Self-consistent mode-coupling theory of electrical conductivity and incoherent excitation transport in disordered media

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(Received 27 May 1986; accepted 16 October 1986)

We present a new method for calculating transport properties of an excitation such as an electron, exciton, or vibron in a disordered medium, in which the dynamics are governed by a Pauli master equation. A hierarchy of self-consistent mode-coupling equations for the master equation propagator is developed, and the first member of the hierarchy is explicitly constructed. This equation can be used to calculate the propagator for an excitation transfer rate with any dependence on the intermolecular separation. The resulting propagator is exactly correct to lowest order in the density and in the ordered lattice limit. Extensive calculations are presented for the site percolation problem, for which a crossover in time to fractal dynamics is observed. The spectral dimension of a percolation cluster in three dimensions is predicted to be 4/3, in agreement with the conjecture of Alexander and Orbach and with recent simulations.

I. INTRODUCTION

A wide variety of dynamical processes in condensed phases can be described with the Pauli master equation (PME), including the motion of electrons, excitons, and vibrons. In general, the PME is valid in the regime in which quantum mechanical phase relationships (coherences) decay on a time scale that is short compared to the time scale associated with the dynamics of the excitation motion.1,2

The excitation motion under these circumstances is referred to as incoherent motion.2,3 In the opposite limit of coherent motion, the quantum coherences play an important role in the dynamics, and must be accounted for explicitly in a theoretical description. The experimental search for evidence of coherent exciton motion in molecular solids at low temperature is an active field of research.3

The incoherent motion condition is realized for materials for which the energetic disorder is in some sense large compared to the intermolecular interactions that underly the dynamics. For example, it has been established that the dynamics of electronic excited states in a dye solution at room temperature are well described by the PME.6,7 In this system, the magnitude of the resonant dipole–dipole (Förster) interactions is small compared to kT. Calculation of the configuration averaged solution of the PME for a disordered system is useful in other contexts besides exciton transport. Montroll has shown that the solution of a random walk problem on a given structure can be used to obtain the vibrational dynamics of a geometrically equivalent structure composed of masses and harmonic springs.8 This mapping of the excitation transport problem onto the vibrational dynamics problem has been used by Alexander, Orbach, and co-workers in their calculations of the density of vibrational modes for disordered, harmonic systems.9–12

The PME, as applied to the excitation transfer problem, is a set of coupled, linear, kinetic equations, describing the time evolution of each of the probabilities that a given molecule (or other entity) in the system is in an excited state [Eq. (2.1)]. In order to describe the dynamics of a disordered material, the transfer rates are taken to be random variables, and the solution of the PME must be averaged over these variables. In general, this averaged solution cannot be obtained exactly, and approximate methods must be developed. Several different theoretical techniques have been applied to this problem, including self-consistent calculations of the Green function.9,13–16 the continuous time random walk formalism,17–20 and the effective medium approximation.21–23 In this work, we present a new approach to performing self-consistent calculations of transport properties for disordered systems for which the dynamics are described by the PME.24 This approach has already been applied to the quantum percolation problem, in which the excitation dynamics are described by a Schrödinger equation, rather than the PME.25 The approach is similar in spirit to the effective dephasing approximation, which has been recently introduced in the context of Anderson localization.26 We focus on two dynamical quantities: D(ke,ε), the generalized diffusion kernel in Fourier–Laplace space [see Eq. (2.7)], and P0(t), the configuration averaged probability that an excitation that occupies a particular position at time τ can be found at that position at a later time t + τ. We begin with an exact relation between P0(τ), the Laplace transform of P0(t), and the diffusion kernel [Eq. (2.8a)]. We then develop a hierarchy of approximations in which the diffusion kernel is expressed as a functional of P0(τ), resulting in a second relation between these two quantities. When the second relation is substituted into the first, we obtain a closed self-consistent equation for P0(τ). The first member of this hierarchy is given in Eqs. (2.14). This equation contains an integration over the wave vector k that is conjugate to the position variable. This type of equation is characteristic of mode-coupling theories of nonlinear hydrodynamics, in which self-consistent equations are derived that contain similar integrations over a wave vector.27–29 An important feature of the mode-coupling theories is their capacity to correctly predict the long-time asymptotic power law decays of

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hydrodynamic variables ("long-time tails"). It can be demonstrated by a scaling argument, that if at long times, there is a single relevant length scale in the problem, then \( P_0(t) \) should decay as \( t^{-d/2} \) in \( d \) dimensions.\(^9\)\(^{17}\)\(^{19}\)\(^{20}\) This scaling argument is outlined in Sec. V. The predictions of the present approach are consistent with this correct asymptotic time dependence. Because of this analogy to the mode-coupling theories of hydrodynamics, we shall refer to our approach as the self-consistent mode-coupling method (SCMC).

In Sec. II, we consider excitation transport among active particles that are randomly distributed on the sites of a crystal lattice, such that a fraction \( c \) of the lattice sites are occupied. We present the SCMC approach, and derive explicitly the first member of a hierarchy of self-consistent equations for \( P_0(\varepsilon) \) [Eqs. (2.14)]. Transport properties that are calculated from this equation have the property that they are exactly correct to lowest order in the density of active particles and are also exactly correct in the limit that all of the lattice sites are occupied by active particles. The major advantage of the SCMC is its capacity to treat a transfer rate with any dependence on the intermolecular separation \( r \). For example, the transfer rate of electronic excitations between molecules with multipolar interactions has an inverse power law dependence on intermolecular separation, \( r^{-\alpha} \), while the rate associated with exchange interactions has the form \( \exp(-r/r_0) \).\(^{20}\)\(^{31}\) In this work we shall perform numerical calculations for the case of a transfer rate that is finite only for molecules occupying nearest neighbor sites on the lattice. Numerical calculations for transfer rates arising from multipolar and exchange interactions will be presented in a future work. The self-consistent equation is analyzed both numerically and analytically in Sec. III for the nearest-neighbor transfer rate. The dynamics for the nearest-neighbor transfer rate are affected by an underlying static phase transition: the site percolation transition.\(^{32}\)\(^{34}\) Below the critical concentration of active particles, \( c^* \), excitations will be confined to finite clusters of particles, and will not be able to move without bound from their initial position. At and above the critical concentration for site percolation, an infinite cluster exists, and excitations on this cluster can move arbitrarily far from their starting point. For one-dimensional systems, the SCMC correctly predicts that \( c^* = 1 \). In one dimension, all excitations are confined to finite clusters, if a finite fraction of the lattice sites are unoccupied by active particles. In two dimensions, the SCMC also yields \( c^* = 1 \), which differs from the correct result. It is known from simulations that the site percolation transition in two dimensions occurs at \( c^* \approx 1 \). For a square lattice,\(^{32}\) simulations yield \( c^* \approx 0.593 \). For a simple cubic lattice, the SCMC predicts a transition at \( c^* = 0.3358 \), which is in good agreement with the accepted value of \( c^* = 0.311 \), which was determined by simulation,\(^{32}\) and also with the predictions of other analytical theories.\(^{15}\)\(^{21}\)\(^{23}\)\(^{24}\)\(^{25}\) We present numerical calculations of \( P_0(t) \), the time dependent mean-squared displacement of an excitation, and the ac electrical conductivity over the full range of concentrations of active sites. There is currently a great deal of interest in the static and dynamic properties of fractal (self-similar) structures.\(^{35}\)\(^{40}\)\(^{41}\)\(^{42}\)\(^{43}\)\(^{44}\)\(^{45}\)\(^{46}\)\(^{47}\)\(^{48}\)\(^{49}\)\(^{50}\) Such a structure has the property that the mass contained in a sphere of radius \( r \) that is centered somewhere in the structure increases as \( r^{d_f} \), where \( d_f \) is the fractal or Hausdorff dimension of the structure, which is less than \( d \), the Euclidean dimension of the space in which the structure is embedded. (For a homogeneous medium, this mass increases as \( r^d \).) In Sec. V, we discuss the scaling argument that demonstrates that if at long times there is a single relevant length scale, then \( P_0(t) \approx t^{-d/2} \). This argument is carried out for a homogeneous (non-fractal) medium. It has been shown by Alexander and Orbach\(^{10}\) and by Rammal and Toulouse\(^{36}\) that in a fractal medium, \( P_0(t) \sim t^{-d/2} \), where \( d_f \) is the spectral or fracton dimension, is less than \( d \), the Euclidean dimension of the embedding space. The mean-squared displacement \( \langle r^2(t) \rangle \) increases as \( t^{d_f/d} \) at long times for a fractal structure, in contrast to the linear time dependence of this quantity for a homogeneous medium.\(^{10}\)\(^{37}\)\(^{38}\) The infinite percolation cluster at the critical point is an example of a fractal structure. The scaling condition that there be a single relevant length scale at long times is clearly satisfied for a random walk on a fractal structure such as the infinite percolation cluster at the critical point. However, \( P_0(t) \) in the site percolation problem is defined as a configuration averaged quantity that contains contributions from all clusters. Thus the scaling argument is not valid for \( P_0(t) \) in the site percolation problem, because at long times there is not a single relevant length scale. The dynamics are influenced by the entire distribution of cluster sizes. It can easily be shown, that for the site percolation problem with \( c < 1 \), \( P_0(t) \) decays not to zero, but to a finite value that is the configuration average of the inverse cluster size.\(^{15}\) If the configuration average were redefined to only include members of the infinite cluster for \( c > c^* \), then the scaling assumption would be valid, and \( P_0(t) \) would decay as \( t^{-d_f/d} \) at \( c = c^* \). The SCMC predicts that \( P_0(t) \) has an inverse power law decay at \( c = c^* \). It is reasonable to interpret this result as representing behavior on the infinite cluster. The predictions of the SCMC for the dynamics at the percolation threshold can thus be translated into predictions of the fractal and spectral dimensions of the infinite percolation cluster. The SCMC yields \( d_f = 2 \) and \( d_s = 4/3 \) in three dimensions. Alexander and Orbach\(^{10}\) have predicted that \( d_s = 4/3 \) for a percolation cluster embedded in a space of Euclidean dimensionality \( d \) with \( d > 2 \). Their conjecture is based on a scaling argument that relates \( d_f \) to critical exponents that are associated with the behavior of static properties at the percolation transition. The values of such exponents are known from computer simulations.\(^{32}\) The validity of the Alexander–Orbach conjecture has been borne out by computer simulations of random walks on percolation clusters. Ben-Avraham and Havlin\(^{30}\) have obtained \( d_s = 1.26 \pm 0.1 \), and Argyrakis and Kopolman\(^{40}\) have obtained \( d_s = 1.32 \pm 0.06 \) from simulations of random walks on percolation clusters on simple cubic lattices. It is well established that the infinite percolation cluster at the critical point is self-similar over length scales that are large compared to the lattice spacing. Let us consider the structure of a finite cluster whose size is large compared to the lattice spacing. There exists a range of length scales that are large compared to the lattice spacing and small compared to the cluster size such
that over these length scales the structure of the cluster cannot be distinguished from that of the infinite cluster at the critical point. Accordingly, there exists a range of time (or frequency) scales, such that the dynamics of an excitation on a finite cluster should be the same as the dynamics on the infinite cluster at the critical point. The existence of such a range of time scales holds also for the infinite cluster above the critical point, as this cluster is known to have a self-similar structure for a range of length scales, but to become homogeneous over large enough length scales. Thus there exists a range of time scales over which the dynamical response of the system is independent of the existence of an infinite cluster and reflects the fractal structure of all clusters. The SCMC predicts the existence of a crossover frequency, such that the system response for much larger frequencies is characteristic of fractal dynamics. [See Eqs. (3.13) and (3.14).] This crossover frequency vanishes at the critical point.

In Sec. IV we compare the SCMC to other theoretical treatments of incoherent transport for the percolation model. Odagaki and Lax have shown that for the special case of the percolation model, the ac conductivity can be calculated exactly in one dimension.41 The results of the SCMC are in excellent agreement with this exact calculation. The predic- tions of the SCMC in three dimensions are compared to those of the effective medium approximation (EMA) of Odagaki and Lax,21 Webman,22 and Korzeniowski, Friesner and Silbey.23 The dynamics predicted by the EMA at the critical concentration are consistent with the infinite cluster having $d^* = 1$ and $d_p = 2$. Our conclusions are summarized in Sec. V. The SCMC should be compared to the EMA and to the self-consistent, diagrammatic theory of incoherent transport that was developed by Loring, Andersen, and Fayer (LAF).15 All three approaches yield transport properties that are correct at low densities of active particles and in the ordered lattice limit. In addition, all three approaches predict a transition in the conductivity in the site percolation problem. The EMA has provided great insight into the dynamics of the site and bond percolation models. Like the SCMC, the EMA predicts a power law time dependence for $\rho_0(t)$ at $c = c^*$, from which the spectral dimension of a percolation cluster can be estimated. However, the EMA cannot be extended in a straightforward manner to investigate the case of a transfer rate of arbitrary distance dependence. The SCMC and LAF theories can be applied to a transfer rate of any distance dependence. A scaling argument [see Eq. (5.11)] shows that if there is a single relevant length scale in the problem at long times, then $\rho_0(t)$ should decay at long times as $t^{-d/2}$. As discussed in Sec. V, the scaling condition should be satisfied for a transfer rate that is a smooth function of distance and that does not have an upper cutoff. The SCMC is consistent with this prediction, while the LAF theory predicts that $\rho_0(t)$ decays exponentially with time at long times.14,16 The SCMC equation in three dimensions represents an improvement over existing theories of incoherent transport, in that it is the only formulation that is correct at low densities and in the ordered lattice limit, that predicts a transition in the self-consistent equation.

II. DERIVATION OF THE SELF-CONSISTENT EQUATION

We consider a lattice with a fraction $c$ of the sites occupied by active particles that are capable of retaining and transferring an excitation. These particles are assumed to be randomly distributed among the lattice sites. The unoccupied sites do not participate in the transport. The dynamics of a particular realization of the random system are governed by a Pauli master equation:

$$\frac{dp}{dt} = W \cdot p.$$  \hspace{1cm} (2.1)

$p$ is an $N$ component vector whose $n$th element is the probability that an excitation resides on the particle labeled $n$. $N$ is the number of active particles. $W$ is an $N \times N$ matrix whose elements are given by

$$W_{nm} = w_{nm} - \delta_{nm} \sum_j w_{jm}.$$  \hspace{1cm} (2.2)

$w_{nm}$ is the rate of excitation transfer between particles labeled $n$ and $m$. We shall assume that $w_{nm} = w_{mn}$. The excitation dynamics in this model are given by $\mathcal{P}(r,t)$, the configuration-averaged probability that an excitation undergoes a displacement $r$ in a time $t$:

$$\mathcal{P}(r,t) = (N-1) \langle [\exp(Wt)]_{12} \delta_{r_{12}} \rangle + \delta_{r,0} \mathcal{P}_0(t),$$  \hspace{1cm} (2.3)

$$\mathcal{P}_0(t) = \langle [\exp(Wt)]_{11} \rangle.$$  \hspace{1cm} (2.4)

$r_{12} = r_1 - r_2$, where $r_n$ is the position of the particle labeled $n$. The angular brackets denote a configuration average.\(^5\) $\mathcal{P}_0(t)$ in Eq. (2.4) is the probability that an excitation that is located at a particular site at a given time can be found at that site after a time $t$ has elapsed. $P(k,e)$, the Fourier–LaPlace transform of $\mathcal{P}(r,t)$, is given by

$$P(k,e) = \sum_t \exp(ikr) \int_0^\infty dt \exp(-\epsilon t) P(r,t),$$  \hspace{1cm} (2.5)

and $P_0(e)$, the Laplace transform of $\mathcal{P}_0(t)$, is given by

$$P_0(e) = \int_0^\infty dt \exp(-\epsilon t) \mathcal{P}_0(t).$$  \hspace{1cm} (2.6)

The diffusion kernel $D(k,e)$ is related to $P(k,e)$ by

$$D(k,e) = [e + k^2 D(k,e)]^{-1}.$$  \hspace{1cm} (2.7)

If $D(k,e)$ approaches a limit $D(0,0)$ as $k$ and $\epsilon$ approach zero, then for sufficiently small $k$ and $\epsilon$, $P(k,e)$ approaches the propagator of an ordinary diffusion equation with diffusion constant $D(0,0)$. Our self-consistent formulation is based on the following pair of coupled equations for $D(k,e)$ and $P_0(\epsilon)$:24

$$P_0(\epsilon) = \Omega_d^{-1} \int d k [e + k^2 D(k,e)]^{-1},$$  \hspace{1cm} (2.8a)

$$D(k,e) = \tilde{D}[k,P_0(\epsilon)].$$  \hspace{1cm} (2.8b)

Equation (2.8a) is an exact relation between $P_0(\epsilon)$ and $D(k,e)$, which follows from the definitions of these quantities in Eqs. (2.4)–(2.7). The integration in Eq. (2.8a) is
carried out over the first Brillouin zone, whose "volume" is 
\( \Omega_d \). \( \Omega_d = (2\pi)^d/V \), where \( V \) is the volume of the unit cell. \( d \) is the spatial dimensionality.

In Eq. (2.8b), \( D(k, \epsilon) \) is expressed as a functional of 
\( P_0(\epsilon) \), which depends implicitly on \( \epsilon \) through its dependence on \( P_0 \). Let us define a function \( F \) such that \( P_0 = F(\epsilon) \). If the inverse of \( F \) exists, so that \( \epsilon = F^{-1}(P_0) \), then any function of \( \epsilon \) can be written as a functional of \( P_0 \). In particular, 
\( D(k, \epsilon) = D[k, F^{-1}(P_0)] \equiv \bar{D}(k, P_0) \). Equation (2.8b) should be regarded as a definition of the functional \( \bar{D} \). The only assumption underlying this definition is that \( F^{-1} \) exists. Since \( \bar{D}(k, P_0) \) cannot be determined exactly for the present model, we shall derive a hierarchy of approximations to this quantity [Eq. (2.12)]. An approximation to \( \bar{D}(k, P_0) \) provides a second, independent relation between \( D(k, \epsilon) \) and \( P_0(\epsilon) \), which, in combination with Eq. (2.8a), yields a pair of coupled equations for these two quantities.

A systematic procedure for constructing \( \bar{D}(k, P_0) \) is developed in Appendix A. We first expand \( \bar{D} \) in a power series in \( c \), the fraction of lattice sites that are occupied by the active particles:

\[
\bar{D} \left[ k, P_0(\epsilon) \right] = \sum_{j=1}^{\infty} c^j \bar{D}_j \left[ k, P_0(\epsilon) \right].
\]  

(2.9)

The expansion of \( \bar{D} \) in Eq. (2.9) should be understood as follows. \( \bar{D} \) depends on \( c \) explicitly, in addition to depending implicitly on \( \epsilon \) through the dependence of \( P_0 \) on \( c \). Equation (2.9) is an expansion of \( \bar{D} \) with respect to its explicit dependence on \( c \). The coefficients \( \bar{D}_j \) depend on \( c \) only through the dependence on \( c \) of \( P_0 \). Each term in the expansion depends on \( c \) to infinite order. Equations (2.8b) and (2.9) can therefore be regarded as a partially resummed density expansion of \( D(k, \epsilon) \). In Appendix A, we present a procedure by which \( \bar{D}_n \) can be uniquely determined from the coefficients of \( c^n \) with \( m < n \) in the ordinary density expansions of \( D \) and \( P_0 \) [Eqs. (A2) and (A3)]. The coefficients of \( c^n \) in the expansions of \( D \) and \( P_0 \) can be obtained from the exact values of these quantities for systems with \( j \) active particles, where \( j = m + 1 \). The expansion in Eq. (2.9) can be truncated to obtain an approximation \( \bar{D}^n \) that is exact to order \( n \) in \( c \),

\[
\bar{D}^{(n)}(k, P_0) = \sum_{j=1}^{n} c^j \bar{D}_j(k, P_0).
\]  

(2.10)

A hierarchy of self-consistent equations can be constructed according to the following procedure. \( \bar{D}^{(n)}(k, P_0) \) is substituted for \( \bar{D}(k, P_0) \) in the right-hand side of Eq. (2.8b). The right-hand side of Eq. (2.8a) is substituted for \( P_0(\epsilon) \) in \( \bar{D}^{(n)}(k, P_0) \). The result is a closed equation for the diffusion kernel. We can improve upon approximations of the form given in Eq. (2.10) by noting that at \( c = 1 \) (no disorder), the diffusion kernel can be calculated exactly since the system is translationally invariant. In this case, \( D(k, \epsilon) \) is independent of \( \epsilon \) and is given by

\[
D(k, \epsilon) = k^{-2} \sum_r w(r) \left[ 1 - \exp(ikr) \right], \quad c = 1. 
\]  

(2.11)

We shall denote \( D(k, \epsilon) \) at \( c = 1 \) by \( \bar{D}(k) \) [Eq. (2.14d)]. Since \( D(k, \epsilon) \) is equal to \( \bar{D}(k, P_0) \), \( \bar{D}(k, P_0) \) must also reduce to \( \bar{D}(k) \) at \( c = 1 \). We now have two pieces of information regarding \( \bar{D} \): a truncated density expansion [Eq. (2.10)] that will be valid for \( c < 1 \) and the exact form at \( c = 1 \) [Eq. (2.11)]. By constructing an approximation that interpolates between Eqs. (2.10) and (2.11), we guarantee that the self-consistent equation will yield exact results at \( c = 1 \). A hierarchy of such approximations can be derived by constructing Padé approximants for \( \bar{D}(k, P_0) \) in the variable \( \gamma = c/(1 - c) \):

\[
\bar{D}(k, P_0) = \left[ \sum_{j=1}^{n} a_j \gamma^j \right] / \left[ 1 + \sum_{j=1}^{n} b_j \gamma^j \right].
\]  

(2.12)

The coefficients \( a_j \) and \( b_j \) in Eq. (2.12) are obtained by requiring that Eq. (2.12) agree with Eq. (2.10) to order \( c^n \), and that it reduce to Eq. (2.11) at \( c = 1 \). Application of these criteria for \( j = 1 \) yields

\[
a_1 = \bar{D}_1(k, P_0),
\]  

(2.13a)

\[
b_1 = \bar{D}_1(k, P_0) / \bar{D}(k).
\]  

(2.13b)

In Appendix A [Eq. (A8)], we show that \( \bar{D}_1(k, P_0) \) can be obtained by calculating \( D_1(k, \epsilon^{-1}) \), the first term in the density expansion of \( D(k, \epsilon) \) [Eq. (A2)], and replacing \( \epsilon^{-1} \) with \( P_0 \). \( D_1(k, \epsilon^{-1}) \) is given in Eq. (A10). The first member of the hierarchy of self-consistent equations for \( P_0 \) is obtained by setting \( n = 1 \) in Eq. (2.12) and substituting the resulting approximation for the diffusion kernel into the right-hand side of Eq. (2.8a) to yield

\[
P_0(\epsilon) = \Omega_d^{-1} \int d k \left[ \epsilon + k^2 \bar{D}(k, P_0) \right]^{-1},
\]  

(2.14a)

\[
\bar{D}(k, P_0) = c \bar{D}_1(k, P_0) / \left[ 1 - c + c \bar{D}_1(k, P_0) / \bar{D}(k) \right],
\]  

(2.14b)

\[
\bar{D}_1(k, P_0) = k^{-2} \sum_r \left[ 1 - \exp(ikr) \right] w(r) / \left[ 1 + 2w(r) P_0 \right],
\]  

(2.14c)

\[
\bar{D}(k) = k^{-2} \sum_r w(r) \left[ 1 - \exp(ikr) \right].
\]  

(2.14d)

Equations (2.14) form the primary result of this article. They provide a self-consistent equation for the dynamics that is valid for any transfer rate \( w(r) \). The summation in Eq. (2.14c) runs over all displacements in the lattice. When Eqs. (2.14d) and (2.14c) are substituted into Eq. (2.14b), and Eq. (2.14b) is substituted into Eq. (2.14a), the result is a closed self-consistent equation for \( P_0(\epsilon) \). The fundamental approximation upon which this equation is based is given in Eq. (2.14b).

An approximation to the propagator \( P(k, \epsilon) \) can be obtained from this equation as follows. The self-consistent equation is solved to yield \( P_0(\epsilon) \). Substitution of this result into Eq. (2.14b) and application of Eq. (2.8b) yields an approximation to \( D(k, \epsilon) \). \( P(k, \epsilon) \) is obtained from \( D(k, \epsilon) \) with Eq. (2.7). All transport properties of an excitation whose dynamics are governed by a Pauli master equation [Eq. (2.1)] can be calculated from \( P(k, \epsilon) \). In the next section, we shall consider the solution of Eqs. (2.14) for a transfer rate that is finite between particles that are nearest neighbors on the lattice, and which vanishes otherwise (site percolation). The asymptotic behavior of \( \bar{S}_0(t) \) for other forms of the transfer rate is discussed in Sec. V.
III. APPLICATION TO SITE PERCOLATION

In this section, we consider the solution of the self-consistent equation [Eqs. (2.14)] for a transfer rate $w(r)$ that is finite for particles that are nearest neighbors on the lattice and that vanishes otherwise. This model provides an approximate description of exciton transport that arises from short-ranged interactions, such as the motion of conduction electrons or triplet excitons. The dynamics for this transfer rate are strongly influenced by an underlying static phase transition: the site percolation transition. In the site percolation problem, one considers a lattice for which a fraction $c$ of the sites are occupied by randomly distributed conducting particles. Particles that occupy nearest-neighbor sites on the lattice are said to form a bond. A cluster is defined as a group of particles connected to each other by bonds. According to percolation theory, there exists a critical concentration $c^*$, such that for $c < c^*$, there is zero probability that a cluster of infinite extent will exist, and that for $c > c^*$, there is unit probability that such a cluster will be formed. Let us now consider transport that arises from a nearest-neighbor transfer rate. For $c < c^*$, all excitations are necessarily confined to finite clusters, and the mean-squared displacement of an exciton must reach a finite limiting value in the limit of long times. For $c > c^*$, the contribution to the mean-squared displacement from excitations on the infinite cluster will ensure that this quantity increases without bound for increasing time.

For a nearest-neighbor transfer rate of magnitude $w$, the first member of our hierarchy of approximations to $D(k,P_0)$ in Eq. (2.14b) has the form

$$\tilde{D}(k,P_0) = \left(2a^2cw/q^3\right) \left[d - \sum_{j=1}^{d} \cos(q_j)\right]^{-1},$$

$$q_j = k \cdot a_j.$$  \hspace{1cm} (3.1a, 3.1b)

In Eq. (3.1b), $a_j$ is the lattice vector in the $j$th direction, which has magnitude $a$. In Eq. (3.1a), the diffusion kernel factors into the product of a term that depends on $P_0$ and a term that depends on the wave vector. Since $\tilde{D}(k,P_0) = D(k,e)$, Eq. (3.1a) yields an approximation to $D(k,e)$ that factors into the product of a term that depends on frequency and a term that depends on the wave vector. Hence, knowledge of $D(0,e)$ is sufficient to construct $D(k,e)$. This factorization of the diffusion kernel in our lowest order approximation is a special feature of the nearest-neighbor transfer rate. For other forms of the transfer rate, our approximation to $D(k,e)$ does not factor in this manner, as can be seen from Eq. (2.14b). Substitution of (3.1) into Eq. (2.14a) yields a pair of self-consistent equations for $P_0(e)$ and $\tilde{D}(0,P_0)$:

$$\tilde{D}(0,P_0) = a^2cw/[1 + 2(1-c)wp_0],$$

$$P_0(e) = \left[a^2/2\tilde{D}(0,P_0)\right] \left[ea^2/2\tilde{D}(0,P_0)\right].$$  \hspace{1cm} (3.2a, 3.2b)

In Eq. (3.2b), $I_d(x)$ is the diagonal element of the lattice Green’s function:

$$I_d(x) \equiv \pi^{-d} \int_0^\infty dq_1 \cdots \int_0^\infty dq_d \left[ x + d - \sum_{j=1}^{d} \cos(q_j) \right]^{-1}.$$  \hspace{1cm} (3.3)

Equations (3.2) can be written as a single equation for $P_0$ or for $\tilde{D}(0,P_0)$. Substituting Eq. (3.2b) into Eq. (3.2a) and noting that $\tilde{D}(0,P_0) = D(0,e)$ yields a self-consistent equation for $D(0,e)$:

$$D(0,e) = ca^2w/[1 + [1 - c]a^2w/D(0,e)] \times I_d \left[ a^2/2D(0,e) \right].$$  \hspace{1cm} (3.4)

The propagator $P(k,e)$ is determined from the solution of Eq. (3.4) as follows. $D(k,e)$ is related to $D(0,e)$ by Eq. (3.1a):

$$D(k,e) = 2q^{-2} \left[d - \sum_{j=1}^{d} \cos(q_j)\right] D(0,e).$$  \hspace{1cm} (3.5)

$P(k,e)$ is obtained from $D(k,e)$ with Eq. (2.7).

We begin our analysis of Eqs. (3.2) [or equivalently, Eq. (3.4)] by considering the asymptotic long time or small frequency limits of the transport properties. Let us consider the solution of Eq. (3.4) in the limit of small $e$. The behavior of this equation in $d$ dimensions depends on the properties of $I_d(x)$, which is defined in Eq. (3.3). The analytic properties of this function are well known. The argument of $I_d$ in Eq. (3.4) is $a^2e^2/2D(0,e)$. For $c > c^*$, the critical concentration for site percolation, we expect that $D(0,e)$ will approach a finite limit as $e$ approaches zero, and hence that the argument of $I_d$ becomes arbitrarily small for sufficiently small $e$. For $c < c^*$, we expect $D(0,e)$ to have the form $A(c)e^{-\epsilon}$, where $A(c)$ is a function of $c$ that diverges as $c$ approaches $c^*$ from below. As $e \to 0$, $a^2/2D(0,e)$ will approach the limit $a^2/A(c)$, which goes to zero as $c$ approaches $c^*$ from below. Thus, in evaluating Eq. (3.4) in the $e \to 0$ limit for $c > c^*$ or $c < c^*$ very close to but less than $c^*$, we need only consider the behavior of $I_d(x)$ for small values of $x$. The limiting behavior of this function in one, two, and three dimensions is

$$\lim_{e \to 0} I_d(x) = \begin{cases} \frac{(2\pi)^{-1/2}}{\Gamma(d/2)}, & d = 1 \\ \frac{2\pi^{-1} \ln(x^{-1})}{\Gamma(3/2)}, & d = 2 \\ \frac{4\pi^{-1/2} \Gamma(d/2)}{\Gamma(3/2)}, & d = 3 \end{cases}$$

with

$$I_5(0) \approx 0.5055.$$  \hspace{1cm} (3.6a, 3.6b)

By substituting the three expressions in Eq. (3.6a) into Eq. (3.4), we obtain self-consistent equations for $D(0,e)$ that are valid for small $e$ and in the concentration regime described above. We shall now analyze the resulting equation in one, two, and three dimensions.

In one dimension ($d = 1$), Eq. (3.4) assumes the form

$$D(0,e)/D_0 = c - (1-c) [D(0,e)/ca^2]^{1/2},$$  \hspace{1cm} (3.7a)

$$D_0 = a^2w.$$  \hspace{1cm} (3.7b)

In the limit of small $e$, the physically reasonable solution of Eq. (3.7a) has the form

$$D(0,e) = \left[\frac{c}{(1-c)}\right]^{a^2} D_0, \quad c < 1.$$  \hspace{1cm} (3.8)

At $c = 1$, the solution of Eq. (3.7a) is $D(0,e) = D_0$, which is the exact correct result for an ordered lattice. The form of our approximation to $D(k,P_0)$ in Eq. (2.14b) guarantees that Eq. (3.4) will be exact at $c = 1$. Equation (3.8) shows that for $d = 1$, $D(0,e)$ vanishes as $e$ approaches zero for
c < 1. The percolation transition is predicted to occur at 
\( c = 1 \), which is the correct result for \( d = 1 \). For \( d = 2 \), substi-
tution of Eqs. (3.6a) into Eq. (3.4) yields

\[
D(0, \varepsilon)/D_0 = c - \frac{1}{\pi \varepsilon} \ln \left[ 2D(0, \varepsilon)/a^2 \varepsilon \right].
\]  
(3.9)

Equation (3.9) can be solved in the limit of small \( \varepsilon \) by postu-
lating a solution of the form \( D(0, \varepsilon) = A \varepsilon^\alpha \), and checking for 
consistency. The result is

\[
D(0, \varepsilon) = \begin{cases} 
\left( a^2 \varepsilon^2 / 2 \right) \exp \{ 2 \pi \varepsilon / (1 - c) \}, & c < 1 \\
D_0, & c = 1 
\end{cases}
\]  
(3.10)

As in \( d = 1 \), \( D(0, \varepsilon) = A \varepsilon \) as \( \varepsilon \) approaches zero for \( c < 1 \), where \( A \) is a function of \( c \) that diverges as \( c = 1 \) is ap-
ached. The percolation transition is thus predicted to oc-
cur at \( c = 1 \) in two dimensions. The site percolation thresh-
old for a square lattice is known to occur at \( c^* \approx 0.593 \). The self-
consistent equation for the nearest-neighbor transfer rate 
[Eq. (3.4)] is thus more accurate for \( d = 1 \) than for \( d = 2 \) in this respect.

\[
D(0, \varepsilon) = \begin{cases} 
\left[ B a^2 (c^* - c)^{-2} - 2 B^2 (a^2 / D_0) (c^* - c)^{-3} (1 - c) \varepsilon^2 \right], & c < c^* \\
D_0 (c - c^*) / (1 - c^*), & c > c^* \\
[D_0 (c - c^*) / 2 \pi]^{2/3} \varepsilon^{1/3}, & c = c^*
\end{cases}
\]  
(3.15)

with

\[
B = \frac{1}{(1 - c)(1 - c^*) / 2 \pi}.
\]  
(3.16)

Equation (3.11) predicts a site percolation transition at 
\( c^* \approx 0.3358 \). For \( c < c^* \), \( D(0, \varepsilon) \) is linear in \( \varepsilon \) for small \( \varepsilon \), with a coeffi-
cient that diverges as \( (c - c^*)^{-2} \). For \( c > c^* \), \( D(0, \varepsilon) \) approaches a constant value for small \( \varepsilon \) that is linear in 
\( c - c^* \). At the critical point \( (c = c^*) \), \( D(0, \varepsilon) \sim \varepsilon^{1/3} \). 
Equation (3.13) shows that for \( \varepsilon \gg \varepsilon_c \), \( D(0, \varepsilon) \) is proportional to 
\( \varepsilon^{1/3} \). This result holds both for \( c < c^* \) and for \( c > c^* \). For \( \varepsilon \ll \varepsilon_c \), the response of the system is different for \( c > c^* \) than for \( c < c^* \), while for \( \varepsilon \approx \varepsilon_c \), the response of the system is insen-
sitive to the presence of an infinite percolating cluster. The crossover frequency \( \varepsilon_c \) vanishes as \( c \) approaches \( c^* \). Thus, at \( c = c^* \), the \( \varepsilon^{1/3} \) behavior is dominant for small frequencies.

Equations (3.15) can be used to determine the behavior at long times of \( \langle r^2(t) \rangle \), the mean-squared displacement of an excitation. The Laplace transform of \( \langle r^2(t) \rangle \) is related to 
\( D(0, \varepsilon) \) by

\[
\int_0^\infty dt \exp (- \alpha t) \langle r^2(t) \rangle = 2d \alpha \varepsilon^{-2} D(0, \varepsilon). 
\]  
(3.17)

The asymptotic behavior of \( \langle r^2(t) \rangle \) can be obtained from Eqs. (3.15) and (3.17), using the Tauberian theorem for Laplace transforms. Substituting Eqs. (3.15) into Eq. (3.17) and inverting the Laplace transform yields

\[
\lim_{t \to \infty} \langle r^2(t) \rangle \sim \begin{cases} 
\frac{a^2 B (c^* - c)^{-2}}{D_0 (1 - c^*)^{-1} (c^*) t}, & c < c^* \\
[D_0 (c - c^*) / 2 \pi]^{2/3} \varepsilon^{1/3}, & c > c^* 
\end{cases}
\]  
(3.18)

The mean-squared displacement reaches a finite asymptotic value at long times for \( c < c^* \), increases linearly with time for \( c > c^* \), and increases as \( t^{2/3} \) at \( c = c^* \). It has been established by computer simulations, that the percolating cluster at

Substitution of Eqs. (3.6a) into Eq. (3.4) yields the following self-consistent equation for \( d = 3 \):

\[
D(0, \varepsilon) [D(0, \varepsilon)/D_0 - (c - c^*) (1 - c^*)^{-1}]^2 = \frac{(a^2 / 2 \pi)^2 (1 - c^*)^2}{\varepsilon},
\]  
(3.11)

\[
c^* = I_3(0) / [1 + I_3(0)] \approx 0.3358.
\]  
(3.12)

The physically reasonable solution to Eq. (3.11) is given by

\[
D(0, \varepsilon) = [D_0 \varepsilon_0 (1 - c) / 4 \pi]^{2/3} \varepsilon^{1/3} \left[ \left[ 1 + (1 + \varepsilon / \varepsilon_c)^{1/2} \right]^{3/5} + \left[ 1 - (1 - \varepsilon / \varepsilon_c)^{1/2} \right]^{3/5} \right]^2,
\]  
(3.13)

\[
\varepsilon_c = (16 \pi^2 / 27) (D_0 / a^2) (1 - c^*)^{-3} (1 - c)^{-2} |c^* - c|^3.
\]  
(3.14)

The "ε+" in Eq. (3.13) should be interpreted as "+" for \( c < c^* \), and as "−" for \( c > c^* \). Expansion of the quantity in brackets on the right-hand side of Eq. (3.13) in powers of \( \varepsilon \) for \( \varepsilon \ll \varepsilon_c \) reveals that \( c = c^* \) is a critical point. For small \( \varepsilon \), Eq. (3.13) reduces to

\[
\sigma(\omega) = (ne^2 / kT) D(0, \varepsilon),
\]  
(3.19a)

\[
\sigma(\omega) = \sigma'(\omega) + i \alpha(\omega).
\]  
(3.19b)

We denote the real and imaginary parts of the complex electrical conductivity by \( \sigma' \) and \( \sigma'' \), respectively. \( n \) is the number density of the charge carriers, and \( e \) is the magnitude of their electrical charge. The ac conductivity is proportional to \( \sigma'(\omega) \). Setting \( \varepsilon = i \omega \) in Eq. (3.13) and taking the real part yields an expression for \( \sigma'(\omega) \) that is valid for small frequencies at concentrations greater than \( c^* \) and at concentrations less than but very close to \( c^* \). This result is given in Eqs. (B1)–(B8) of Appendix B, and has the form

\[
\sigma(\omega) = (ne^2 / kT) D(0, \varepsilon),
\]  
(3.19a)

\[
\sigma(\omega) = \sigma'(\omega) + i \alpha(\omega).
\]  
(3.19b)
\[ \sigma'(\omega) = \sigma_0[(1 - c)/2\pi]^{2/3}(\omega/\omega_c)^{1/3}F(\omega/\omega_c) \]  
(3.20a)

\[ \sigma_0 = ne^2D_o/(kT) \]  
(3.20b)

\[ F(\omega/\omega_c) \sim \begin{cases} 
1, & \omega \gg \omega_c, \\
\omega^{5/3}, & \omega \ll \omega_c, \ c < c^* \\
\omega^{-1/3}, & \omega \ll \omega_c, \ c > c^* 
\end{cases} \]  
(3.20c)

The crossover frequency \( \omega_c \) is equal to \( \varepsilon_c \), which is defined in Eq. (3.14). In all of the numerical calculations presented here, \( \sigma(\omega) \) is given in units of \( \sigma_0 \) [Eq. (3.20b)]. For \( c > c^* \) and \( \omega \ll \omega_c \), we have

\[ \sigma'(0) = \sigma_0(1 - c^*)^{-1}(1 - c^*) . \]  
(3.21)

On the insulating side of the transition \( (c < c^*) \), \( \sigma'(\omega) \) will be proportional to \( \omega^2 \) for \( \omega \ll \omega_c \):

\[ \sigma'(\omega) = 2\sigma_0 B^2(c^* - c)^{-3}(1 - c^*)(\omega/\omega_c)^2. \]  
(3.22)

From Eq. (3.15) [or Eqs. (B1)–(B8)], we see that for \( \omega \gg \omega_c \) and \( c > c^* \) or \( c < c^* \),

\[ \sigma'(\omega) = \sigma_0(3^{1/2}/2)[(1 - c)/2\pi]^{2/3}(\omega/\omega_c)^{1/3} . \]  
(3.23)

Calculations of \( \sigma'(\omega) \) for small frequencies in the vicinity of the critical point from Eqs. (B1)–(B8) are shown in Fig. 1(A) for \( c = c^*, \ c^* \pm 0.005, \) and \( c^* \pm 0.01 \). The crossover frequency for these concentrations can be calculated from Eq. (3.14). For \( c = c^* \pm 0.005 \), \( \log(\omega_c/2\omega) \approx -5.5 \), and for \( c = c^* \pm 0.01 \), \( \log(\omega_c/2\omega) \approx -4.6 \). The crossover to the \( \omega^{1/3} \) behavior of Eq. (3.23) is clearly illustrated, as is the vanishing of \( \omega_c \) as \( c \) approaches \( c^* \). From Eq. (3.14), we see that \( \omega_c \sim |c - c^*|^3 \). \( \sigma'(\omega) \) is shown in Fig. 1(B) for the values of \( c \) that were used in Fig. 1(A).

Using Eq. (3.6a), we have explored the asymptotic behavior of the solution of Eq. (3.4) at small frequencies for \( d = 1, 2, \) and 3. We next turn to the calculation of transport properties of linear and simple cubic lattices for all times and concentrations. In one dimension, the diagonal element of the lattice Green's function \( I_1(x) \), defined in Eq. (3.3), can be evaluated in closed form:

\[ I_1(x) = [x^2 + 2x]^{-1/2} . \]  
(3.24)

Substitution of Eq. (3.24) into the self-consistent equation for \( P^o_0(\varepsilon) \) [Eqs. (3.2)] yields a cubic equation for this quantity:

\[ 2w(1 - c)e^2P^3_0 + (e^2 + 4wce)P^2_0 - 2w(1 - c)P_0 - 1 = 0 . \]  
(3.25)

We have determined \( \mathcal{P}_0(t) \) by obtaining the approximate root of Eq. (3.25) and inverting the Laplace transform numerically with the Stehfest algorithm.\(^{45}\) The results for \( c = 0.2, 0.4, 0.6, 0.8, \) and 1 are shown in Fig. 2. At \( c = 1 \), Eq. (3.25) yields the exactly correct result, which decays as \( t^{-1/2} \) for long times. For \( c < 1 \), \( \mathcal{P}_0(t) \) decays to a finite value at long times, indicating that all excitations are localized on clusters of finite size.

The wave vector integration in Eq. (3.3) cannot be carried out analytically in three dimensions to yield an expression for \( I_1(x) \) in closed form. Therefore, the self-consistent equation [Eqs. (3.2) or Eq. (3.4)] must be solved numerically in three dimensions. The results for \( c = 0.2, 0.3, 0.4, 0.6, \) and 1 are shown in Fig. 3, and for a range of concentrations about \( c^* = (c = 0.3, 0.32, 0.34, 0.36, \) and 0.38) in Fig.

**FIG. 1.** (A) The ac conductivity \( \sigma'(\omega) \), calculated from Eqs. (B1)–(B8), is shown for \( c = c^*, c^* \pm 0.005, \) and \( c^* \pm 0.01 \). \( \omega_c \) is proportional to \( \omega^2 \) for \( c < c^* \), and is independent of frequency for \( c > c^* \). For \( \omega \gg \omega_c \), \( \sigma'(\omega) \sim \omega^{1/3} \) for \( c > c^* \) and for \( c < c^* \). The crossover frequency \( \omega_c \) vanishes as \( |c - c^*|^3 \). For \( c = c^* \pm 0.005 \), \( \log(\omega_c/2\omega) \approx -5.5 \), and for \( c = c^* \pm 0.01 \), \( \log(\omega_c/2\omega) \approx -4.6 \). (B) The imaginary part of the complex conductivity \( \sigma''(\omega) \) is shown for the same values of \( c \) that were used in Fig. 1.

4. For \( c < c^* \), \( \mathcal{P}_0(t) \) decays to a finite value at long times, and for \( c > c^* \), it decays to zero as \( t^{-1/2} \). [At \( c = c^* \), \( \mathcal{P}_0(t) \) decays as \( t^{-2/3} \).] The interpretation of this exponent in terms of fractal dynamics will be discussed in Sec. IV.] It can easily be shown that for \( c < 1 \), \( \mathcal{P}_0(t) \) for the percolation problem should decay to a finite value equal to the configuration average of the inverse cluster size.\(^{13}\) Since finite clusters still exist for \( c > c^* \), \( \mathcal{P}_0(t) \) should decay to a nonzero value at long times for all \( c < 1 \). The appearance of the infinite cluster at \( c = c^* \) should not drastically affect the long time behavior of \( \mathcal{P}_0 \) in contrast to the predictions of the SMC. It should be
FIG. 2. $\Phi(t)$, the probability that an excitation remains at its initial site, is calculated from Eq. (3.25) for a substitutionally disordered simple cubic lattice with nearest-neighbor interactions, for $c = 0.2, 0.4, 0.6, 0.8, and 1.0$. At $c = 1.0$ (the ordered limit), the SCMC gives the exact result, which decays as $t^{-1/2}$ at long times. For $c < 1.0$, $\Phi(t)$ decays to a finite value at long times. For purposes of comparison, a function proportional to $t^{-1/2}$ (broken curve) is shown.

noted that all other analytical theories of excitation dynamics that predict a critical point in the percolation model also predict that $\Phi$ decays to zero for $c > c^*$. It is beyond the scope of a theory whose microscopic input is the exact dynamics of a small number of particles to predict the correct long-time behavior of $\Phi$. This behavior reflects the entire distribution of cluster sizes, which can only be obtained from computer simulations. However, we can attach physical significance to the SCMC prediction of $\Phi$ for $c > c^*$. Suppose that the configuration average in the definition of $\Phi$ [Eq. (2.4)] were redefined to only include members of the infinite cluster for $c > c^*$. This redefined $\Phi$ should decay as $t^{-d/2}$ at long times in $d$ dimensions for $c > c^*$. This prediction follows from the scaling assumption that at long times there is a single relevant length scale in the problem. This scaling assumption is not valid for the full percolation problem, in which the long-time dynamics reflect the entire distribution of cluster sizes, and there is a corresponding range of relevant length scales. If we only consider dynamics on the infinite cluster, then the scaling assumption will hold. Since the SCMC predicts that $\Phi$ decays as $t^{-3/2}$ at long times for $c > c^*$ in $d = 3$, it is reasonable to interpret this long-time behavior as representing dynamics on the infinite cluster.

The asymptotic behavior at long time of $\langle r^2(t) \rangle$, the mean-squared displacement of an excitation, for a cubic lattice is given in Eq. (3.18). In the long time limit, this quantity depends linearly on time for $c < c^*$, has a constant value for $c < c^*$, and is proportional to $t^{2/3}$ at $c = c^*$. If the excitation dynamics were described by an ordinary diffusion equation, $\langle r^2(t) \rangle$ would depend linearly on time, for all times. A time-dependent derivative of $\langle r^2(t) \rangle$ is a signature of deviations from simple diffusive behavior. Figure 5 shows the time dependence of $d \langle r^2(t) \rangle / dt$ for a cubic lattice with $c = 0.2, 0.3, c^*, 0.4, 0.6$, and 1. These calculations were performed by solving Eq. (3.4) numerically, and applying Eq. (3.17). For $c < c^*$, the derivative goes to zero at long times, indicating that the excitations are localized on clusters of finite size. At $c = c^*$, the derivative decays as $t^{-1/3}$, as can be seen from Eq. (3.18). For $c > c^*$, the behavior of $\langle r^2(t) \rangle$ is dominated at long times by contributions from the infinite cluster, and the derivative approaches a finite value.

The ac conductivity arising from the incoherent motion of localized charge carriers is related to the diffusion kernel in Eqs. (3.19). We defer presentation of calculations of $\sigma(\omega)$.
FIG. 5. The time derivative of the mean-squared displacement is calculated from Eqs. (3.4) and (3.17) for a substitutionally disordered simple cubic lattice with nearest-neighbor interactions for \( c = 0.2, 0.3, 0.3358, 0.36, 0.4, 0.6, \) and 1.0. For \( c > c^* \), \( \langle r^2(t) \rangle \) is linear in time at long times, because of the presence of an infinite cluster. Its derivative therefore decays to a finite value at long times. For \( c < c^* \), all excitations are localized on finite clusters, and \( \langle r^2(t) \rangle \) attains a finite value at long times. Its derivative therefore decays to zero. At \( c = c^* \), \( d (\langle r^2(t) \rangle) / dt \) decays as \( t^{-1/2} \), reflecting the fractal structure of the infinite cluster.

FIG. 6. (A) The ac conductivity \( \sigma'(\omega) \) is calculated from Eqs. (3.4) and (3.19) for a substitutionally disordered simple cubic lattice with nearest-neighbor interactions for \( c = 0.2, 0.4, 0.6, \) and 0.8, \( \sigma_0 = 1.0. \) For \( c < c^* \), \( \sigma'(\omega) \) takes on a finite value in the limit of zero frequency; the dc conductivity. For \( c > c^* \), \( \sigma'(\omega) \) vanishes as \( \omega^2 \) for small frequency. A metal-insulator transition is predicted at \( c^* = 0.3358. \) (B) The imaginary part of the complex conductivity \( \sigma'(\omega) \) is calculated from Eqs. (3.4) and (3.19) for a substitutionally disordered simple cubic lattice with nearest-neighbor interactions for the same values of \( c \) chosen in Fig. 6(A).

FIG. 7. (A) The ac conductivity \( \sigma'(\omega) \) is calculated from Eqs. (3.4) and (3.19) for a substitutionally disordered simple cubic lattice with nearest-neighbor interactions for \( c = 0.30, 0.32, 0.34, 0.36, \) and 0.38. \( \sigma_0 = 1.0. \) For \( c > c^* \), \( \sigma'(\omega) \) takes on a finite value in the limit of zero frequency; the dc conductivity. For \( c < c^* \), \( \sigma'(\omega) \) vanishes as \( \omega^2 \) for small frequency. A metal-insulator transition is predicted at \( c^* = 0.3358. \) (B) The imaginary part of the complex conductivity \( \sigma'(\omega) \) is shown for \( c = 0.38 \) and 0.30. Comparisons with Fig. 7(A) shows that \( \sigma'(\omega) \) is less sensitive to variations in \( c \) near the critical point than is \( \sigma'(\omega). \)

in one dimension to Sec. IV. Odagaki and Lax have shown that for the percolation model in one dimension, \( \sigma(\omega) \) can be calculated exactly. Determination of this quantity provides a unique opportunity to compare the predictions of the SCMe to an exact result. In Sec. IV, we compare the SCMC, the EMA, and the exact result. The agreement between the exact result and the SCMC is remarkable. Of course, \( \sigma(\omega) \) cannot be determined exactly in three dimensions for the percolation model. We have calculated \( \sigma(\omega) \) for a disordered cubic lattice by solving Eq. (3.4) numerically to obtain \( D(0,\varepsilon) \), obtaining the inverse Laplace transform of this quantity numerically, and then performing a numerical fast Fourier transform from the time domain to the frequency domain. In the Fourier transform, \( 2^{15} \) points were used with a time step of 0.038 35\( w^{-1} \), which yields a frequency step of 0.005\( w \). The results are shown in Figs. 6–8. The real and imaginary parts of the complex conductivity are given in units of \( \sigma_0 [\text{Eq. (3.20b)}]. \) Figure 6(A) shows \( \sigma'(\omega) \) for...
discriminate between the two species (diagonal disorder). This approach was generalized to treat excitation transport by Odagaki and Lax, and Korzeniowski, Friesner, and Silbey, who considered a model based on the Pauli master equation [Eq. (2.1)] with nearest-neighbor hopping rates. The CPA method, when applied to the transport problem, is referred to as the effective medium approximation (EMA). In the previous section, we considered the site percolation problem, in which a fraction $c$ of the lattice sites are occupied by randomly distributed active particles. Odagaki and Lax treated the bond percolation problem, in which the hopping rate between a nearest-neighbor pair of sites has a finite value with probability $c$ and is zero with probability $1 - c$. In our approach, an effective, frequency dependent hopping rate $w_{\text{eff}}(\epsilon)$ is defined for the $d$-dimensional analog of a simple cubic lattice by the relation

$$P(k,\epsilon) = \left[ \epsilon + 2w_{\text{eff}}(\epsilon) \left[ d - \sum_{j=1}^{d} \cos(k a_j) \right] \right]^{-1}.$$  

$P(k,\epsilon)$ is the propagator defined in Eq. (2.5). $a_j$ is the lattice vector in the direction $j$. If $w_{\text{eff}}$ in Eq. (4.1) is taken to be independent of frequency, the resulting expression gives the propagator for an ordered lattice with a nearest-neighbor hopping rate $w_{\text{eff}}$. In the EMA, the disordered system is mapped onto an effective, ordered system with a frequency dependent transfer rate. The effective transfer rate is obtained with the following self-consistent procedure. The propagator is calculated for a lattice in which all of the bonds except one have the value $w_{\text{eff}}(\epsilon)$, and the remaining bond is treated exactly, i.e., it has a probability $c$ of assuming the value $w$ and a probability $1 - c$ of having the value zero. This propagator can be averaged exactly, since only one bond is characterized by disorder. The averaged propagator is equated to $P(k,\epsilon)$ in Eq. (4.1), resulting in a self-consistent equation for $w_{\text{eff}}$. For the mathematical details of the derivation of this self-consistent equation, the reader is referred to Refs. 21–23. The EMA equation can be written in the form

$$w_{\text{eff}}(\epsilon) = \left( 1 - c^{*} ight) + c^{*} \left[ (\epsilon/2w_{\text{eff}}) - (\epsilon/2w_{\text{eff}}) \right] + I_d(\epsilon/2w_{\text{eff}}) = 0,$$ 

$$c^{*} = 2/\pi.$$

$I_d$ is the diagonal element of the lattice Green function, as defined in Eq. (3.3). $z$ is the coordination number of the lattice. Korzeniowski, Friesner, and Silbey developed an EMA for the site percolation problem, which to lowest order results in a self-consistent equation for $w_{\text{eff}}$ that is identical to Eq. (4.2). We shall therefore compare the results of the previous section for the site percolation problem to the predictions of Eq. (4.2). An important advantage of the self-consistent mode-coupling (SCMC) method over the EMA is that the former method can be applied to a transfer rate of arbitrary distance dependence, while the EMA is restricted to transfer rates of finite range (e.g., the nearest-neighbor transfer rate). In Sec. III, we analyzed the SCMC equation [Eqs. (2.14)] for the special case of a nearest-neighbor transfer rate. The predictions of the SCMC equation for transfer rates with exponential and inverse power dependences on the intermolecular separation will be considered.
in a future publication. For the special case of the nearest-neighbor transfer rate, the SCMC procedure is similar to the EMA in that the configuration averaged propagator for the disordered system is mapped onto an effective propagator of the form given in Eq. (4.1). In both methods, the averaged propagator for the disordered system with a nearest-neighbor transfer rate is mapped onto the propagator for an effective ordered system with a frequency-dependent nearest-neighbor transfer rate. In general, inspection of Eqs. (2.14) shows that the SCMC method does not map the averaged propagator for a disordered system with arbitrary transfer rate \( w(r) \) onto the propagator for an effective ordered system with a frequency dependent transfer rate that has the same distance dependence as the transfer rate of the original problem. We can recast the results of Sec. II in a form that is similar to the EMA equations [Eqs. (4.1)–(4.2)] by noting that the SCMC propagator is given by Eq. (4.1), where \( w_{\text{eff}}(e) = a^{-2}D_0(e) \), and \( D_0(e) \) is obtained by solving Eq. (3.4). Thus, the SCMC equation for \( w_{\text{eff}}(e) \), which should be compared to the EMA equation [Eq. (4.2)], is

\[
w_{\text{eff}} + w(1 - c)I^0_0(e/2w_{\text{eff}}) - c = 0.
\]

(4.4)

Inspection of the EMA equation [Eq. (4.2)] shows that \( c^* = 2/\zeta \) is a critical point, such that \( w_{\text{eff}} \) vanishes in the limit of small \( c \) for \( c < c^* \) and approaches a finite value in this limit for \( c > c^* \). For a linear chain (\( z = 2 \)), the EMA correctly predicts a percolation transition at \( c^* = 1 \). The EMA critical concentrations of \( 1/2 \) and \( 1/3 \) for the square and cubic lattices, respectively, are in good agreement with the best values from simulations of \( 0.593 \) for the square lattice and \( 0.311 \) for the cubic lattice. The SCMC critical concentrations for the linear, square, and cubic lattices are, respectively, 0.1, 1, and 0.3358 [see Eqs. (3.8), (3.10), and (3.12)]. In two dimensions, the EMA correctly predicts a transition for \( c^* < 1 \). Let us consider in greater detail the solution of Eq. (4.2) for \( d = 3 \) in the limit of small \( e \), in the vicinity of the critical point. In this limit, we may replace \( I_3(e/2w_{\text{eff}}) \) in Eq. (4.2) by the constant \( I_3(0) \), which is given in Eq. (3.6b). This assumption, which can be justified a posteriori, is based on the following logic. For \( c > c^* \), \( w_{\text{eff}} \) has an \( e \) dependence that is weaker than linear for small \( e \). For \( c < c^* \), \( w_{\text{eff}} \) is linear in \( e \) for small \( e \), with a coefficient that diverges as \( c \) approaches \( c^* \). Thus, even though \( e/2w_{\text{eff}} \) is independent of \( e \) in this case, this ratio becomes arbitrarily small for \( c \) near \( c^* \). In this limit, Eq. (4.2) becomes a quadratic equation in \( w_{\text{eff}} \). In the limit of small \( e \), the solution to this quadratic equation is

\[
w_{\text{eff}} = \{w(c - c^*)/[2(1 - c^*)]\}[1 \pm [1 + e/e_c]^{1/2}],
\]

(4.5)

\[
e_c = \{(c^* - c)^2/[2(1 - c^*)]I_3(0)\}
\]

(4.6)

The “±” in Eq. (4.5) should be interpreted as + for \( c > c^* \) and as − for \( c < c^* \). This result for the EMA should be compared to Eqs. (3.13) and (3.14) for the SCMC, by noting that \( D_0 = a^2w \), and that \( D_0(0,e) = aw_{\text{eff}}(e) \), where \( a \) is the lattice spacing. Both the EMA and the SCMC predict the existence of a crossover frequency \( e_c \), such that \( w_{\text{eff}} \) has the same frequency dependence for \( e < e_c \) and \( e > e_c \). For the SCMC, \( w_{\text{eff}} \sim e^{1/2} \) for \( e < e_c \). Inspection of Eq. (4.5) shows that for \( e > e_c \), \( w_{\text{eff}} \sim e^{1/2} \) on both sides of the transition. For \( e < e_c \), \( w_{\text{eff}} \) is linear in \( e \) for \( c < c^* \), and approaches a finite value for \( c > c^* \). Within the EMA, the crossover frequency vanishes as \( c \) approaches \( c^* \) as \( (c^* - c)^2 \), in contrast to the crossover frequency within the SCMC, which vanishes as \( |c - c^*|^3 \). [See Eq. (3.14).] Taking the limit of Eq. (4.5) for \( e < e_c \) yields

\[
w_{\text{eff}}(e) = \begin{cases} \frac{w(c - c^*)}{2(1 - c^*)} & c < c^* \\ \frac{w(c - c^*)(1 - c^*)}{2(1 - c^*)} & c > c^* \\ \frac{w(c - c^*)}{2(1 - c^*)} & c = c^* \end{cases},
\]

(4.7)

This result for the EMA should be compared to Eq. (3.15) for the SCMC equation. It should be noted that because Eq. (4.5) is based on the assumption that \( e/w_{\text{eff}} \ll 1 \), the expression for \( c < c^* \) in Eq. (4.7) is only valid for \( c \) very close to \( c^* \). For example, analysis of the exact EMA equation [Eq. (4.2)] reveals that there is a contribution to \( w_{\text{eff}} \) for \( c < c^* \) that is proportional to \( e \) and which diverges as \( (c^* - c)^{-1/2} \). For \( c \) sufficiently close to \( c^* \) this term is negligible compared to the contribution that diverges as \( c^* - c \), which is given in Eq. (4.7). An expansion of \( w_{\text{eff}} \) to second order in \( e \) that is valid for any \( c \) less than \( c^* \) is given in Eq. (4.10) of Ref. 21. Comparison of Eqs. (3.15) and (4.7) shows that for \( c > c^* \), the zero frequency limit of \( w_{\text{eff}} \) has the same form in the EMA and the SCMC. For \( c < c^* \), both theories predict that \( w_{\text{eff}} \) is proportional to \( e \) for small \( e \), and has a correction that goes as \( e^2 \). However, the concentration dependence of the coefficients of these terms is very different in the two theories. In the EMA, the coefficient of the first term diverges as \( (c^* - c)^{-1} \), and that of the second term diverges as \( (c^* - c)^{-3} \), as \( c \) approaches \( c^* \) from below. Equation (3.15) shows that these coefficients within the SCMC diverge, respectively, as \( (c^* - c)^{-2} \) and \( (c^* - c)^{-3} \). The two theories also predict different behavior at \( c = c^* \): in the EMA, \( w_{\text{eff}} \sim e^{1/2} \), whereas \( w_{\text{eff}} \sim e^{1/3} \) in the SCMC. By applying Eq. (3.17) to Eq. (4.7), we can determine the asymptotic behavior of \( \langle r^2(t) \rangle \), the mean-squared displacement, that is predicted by the EMA for long times:

\[
\lim_{t \to \infty} \langle r^2(t) \rangle = \begin{cases} a^2[c^*(I_3(0)/2)(c^* - c)^{-1}] & c < c^* \\ a^2w(1 - c^*)^{-1}(c - c^*)t & c > c^* \\ a^2[c^*(I_3(0)/2)(2(1 - c^*))^{1/2}t^{1/2}] & c = c^* \end{cases}
\]

(4.8)

The mean-squared displacement increases linearly with time for \( c < c^* \), reaches a finite asymptotic value for \( c < c^* \), and increases as \( t^{1/2} \) for \( c = c^* \). Equation (4.8) should be compared to Eq. (3.18), which gives the long-time behavior of \( \langle r^2(t) \rangle \) for the SCMC. The time dependence of \( \langle r^2(t) \rangle \) at long times for \( c > c^* \) is the same in Eq. (3.18) as in Eq. (4.8).
The finite limiting value attained by \( \langle r^2(t) \rangle \) at long times for \( c < c^* \) diverges as \( (c^* - c)^{-1} \) in the EMA and as \( (c^* - c)^{-2} \) in the SCMC. Within the EMA, \( \langle r^2(t) \rangle \) grows as \( t^{1/2} \) at \( c = c^* \), and within the SCMC, it increases as \( t^{2/3} \) at \( c = c^* \).

The time dependence of \( \langle r^2(t) \rangle \) at long times at \( c = c^* \) is dominated by the contribution from random walks on the single, infinite percolating cluster that comes into existence at the critical point. This time dependence \( (t^{2/3}) \) in the SCMC and \( t^{1/2} \) in the EMA) provides information on the structure of this infinite cluster. The infinite cluster at \( c = c^* \) is a self-similar or fractal structure, that is characterized by a fractal dimension, \( d_f \). If one considers a set of points that are randomly distributed in a space of Euclidean dimension \( d \), then the number of points in a sphere of radius \( r \) is proportional to \( r^d \). For a fractal structure embedded in a space of dimension \( d \), this quantity is proportional to \( r^{d_f} \), where \( d_f < d \). The term “spectral dimension” arises from the fact that the density of vibrational modes on a fractal \(^10\) is proportional to \( \omega^{-d_f} \), in contrast to the Euclidean result of \( \omega^{-d} \). The mean-squared displacement for a random walk on a fractal grows at long times as \( t^{d/d_f} \).

\[ \langle r^2(t) \rangle \sim t^{d/d_f}, \]  
\[ \mathcal{P}_0(t) \sim t^{-2/d_f}. \]  

Comparison of Eqs. (4.9) and (4.10) to Eqs. (4.13) and (4.14) yields

\[ d_s = 4/3, \]  
\[ d_f = 2. \]  

The EMA and the SCMC both predict \( d_f = 2 \), but differ in their predictions of \( d_s \). The prediction of \( d_s = 2 \) is in good agreement with the current best estimate\(^10\) of \( d_s \approx 2.5 \). This latter value is obtained by a scaling relation that connects \( d_f \) to \( d_s \) and to critical exponents associated with the static percolation problem. The current best estimate of the spectral dimension of the infinite cluster at \( c = c^* \) is \( d_s \approx 4/3 \), exactly the value predicted by the SCMC. Alexander and Orbach\(^10\) have used a scaling argument to conjecture that \( d_s \approx 4/3 \) for \( d > 2 \). Recent simulations of random walks on percolation clusters on simple cubic lattices by Ben-Avraham and Havlin\(^39\) and by Argyriakis and Kopelman\(^40\) have yielded \( d_s = 1.26 \pm 0.01 \) and \( d_s = 1.32 \pm 0.06 \), respectively. This value is also consistent with experimental data. Orbach\(^36\) has pointed out that the measurements of the vibrational density of states of fused silica, carried out by Buchenau et al.,\(^47\) are consistent with \( d_s \approx 1.4 \). Thus, the value of \( d_s \) in \( d = 3 \) predicted by the SCMC is in perfect agreement with the currently accepted value of this quantity. The SCMC is the only analytical theory of motion in disordered media that predicts the correct value of the spectral dimension of a percolation cluster in \( d = 3 \). We next turn to the predictions of the SCMC for \( d > 3 \). In order to analyze the solution of Eq. (4.4) in the vicinity of \( c^* \), we need the behavior of \( I_\beta \) for small values of its argument. [This asymptotic behavior is given in Eq. (3.6) for \( d = 1, 2, \) and 3.] Analysis of the definition of \( I_\beta \) in Eq. (3.3) shows that \( I_\beta(x) = A_\beta + B_\beta x \ln(x) \) and that \( I_{d_f}(x) = A_{d_f} + B_{d_f} x \) for \( d > 4 \), in the limit \( x < 1 \), where \( A_\beta \) and \( B_\beta \) are numbers. Substitution of the latter expression into Eq. (4.4) and solution of the resulting equation at \( c = c^* \) yields \( d_f = 2 \) and \( d_s = 1 \) for \( d > 4 \). At \( d = 4 \), there is a logarithmic correction to the power law behavior. The marginal dimensionality \( d^* \) for a phase transition is the dimensionality such that for \( d > d^* \), the critical exponents are independent of dimensionality and take on their mean-field values. For percolation,\(^10\) \( d^* = 6 \), and \( d_f = 4 \) and \( d_s = 4/3 \) for \( d > 6 \). The SCMC predicts the existence of a marginal dimensionality, but at \( d^* = 4 \) rather than \( d^* = 6 \).

In addition to predicting the parameters \( d_f \) and \( d_s \) associated with the infinite percolation cluster at \( c = c^* \), both the EMA and the SCMC predict the existence of a crossover frequency \( \epsilon_\infty \) [Eq. (3.14) for the SCMC and Eq. (4.6) for the EMA], such that for \( \epsilon > \epsilon_\infty \), the frequency dependence of \( \omega_{\infty} \) for \( c < c^* \) and \( c > c^* \) is the same as the frequency dependence of \( \omega_{\infty} \) at \( c = c^* \). In both theories, \( \epsilon_\infty \) vanishes as \( c \) approaches \( c^* \), although each theory predicts a different exponent. This crossover frequency has the following physical significance. The percolation cluster at \( c = c^* \) is a self-similar (fractal) structure for length scales that are large compared to the lattice spacing. Finite clusters that are sufficiently large will appear to be self-similar for a range of length scales that are
large compared to the lattice spacing, but small compared to the
cluster size. The infinite cluster for \( c > c^* \) is also self-
similar over a range of length scales. For sufficiently large
lengths, the infinite cluster at \( c > c^* \) becomes homogeneous
(not self-similar). Thus, all clusters that are sufficiently
large are characterized by a range of length scales for which
they are self-similar and over which they therefore resemble
the infinite cluster at \( c = c^* \). Therefore, the dynamics of such
clusters should be characterized by a range of frequencies
over which these dynamics are similar to those on the infinite
cluster at \( c = c^* \). For \( \varepsilon \ll \varepsilon_c \), the dynamics are sensitive to the
existence of an infinite cluster, and the system response is
different for \( c > c^* \) than for \( c < c^* \). For \( \varepsilon \gg \varepsilon_c \), the dynamics
for \( c > c^* \) and for \( c < c^* \) are the same as the dynamics at
\( c = c^* \). Orbach and Alexander have derived a scaling rela-
tion that relates the exponent describing the vanishing of \( \varepsilon_c \)
at \( c = c^* \) to the spectral dimension, the fractal dimension,
and the correlation length exponent.\(^{10}\) In order to obtain this
relation, we consider two lengths. The first length is \( \xi \), the
usual correlation length, which is related to a characteristic
cluster size.\(^{32}\) This length diverges as \( c \) approaches \( c^* \) with an
exponent \( \nu \):

\[
\xi \sim |c - c^*|^{-\nu}.
\]

The second length is \( L(\varepsilon) \), the diffusion length, which is
associated with the displacement undergone by a random walker.
From dimensional analysis, we see that \( L(\varepsilon) \sim \varepsilon (r^2(\varepsilon))^{1/2} \)
where \( \langle r^2(\varepsilon) \rangle \) is the Laplace transform of \( \langle r^2(t) \rangle \). Taking the Laplace transform of Eq. (4.10) yields

\[
L(\varepsilon) \sim \varepsilon^{-d/v_d}.\]

The crossover frequency is that frequency for which \( L(\varepsilon) \)
equals \( \xi \). The concentration dependence of \( \varepsilon_c \) is obtained by
equating Eqs. (4.17) and (4.18):

\[
\varepsilon_c \sim |c - c^*|^{2d/v_d}/d.
\]

In order to determine whether or not the EMA and the SCMC satisfy Eq. (4.19), we must calculate \( \nu \) within each theory. This exponent is determined by noting that for \( c < c^* \)
and very small \( \varepsilon \), \( \langle r^2(\varepsilon) \rangle \sim \varepsilon^{2/7} \). Comparison of this result to Eq. (3.15) for the SCMC and to Eq. (4.7) for the EMA
shows that \( \nu = 1 \) for the SCMC and \( \nu = 1/2 \) for the EMA.
Substituting \( \nu = 1, d_\nu = 2, \) and \( d = 4/3 \) into Eq. (4.19) results
in an exponent of 3 for the SCMC. Inspection of Eq. (3.16)
shows that \( \varepsilon_c \) does vanish as \( |c - c^*|^{1/3} \) for the SCMC,
and hence that the SCMC is consistent with the scaling rela-
tion in Eq. (4.19). Performing this manipulation for the EMA
shows that although the predictions of \( v \) and \( d_\nu \) are different for the two theories, the EMA also obeys Eq. (4.19).

Figure 9(A) shows \( \sigma(\omega) \), the ac conductivity, calcu-
lated at \( c = c^* \) for the EMA and the SCMC. In Figs. 9(A) and
9(B), the conductivity is given in units of \( \sigma_0 \), which is
defined in Eq. (3.20b). Since both theories are correct to first
order in \( \varepsilon \), both curves have the correct large frequency
limit of \( c^* \sigma_0 \). The difference in the value of \( c^* \) predicted by the two
theories is too small to be seen in Fig. 9(A), so the curves
overlap at high frequency. The regime of fractal dynamics
[\( \sigma(\omega) \sim \omega^{1/2} \) for the SCMC and \( \sigma(\omega) \sim \omega^{1/2} \) for the EMA]
is indicated by the linear portion in these logarithmic plots.

![A](image1.png) ![B](image2.png)

**FIG. 9.** (A) The ac conductivity \( \sigma(\omega) \) is calculated for a substitutionally
ordered simple cubic lattice with nearest-neighbor interactions at \( c = c^* \)
with the EMA (broken curve) and the SCMC (solid curve). \( \sigma_0 = 1. \) For
\( \omega < 2\omega_1, \sigma(\omega) \) is proportional to \( \omega', \) where \( r = 1/3 \) in the SCMC
and \( r = 1/2 \) in the EMA. This behavior is a signature of the fractal structure of the
infinite percolation cluster at \( c = c^* \). (B) The imaginary part of the complex
conductivity \( \sigma' \) is shown for a substitutionally ordered simple cubic
lattice with nearest-neighbor interactions at \( c = c^* \) for the EMA (broken
curve) and for the SCMC (solid curve).

Both theories predict fractal dynamics at \( c = c^* \) for \( \omega / 2\omega_1 \ll 1. \) The frequency dependency of \( \sigma'' \) at \( c = c^* \)
calculated with the EMA (broken curve) and the SCMC (solid curve)
shown in Fig. 9(B).

Odagaki and Lax have demonstrated that \( \sigma''(\omega) \) can be
calculated exactly in one dimension for the bond percolation
model.\(^{41}\) Their procedure is also valid for the site percolation
model, and yields the same result. This quantity thus provides
an opportunity to compare the predictions of the
SCMC to an exact result. Figures 10(A) and 10(B) show
\( \sigma''(\omega) \) and \( \sigma''(\omega) \), respectively, for \( c = 0.2, 0.4, \) and \( 0.8, \)
calculated with the SCMC (solid curve), the EMA\(^{21-23} \)
dashed curve), and the exact formula of Odagaki and Lax\(^{41}
(dashed curve). In Figs. 10(A) and 10(B), the conductivity
is given in units of \( \sigma_0 \), which is defined in Eq. (3.20b). The
exact calculations were performed using Eqs. (5), (7), and
(10) of Ref. 41. Since both the SCMC and the EMA are
exact to lowest order in concentration, the agreement with
the exact result is best for both theories at low concentrations.

and large frequencies. The SCMC shows excellent agreement with the exact result for all concentrations and frequencies.

V. DISCUSSION AND SUMMARY

In this work we have presented a new approach to the investigation of the incoherent transport of localized excitations in a disordered medium. We have developed a hierarchy of self-consistent equations for the master equation propagator \( P(k,e) \) [defined in Eq. (2.5)], from which all transport properties such as \( \mathcal{D}_0(t) \), the probability that an excited molecule retains its excitation after a time \( t \), and \( \sigma(\omega) \), the complex conductivity, can be calculated. Our procedure is based on deriving a pair of coupled equations for two unknown quantities: \( P_0(e) \) [the Laplace transform of \( \mathcal{D}_0(t) \)] and \( D(k_e) \) (the generalized diffusion kernel). Equation (2.8a), which follows from the definitions of these quantities, provides an exact relation between them. A hierarchy of approximate relations between them is constructed in Eqs. (2.9)–(2.12). Successive members of the hierarchy are exactly correct to successively higher orders in \( c \), the concentration of active molecules. The microscopic input to each level of approximation is a knowledge of the exact dynamics for a small number of interacting molecules. To obtain results that are exact to order \( c^n \), one must solve the problem with \( n + 1 \) and fewer particles. Each member of the hierarchy is exactly correct at \( c = 1 \), the limit of a filled, ordered lattice. The explicit form of the first member of the hierarchy is given in Eq. (2.14b). Substitution of each member of the hierarchy of approximate relations between \( D(k,e) \) and \( P_0(e) \) into Eq. (2.14a) yields a pair of coupled equations for these two quantities. The first member of this hierarchy of self-consistent equations is given in Eqs. (2.14). The solution of these equations yields a self-consistent approximation to \( D(k,e) \), from which the propagator \( P(k,e) \) can be calculated with Eq. (2.7). In this work we have focused exclusively on the first member of this hierarchy of coupled equations, which yields transport properties that are correct to first order in concentration and at \( c = 1 \). The microscopic input to this approximation is the exact dynamics of an excitation on a pair of interacting molecules [Eq. (A10)]. Equations (2.14) are the primary formal results of this work. From them, transport properties can be calculated for a transfer rate \( w(r) \) with any dependence on \( r \), the intermolecular separation.

In Secs. III and IV, we specialized to the case of the site percolation problem, in which \( w(r) \) is finite only for nearest neighbors on the lattice. This model is appropriate for the description of transport arising from short-ranged interactions, such as electrical conduction in glasses or solutions, or triplet exciton motion in molecular crystals. In this case, the self-consistent equation for \( P_0(e) \) simplifies considerably to the form given in Eq. (3.2). The following behavior is predicted by the SCMC for a simple cubic lattice with site disorder. A percolation transition is predicted at \( c^* \approx 0.3358 \), which is in good agreement with the current best estimate from simulations\(^\text{12}\) of 0.311. (This result also agrees with the predictions of other analytic theories. The EMA\(^\text{21-23}\) gives \( c^* = 1/3 \), and the diagrammatic theory of Loring, Andersen, and Fayer\(^\text{15}\) yields \( c^* \approx 0.353 \).) For \( c > c^* \), the mean-squared displacement of an excitation \( \langle r^2(t) \rangle \) increases linearly with time at long times, as is consistent with diffusive behavior. For \( c < c^* \), \( \langle r^2(t) \rangle \) reaches a finite limit at long times, indicating that all excitations are confined to clusters of finite size. At \( c = c^* \), \( \langle r^2(t) \rangle \sim t^{2/3} \). This power-law time dependence with an exponent less than one, which is a signature of fractal dynamics, is consistent with the fact that the infinite percolation cluster at \( c = c^* \) is known to be a fractal or self-similar structure. The behavior of \( \mathcal{D}_0(t) \) for different values of \( c \) is depicted in Figs. 2–4. For \( c < c^* \), this quantity decays to a finite limiting value at long times, which is con-
sistent with all excitations being localized on finite clusters. For $c < c^*$, however, $\mathcal{P}_0(t)$ decays to zero. It can be easily shown that for the site percolation problem, $\mathcal{P}_0(t)$ should decay to the configuration average of the inverse cluster size. Thus, $\mathcal{P}_0(t)$ should decay to a finite limit for all $c < 1$. The appearance of an infinite cluster at $c = c^*$ does not strongly affect the asymptotic value of $\mathcal{P}_0(t)$. It should be noted that all previous theories of transport for the site percolation model that are capable of predicting a transition also have the property that $\mathcal{P}_0(t)$ decays to a nonzero constant for $c < c^*$, and to zero for $c > c^*$. Determining the true asymptotic behavior of $\mathcal{P}_0$ requires a detailed knowledge of the distribution of cluster sizes, which is beyond the scope of analytical theories such as these. Such knowledge can only come from computer simulations. Despite the disagreement between the true long-time behavior of $\mathcal{P}_0$ for $c > c^*$ and the behavior predicted by the SCMC, we can provide a physical interpretation of the SCMC prediction. If we restrict our attention to the dynamics on the infinite cluster, and neglect the contributions to $\mathcal{P}_0$ from finite clusters for $c > c^*$, then this redefined $\mathcal{P}_0$ will decay to zero. For this reason, we shall interpret the long-time behavior of the SCMC $\mathcal{P}_0$ for $c > c^*$ as representing the contribution from the infinite cluster. If we interpret the behavior of $\mathcal{P}_0(t)$ for $c > c^*$ as deriving from the dynamics on the infinite cluster, we can use Eqs. (4.9) and (4.10) to obtain $d_f$, the fractal dimensionality, and $d_s$, the spectral dimensionality of the infinite cluster. The SCMC predicts $d_f = 2$ and $d_s = 4/3$ in three dimensions. The value of $d_f$ is in good agreement with the current best estimate from simulations of 2.5, and the value of $d_s$ is identical to the value conjectured by Alexander and Orbach from scaling considerations.

Recent computer simulations of random walks on fractals by Ben-Avraham and Havlin and by Argyriakis and Kopelman yield values very close to $4/3$. In addition to predicting fractal dynamics at $c = c^*$, the SCMC predicts the existence of a range of time scales over which fractal dynamics obtain for any value of $c$. The crossover frequency at which the fractal regime begins is given in Eq. (3.14) and vanishes at $c = c^*$. This range of time scales is a reflection of the fact that all percolation clusters that are sufficiently large resemble the percolation cluster at $c = c^*$ over some range of length scales. Hence there exists a range of time scales for which the system response is insensitive to the existence of an infinite cluster. The crossover between fractal and homogeneous behavior is of great interest in the context of the vibrational dynamics of disordered, harmonic networks. It has been suggested that such a crossover is consistent with experimentally measured densities of vibrational modes of amorphous materials such as fused silica. This crossover has been investigated by Derrida, Orbach, and Yu, who made use of the connection between the incoherent motion problem and the vibrational dynamics problem and applied the EMA. The SCMC is applied to the vibrational dynamics problem in Ref. 48.

We conclude this discussion by considering the asymptotic behavior of $\mathcal{P}_0(t)$ at long times for a general transfer rate $w(r)$. If at long times, there is only one length scale that is relevant to the dynamics, then the propagator $\mathcal{P}(r,t)$ has the form of a solution of the diffusion equation in $d$ dimensions: $\mathcal{P}(r,t) = A_d \left\langle r^2(t) \right\rangle^{-d/2} \exp \left\{ -B_d r^2 / \left\langle r^2(t) \right\rangle \right\}.$ (5.1) $A_d$ and $B_d$ are constants that depend on the dimensionality.

The single relevant length scale in the problem is $\left\langle r^2(t) \right\rangle^{1/2}$. Setting $r = 0$ in Eq. (5.1) shows that if $\left\langle r^2(t) \right\rangle$ is linear in time, then $\mathcal{P}_0(t)$ decays as $t^{-d/2}$ at long times. For a random walk on a fractal structure, $\mathcal{P}_0 \sim t^{-d_s/2}$, where the spectral dimension $d_s$ is less than $d$.

We have noted that for the percolation problem treated here, $\mathcal{P}_0(t)$ should decay to a finite value at long times for all $c < 1$. The scaling assumption is not applicable to the percolation problem because the dynamics at long times are not determined by a single relevant length, but rather by the entire distribution of cluster sizes. The existence of clusters on which an excitation is confined for all times is a unique and in some sense pathological attribute of models in which $w(r)$ is identical zero for values of $r$ greater than some maximum value. If $w(r)$ is a smooth function of $r$ with no upper cutoff (e.g., power law or exponential), then an excitation can explore the entire system in an arbitrarily long period of time. Thus for a transfer rate without an upper cutoff, we expect the scaling argument to hold at long times, and hence that the transport will be described by a diffusion equation. In a subsequent publication, we shall present the results of the SCMC for transfer rates arising from multipolar and exchange interactions. For such models, the SCMC yields the correct asymptotic behavior of $\mathcal{P}_0(t)$, namely $\mathcal{P}_0(t) \sim t^{-d/2}$. The following argument demonstrates that the solution of any member of the SCMC hierarchy of equations for $P_0(e)$ [Eq. (2.14a)] must be consistent with the above scaling argument. We begin by postulating a solution to Eq. (2.14a) with the property that a diffusion constant exists in the limit of small frequencies and wave vectors. In this case the integral over the wave vector in Eq. (2.14a) can be divided into the sum of a contribution from wave vectors that are sufficiently small that $D(k,e)$ can be taken to be independent of $k$, and the contribution from the rest of the Brillouin zone:

$$P_0(e) = \mathcal{P}_0^{-1} \left[ (\theta_d/D) K_d(e/D) + F_d(q,e) \right],$$

(5.2)

$$K_d(x) \equiv \int_0^\infty k^{d-1} dk \left[ k^2 + x \right]^{-1}.$$

(5.3)

The cut-off wave vector $q$ is defined to be sufficiently small that $D(k,e)$ can be replaced by a constant, $D$. $\theta_d$ is the integral over solid angle in $d$ dimensions. $F_d(q,e)$ is the integral of the integrand on the right-hand side of Eq. (2.14a) over a volume that is obtained from the Brillouin zone by subtracting a $d$-dimensional sphere of radius $q$ that is centered at $k = 0$. For small values of $x$, $K_d(x)$ has the asymptotic form

$$K_d(x) \sim \begin{cases} \left(\pi/2\right)x^{-(d/2) - 1}, & d = 1 \\ (1/2)\ln(q^2/x), & d = 2 \\ (q - \pi/2)x^{(d/2) - 3}, & d = 3 \end{cases}.$$

(5.4)

We next consider the limiting behavior of Eq. (5.2) for small values of $e$. $F_d(q,0)$ is finite, because the cut-off wave vector $q$ prevents the denominator of the integrand in Eq. (2.14a) from vanishing. Substituting Eqs. (5.4) into Eq. (5.2) yields
The asymptotic, long-time behavior of $\mathcal{P}_0(t)$ can be obtained by applying the Tauberian theorem for Laplace transforms\textsuperscript{44} to Eq. (5.5). $\mathcal{P}_0(t)$ decays as $t^{-1/2}$ for $d = 1$ and as $t^{-3/2}$ for $d = 3$. Thus, if the self-consistent equation [Eq. (2.14a)] has a solution for which a diffusion constant can be defined at small frequencies and wave vectors, then the resulting approximation for $\mathcal{P}_0(t)$ is consistent with the scaling argument. The SCMC is the only theory of excitation transport on disordered lattices that interpolates between exact results at high and low concentrations, that predicts a transition in the site percolation problem, that can be applied in a straightforward manner to any $w(r)$, and that predicts an asymptotic time dependence for $\mathcal{P}_0(t)$ that is consistent with scaling arguments.

**ACKNOWLEDGMENTS**

The support of the National Science Foundation, the Office of Naval Research, the U.S. Army Research Office, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

**APPENDIX A**

In this work, we have made the ansatz that the diffusion kernel could be expressed as a functional of $P_0$ [Eq. (2.8b)]:

$$D(k,\varepsilon,c) = D'[k,P_0(\varepsilon,c),c]. \quad (A1)$$

We write $P_0$ as $P_0(\varepsilon,c)$, $D$ as $D(k,\varepsilon,c)$, and $D$ as $\bar{D}(k,P_0(c))$ to emphasize the dependence of these quantities on concentration. Equation (A1) is a definition of the functional $\bar{D}$. In this Appendix, we present a systematic prescription for evaluating $\bar{D}$. We begin by expanding $D$ and $P_0$ in powers of $c$:

$$D(k,\varepsilon,c) = \sum_{j=1}^{\infty} c^j D_j(k,\varepsilon^{-1}), \quad (A2)$$

$$P_0(\varepsilon,c) = c^{-1} + \sum_{j=1}^{\infty} c^j Q_j(\varepsilon^{-1}). \quad (A3)$$

$D_j$ and $Q_j$ can be calculated from the exact solution of the transport problem for $j + 1$ or fewer particles. We shall take $\{D_j\}$ and $\{Q_j\}$ as given and use them to construct an expression for $\bar{D}$. $\bar{D}(k,P_0(c))$ depends explicitly on $c$, as well as depending implicitly on $c$ through the $c$ dependence of $P_0$. We expand $\bar{D}$ in a power series with respect to its explicit $c$ dependence:

$$\bar{D}(k,P_0(c)) = \sum_{j=1}^{\infty} c^j \bar{D}_j(k,P_0). \quad (A4)$$

The function $D_n(k,\varepsilon^{-1})$ in Eq. (A2) is given by

$$D_n(k,\varepsilon^{-1}) = \frac{1}{n!} \frac{\partial^n}{\partial \varepsilon^n} D(k,\varepsilon,c) \bigg|_{\varepsilon=0} = \frac{1}{n!} \frac{\partial^n}{\partial \varepsilon^n} \bar{D}(k,P_0) \bigg|_{\varepsilon=0}. \quad (A5)$$

The second equality in Eq. (A5) follows from the definition of $\bar{D}$ in Eq. (A1). Substitution of Eq. (A4) into Eq. (A5) and application of Leibnitz’ rule for the nth derivative of a product yields

$$D_n(k,\varepsilon^{-1}) = \sum_{j=1}^{n} \frac{1}{(n-j)!} \frac{\partial^{n-j}}{\partial \varepsilon^{n-j}} \bar{D}_j(k,P_0(c)) \bigg|_{\varepsilon=0}. \quad (A6)$$

An expression for $\bar{D}_n(k,P_0)$ is obtained by solving Eq. (A6) for $\bar{D}_n(k,\varepsilon^{-1})$ and replacing $\varepsilon^{-1}$ with $P_0$:

$$\bar{D}_n(k,P_0) = D_n(k,P_0) - \sum_{j=1}^{n-1} \frac{1}{(n-j)!} \frac{\partial^{n-j}}{\partial \varepsilon^{n-j}} \bar{D}_j(k,P_0) \bigg|_{\varepsilon=0}. \quad (A7)$$

Equation (A7) relates $\bar{D}_n$ to $\bar{D}_m$ with $j < n$. Using Eqs. (A2), (A3), and (A7), we can relate the unknown function $\bar{D}_n$ to the known functions $D_j$ and $Q_j$ with $j < n$. In this manner, we may calculate each term in the series for $\bar{D}$ in Eq. (A4). For illustrative purposes, we will calculate $\bar{D}_1(k,P_0)$ explicitly for $n = 1$ and $n = 2$.

For $n = 1$, Eq. (A7) becomes

$$\bar{D}_1(k,P_0) = D_1(k,P_0). \quad (A8)$$

For $n = 2$, we have

$$\bar{D}_2(k,P_0) = D_2(k,P_0) - \frac{\partial}{\partial \varepsilon} \bar{D}_1(k,P_0) \bigg|_{\varepsilon=0}$$

$$= D_2(k,P_0) - \frac{\partial \bar{D}_1(k,y)}{\partial y} \bigg|_{y=P_0} \frac{\partial P_0(x,c)}{\partial c} \bigg|_{c=0}$$

$$= D_2(k,P_0) - Q_1(P_0) \frac{\partial D_1(k,y)}{\partial y} \bigg|_{y=P_0}. \quad (A9)$$

In order to construct the first member of the hierarchy of SCMC equations for $P_0(\varepsilon)$, we need $D_1(k,\varepsilon^{-1})$, the coefficient of $c$ in the expansion of the diffusion kernel in Eq. (A2). This quantity can be calculated in a straightforward fashion from the exact solution of the Pauli master equation [Eq. (2.1)] for two particles\textsuperscript{13-16}:

$$\frac{\partial D_1}{\partial \varepsilon} = \sum_{r} \frac{[1 - \exp(ikr)] \omega(r) / [1 + 2\omega(r)\varepsilon^{-1}].} \quad (A10)$$

Replacing $\varepsilon^{-1}$ with $P_0$ in Eq. (A10) according to Eq. (A8) yields Eq. (2.14c).

**APPENDIX B**

In this Appendix, we present an explicit formula for the ac conductivity $\sigma'(\omega)$, that is obtained by substituting $i\omega$ for $\varepsilon$ in Eq. (3.13) and taking the real part of the resulting expression. As discussed in the derivation of Eq. (3.13), this result is valid for small frequencies for $c$ greater than $c^*$, and for $c$ less than but very close to $c^*$. Performing this manipulation yields

$$\quad$$

\[ \sigma'(\omega) = \sigma_0 \left[ (1 - c)/2\pi \right]^{2/3} (\omega/m)^{1/2} F(\omega/\omega_c) \cdot \] \hspace{2cm} (B1)

For \( c < c^* \), the scaling function \( F \) has the form

\[ F(y) = (4y^{1/3}) \left\{ A^+_+ \cos(2C_+) + A^-_- \cos(2C_-) \right\} - 2A^+_- A^-_+ \cos(C_+ - C_-) \right\}, \] \hspace{2cm} (B2)

\[ A_{\pm} = \left( (y^2 + 1)^{1/2} + y \pm \left( (4y^2)(y^2 + 1) \right)^{1/4} \times \left\{ \sin[(1/2)\tan^{-1}y] + \cos[(1/2)\tan^{-1}y] \right\} \right)^{1/6}, \] \hspace{2cm} (B3)

\[ C_{\pm} = \left(1/3\right) \tan^{-1}(Z_\pm/X_\pm), \] \hspace{2cm} (B4)

\[ Z_\pm = \left( y^2 + 1 \right)^{1/4} \sin[(1/2)\tan^{-1}y] \pm (y/2)^{1/2}, \] \hspace{2cm} (B5)

\[ X_\pm = \left( y^2 + 1 \right)^{1/4} \cos[(1/2)\tan^{-1}y] \pm (y/2)^{1/2}. \] \hspace{2cm} (B6)

For \( c > c^* \), \( F(y) \) takes the form

\[ F(y) = (4y^{1/3}) \left\{ A^+_+ \cos(2B_+) + A^-_- \cos(2B_-) \right\} + 2A^+_- A^-_+ \cos(B_+ - B_-) \right\}, \] \hspace{2cm} (B7)

\[ B_{\pm} = \left(1/3\right) \tan^{-1}(X_\pm/Z_\pm). \] \hspace{2cm} (B8)

If the limits \( y > 1 \) and \( y < 1 \) are taken in Eqs. (B2)–(B8), the asymptotic behavior of the scaling function shown in Eq. (3.20c) can be verified.

44G. H. Hardy, Divergent Series (Oxford University, Oxford, 1949).