to the U.S. Air Force Office of Scientific Research (AFOSR) and the U.S. Army Research Office (ARO). We thank D. F. Shriver and D. H. Whitmore for helpful remarks.

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