Journal of Statistical Physics, Vol. 31, No. 3, 1983

Localized Excitation Transport on Substitutionally Disordered Lattices

G. Korzeniewski,[1] R. Friesner,[1] and R. Silbey[1]

Received August 17, 1982; revised November 10, 1982

Average-T-matrix and coherent medium theories are used to study the motion of localized excitations on substitutionally disordered lattices. We derive equations which relate coherent medium results for bond and site averaging and show how these reduce to the two-body solution results of Gochanour, Andersen, and Fayer. Numerical results for $P_0(t)$, the probability of remaining at the origin for two-dimensional nearest-neighbor lattices are presented.

KEY WORDS: Disordered lattice; coherent medium; master equation.

1. INTRODUCTION

There are many systems where it is possible to study the dynamics of localized excitations which move among randomly placed sites or molecules. Exciton transport on protonated molecules in deuterated molecular host crystals,[1] vibrational energy transfer in matrix isolation systems,[2] and fluorescence-line-narrowing experiments in a wide variety of amorphous crystals and glasses[3] are some examples of systems which have been studied experimentally and where a hopping mechanism for transport is possible.

Because transport in these systems does not occur among a periodic array of sites, it is possible that the motion of the excitation will not be diffusive, even at fairly long times. At any given density, isolated clusters of sites will be present, and if the excitation transfer range is small, the excitation may get trapped in these small clusters. In the case where only

Supported in part by the National Science Foundation. (CHE81-00407).

[1] Department of Chemistry and Center for Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 USA.

0022-4715/83/0600-0451$03.00/0

nearest-neighbor jumps on a lattice are possible, percolative behavior will be seen.

The main theoretical effort directed at characterizing this behavior for various time and density regimes has followed two lines: One is use of the continuous time random walk (CTRW) method[4] in which the random lattice is replaced by a periodic one with a distribution of waiting times at each site before the excitation can move to another site. The other approach has been solution of an averaged (generalized) master equation, where the average is over all random configurations of sites or molecules which can carry the excitation.[5] Klafter and Silbey[6] have shown that these two approaches are equivalent and give exact formal expressions which relate the CTRW functions to a self-energy for the averaged master equation.

Various solutions of the averaged master equation (and therefore the CTRW waiting time function) are possible depending on the type of system and disorder considered. Gochanour, Andersen, and Fayer[7] have derived an exact equation, in terms of an expansion in an n-body self-energy, for the case where the excitation can move on a continuum of sites as in a solution. On a lattice, however, in dimensions higher than one, exact analytic expressions have not been found (as will be discussed later) and one must resort to approximate schemes. The most successful of these schemes to date appears to be the coherent medium approximation. The coherent medium approach involves finding a medium in which some scattering vanishes to low order. All other scattering is then neglected and self-consistent equations are obtained. Coherent medium theories have been presented by Odagaki and Lax[8] and by Webman.[9] Their application has been for the case where *bond* disorder is present. In bond disordered systems, such as random resister networks, transport through the lattice may be blocked by "closed" bonds, but all sites connected by "open" bonds are accessible.

If the guest and host molecules in a matrix have similar physical properties, and the guest–host interaction is weak, then transport may be viewed as occurring among substitutional sites on an ordered lattice. In these *site* disordered systems, transport through the lattice may be blocked by closed sites, but all bonds between open sites are also open. Most of the systems mentioned above may be viewed, at least to a first approximation, as substitutionally disordered. Both solution and bond averaging have been suggested and used as approximate methods of calculating transport properties for substitutionally disordered lattices.[7,8,10] For this reason, it is important to construct a theory for these systems and find relationships between the various types of disorder.

In the following we present average-T-matrix and coherent medium theories for substitutionally disordered lattices. Relationships between the above types of disorder (site, bond, solution) are found. Finally we present numerical coherent medium and solution results and discuss some properties of the exact solution which are incorrectly accounted for by coherent medium techniques.

2. MODEL

The model we wish to consider is similar to one presented earlier by Klafter and Silbey[6] and will be reviewed here. We will be concerned with transport among randomly placed substitutional guest sites on a superlattice which is otherwise translationally invariant. The electronic or vibrational states of the impurity sites are taken to be localized so transport occurs "incoherently" via a "hopping" mechanism. The host sites take no part in the transport and no traps are present. The transport observables may be calculated if the probability of the excitation being on any site n at time t, $p_n(t)$, is known. This can be obtained for a given guest site configuration by solution of the master equation

$$\dot{p}_n(t) = \sum_m W'_{mn} p_m(t) \tag{1}$$

$$W'_{mn} = (1 - \delta_{mn}) w'_{mn} - \delta_{mn} \sum_{j \neq n} w'_{nj} \tag{2}$$

w'_{mn} is the rate of hopping from site m to n. In the following we will take the high-temperature limit so that $w'_{mn} = w'_{nm}$. The sums in (1) and (2) go over guest occupied sites only, and may be converted to sums over the superlattice if each w'_{mn} in (2) is multiplied by functions $\xi_m \xi_n$, where

$$\xi_i = \begin{cases} 1 & \text{site } i \text{ guest site} \\ 0 & \text{site } i \text{ host site} \end{cases}$$

so that (1) becomes

$$\begin{aligned} \dot{p}_n(t) &= \sum_m \left[(1 - \delta_{mn}) w_{mn} - \delta_{mn} \sum_j w_{nj} \right] p_m(t) \\ w_{mn} &= w'_{mn} \xi_m \xi_n \end{aligned} \tag{3}$$

and the sums in (3) now go over all sites in the superlattice. Since the actual guest site configuration is not known either experimentally or theoretically (through knowledge of the ξ_i's), and since we will be mainly interested in the long-time, long-distance properties of the transport, the quantity of interest is the site occupation probability averaged over all random guest

site configurations:

$$\langle \dot{p}_n(t) \rangle = \sum_m \langle W_{mn} p_m(t) \rangle \tag{4}$$

where W_{mn} contains the w_{mn}'s. The average in (4) operates only on the ξ_i's with (in the thermodynamic limit) $\langle \xi_i^n \rangle = \rho$ and $\langle \xi_i \xi_j \ldots \xi_n \rangle$ (no sites equal) $= \rho^n$ where ρ is the number density of guest sites. The Laplace transform of (4) may be taken via

$$f(u) = \int_0^\infty e^{-ut} f(t)\, dt \tag{5}$$

and a solution found

$$\langle p_n(u) \rangle = \sum_j \langle [u - \mathsf{W}]^{-1}_{nj} p_j(t = 0) \rangle \tag{6}$$

Assuming that at $t = 0$ the excitation is on site 0, and that it can never be on a host site, the initial condition is

$$p_j(t = 0) = \delta_{j0} \xi_0 \tag{7}$$

A Green's function for the averaged system may be defined

$$\langle \mathbf{p}(u) \rangle = \langle \mathsf{G} \rangle \langle \mathbf{p}(t = 0) \rangle \tag{8}$$

$$\langle G \rangle_{ij} = \frac{1}{\rho} \left[(u - \mathsf{W})^{-1} - \frac{1}{u}(1 - \rho) \right]_{ij} \tag{9}$$

Equation (9) is obtained by noting that every term after the first in the expansion of $[u - \mathsf{W}]^{-1}_{00}$ or $[u - \mathsf{W}]^{-1}_{0n}$ contains ξ_0 and that $\xi_0^n = \xi_0$.

It has been shown[6] that Green's functions of the form

$$\langle \mathsf{G}' \rangle = \langle [u - \mathsf{W}]^{-1} \rangle \tag{10}$$

can be formally rewritten in both real and k-space representations:

$$\langle \mathsf{G}'(u) \rangle = [u - \Sigma(u)]^{-1} \tag{11}$$

$$G'(\mathbf{k}, u) = [u + \Sigma(\mathbf{k} = 0, u) - \Sigma(\mathbf{k}, u)]^{-1} \tag{12}$$

where

$$\Sigma(\mathbf{k}, u) = \sum_{n \neq 0} \exp(i\mathbf{k} \cdot \mathbf{R}_{n0}) \Sigma_{0n}(u) \tag{13}$$

$\Sigma(u)$ is a matrix which contains all the averaging and will hereafter be referred to as the self-energy matrix. Once $\Sigma(u)$ is obtained, all transport properties of the system can be found. For example, a generalized diffusion coefficient may be defined[6]

$$D(\mathbf{k} = 0, u) = \lim_{k \to 0} \frac{1}{k^2} [\Sigma(\mathbf{k} = 0, u) - \Sigma(\mathbf{k}, u)] \tag{14}$$

and the mean square displacement at long times found[6]

$$\langle R^2(u)\rangle = \lim_{u\to 0} \frac{1}{u^2} D(\mathbf{k}=0, u) \tag{15}$$

The extension of the above formalism to Green's functions of the type (9) is straightforward.[11]

As noted in the introduction, it is not, in general, possible to obtain exact expressions for $\Sigma(u)$. In the following we obtain $\Sigma(u)$ through average-T-matrix and coherent medium approximations.

3. DERIVATION OF THE SELF-ENERGY

We start by adding and subtracting a *nonfluctuating and translationally invariant* matrix S in the denominator of G' appearing in the Green's function (9):

$$\langle \mathsf{G}\rangle = \frac{1}{\rho}\left[\left\langle \frac{1}{u-\mathsf{S}-\delta\mathsf{W}}\right\rangle - \frac{1}{u}(1-\rho)\right] \tag{16}$$

$$\delta\mathsf{W} = \mathsf{W} - \mathsf{S} \tag{17}$$

and the matrix elements of S are

$$S_{mn} = (1-\delta_{mn})s_{mn} - \delta_{mn}\sum_{j\neq n} s_{nj} \tag{18}$$

The sum in (18) goes over the superlattice and the explicit form of the s_{ij}'s will be determined later. $\langle \mathsf{G}\rangle$ can now be rewritten

$$\langle \mathsf{G}\rangle = \mathsf{G}^{(0)} + \mathsf{G}^{(0)}\langle \mathsf{T}\rangle \mathsf{G}^{(0)} \tag{19}$$

$$\mathsf{G}^{(0)} = \left[u - \mathsf{S}\right]^{-1} \tag{20}$$

$$\mathsf{T} = \left[\delta\mathsf{W}(1-\mathsf{G}^{(0)}\delta\mathsf{W})^{-1} + (1-\rho)\mathsf{S}(1+\mathsf{G}^{(0)}\mathsf{S})^{-1}\right] \tag{21}$$

In order to do an average-T-matrix or coherent medium theory, we will express T as an expansion in two-body t matrices. To do this we switch over to an operator representation.

$$\delta\hat{W} = \frac{1}{2}\sum_{j,k}{}' \delta\hat{w}_{jk} \tag{22}$$

$$\delta\hat{w}_{jk} \equiv (|j\rangle - |k\rangle)(w_{jk} - s_{jk})(\langle k| - \langle j|) \tag{23}$$

$$\hat{S} = \frac{1}{2}\sum_{j,k}{}' \hat{s}_{jk} \tag{24}$$

$$\hat{s}_{jk} \equiv (|j\rangle - |k\rangle)s_{jk}(\langle k| - \langle j|) \tag{25}$$

The functions $|j\rangle, |k\rangle$, are orthogonal localized site functions and the primes on the summations restrict j from being equal to k. $\delta\hat{w}_{jk}$ and $\hat{s}_{jk}$ have been defined so that the matrix elements of $\delta\hat{W}$ and $\hat{S}$ are the same as the matrix element of $\delta\mathbf{W}$ and $\mathbf{S}$. Below, we will use operator and matrix notation interchangeably whenever an operator and matrix are equivalent in the sense that for a matrix $\mathbf{M}$, there is an operator $\hat{M}$ such that $\mathbf{M}_{jk} = \langle j|\hat{M}|k\rangle$.

Two-body operators can now be defined

$$\hat{t}_{jk} = \delta\hat{w}_{jk}\left(1 - \hat{G}^{(0)}\delta\hat{w}_{jk}\right)^{-1} = (|j\rangle - |k\rangle)t_{kl}(\langle k| - \langle j|) \tag{26}$$

$$t_{jk} = \frac{w_{jk} - s_{jk}}{1 + 2(\langle j|G^{(0)}|j\rangle - \langle j|G^{(0)}|k\rangle)(w_{jk} - s_{jk})} \tag{27}$$

$$\hat{q}_{jk} = \hat{s}_{jk}\left(1 + G^{(0)}\hat{s}_{jk}\right)^{-1} = (|j\rangle - |k\rangle)q_{jk}(\langle k| - \langle j|) \tag{28}$$

$$q_{jk} = \frac{s_{jk}}{1 - 2(\langle j|G^{(0)}|j\rangle - \langle j|G^{(0)}|k\rangle)s_{jk}} \tag{29}$$

using (21), (22), (24), (26), and (28) an expansion for $\hat{T}$ in terms of $\hat{t}$'s and $\hat{q}$'s may be obtained:

$$\begin{aligned}\hat{T} = {} & \frac{1}{2}\sum_{j,k}{}' \hat{t}_{jk} + \frac{1}{4}\sum_{\substack{j,k \\ (j,k)\neq(m,n)}}{}' \sum_{m,n}{}' \hat{t}_{jk}G^{(0)}\hat{t}_{mn} \\ & + \frac{1}{8}\sum_{j,k}{}' \sum_{\substack{m,n \\ (j,k)\neq(m,n) \\ (m,n)\neq(p,r)}}{}' \sum_{p,r}{}' \hat{t}_{jk}G^{(0)}\hat{t}_{m,n}G^{(0)}\hat{t}_{p,r} + \cdots \\ & + (1-\rho)\left[\frac{1}{2}\sum_{j,k}{}' \hat{q}_{jk} - \frac{1}{4}\sum_{\substack{j,k \\ (j,k)\neq(m,n)}} \sum_{m,n} \hat{q}_{jk}G^{(0)}\hat{q}_{mn} + \cdots\right]\end{aligned} \tag{30}$$

Note $\hat{t}_{jk}$ (and $\hat{q}_{jk}$) has been defined in such a way as to give the most cancellation in the expression for $\hat{T}$. If the factor of $1/2$ in (22) or (24) is left out altogether (resulting in a nonhomomorphic partition[12]) or included in the definition of t (as in Webman's treatment[9]) additional terms appear in each order after the first which include factors of $\hat{t}_{jk}G^{0}\hat{t}_{mn}$ with $(j,k) = (m,n)$.

This expression for T is rather complex. In order to go further and find an approximate formula for $\langle\hat{T}\rangle$, we can make the average t matrix approximation (ATA), which assumes factorization of *all* products of $\hat{t}$'s in (30). When this is done, the summation can be done, and we find in the

ATA

$$\langle \hat{T} \rangle_{\mathrm{ATA}} = \frac{1}{\rho} \left\{ \hat{M}(u) \left[1 - \hat{G}^{(0)} \hat{M}(u) \right]^{-1} + (1-\rho) \hat{S} (1 + G^{(0)} \hat{S})^{-1} \right\} \tag{31}$$

where

$$\hat{M}(u) = \sum_{j,k}{}' \langle t_{jk} \rangle \left[1 - 2(\langle j | G^{(0)} | j \rangle - (\langle j | G^{(0)} | k \rangle) \langle t_{jk} \rangle \right]^{-1} \times \left[-|j\rangle\langle j| + |j\rangle\langle k| \right] \tag{32}$$

The average in (32) can be done to give

$$\langle t_{jk} \rangle = \frac{\rho^2 (w_{jk} - s_{jk})}{1 + \alpha_{jk}(w_{jk} - s_{jk})} - \frac{(1-\rho^2) s_{jk}}{1 - \alpha_{jk} s_{jk}} \tag{33}$$

$$\alpha_{jk} = 2(\langle j | \hat{G}^{(0)} | j \rangle - |j| \hat{G}^{(0)} | k \rangle) \tag{34}$$

For notational convenience, we have dropped the prime on w_{ij} (see eq. (3)). The matrix S still needs to be determined. If S is set equal to zero, then,

$$\langle t_{jk} \rangle \overset{S=0}{=} \frac{\rho^2 w_{jk}}{1 + (2/u) w_{jk}} \tag{35}$$

$$\langle G \rangle_{ij} = \frac{1}{\rho} \left[(u - \mathsf{M}(u))^{-1} + \frac{1}{u} (\rho - 1) \right]_{ij} \tag{36}$$

a diffusion coefficient for (36) may be defined[11]

$$D(\mathbf{k} = 0, u) = \frac{1}{\rho} \lim_{k \to 0} \frac{1}{k^2} M(\mathbf{k}, u) \tag{37a}$$

$$M(\mathbf{k}, u) = \sum_{j \neq 0} \left[\exp(i\mathbf{k} \cdot \mathbf{R}_{0j}) - 1 \right] \frac{\rho^2 w_{0j}}{1 + (2/u)(1-\rho^2) w_{0j}} \tag{37b}$$

A coherent medium approximation may be obtained if, instead of setting $\mathsf{S} = 0$, S is chosen so that $\langle \mathsf{T} \rangle = 0$. It is not possible to do this exactly, but one possible approximate way is to choose S so that the average of the lowest-order terms in (30) vanish. Then, for example

$$\sum_{j,k} \langle \hat{t}_{jk} \rangle + (1-\rho) \sum_{j,k} \hat{q}_{j,k} = 0 \tag{38}$$

$\langle \hat{t}_{jk} \rangle$ is given by (26) and (33). If the coherent medium approximation of (38) is made, then

$$\langle \mathsf{G} \rangle_{\mathrm{cm}} = \mathsf{G}^{(0)} = \frac{1}{u - \mathsf{S}} \tag{39}$$

and the diffusion coefficient is given by (14) with $\Sigma = \mathsf{S}$. The matrix elements of S are defined by (38) and physical solutions can be obtained if

real positive s_{jk} exist such that

$$s_{jk}^{\mathrm{cm}} = \frac{(1 + \alpha_{jk} w_{jk}) - \left[(1 + \alpha_{jk} w_{jk})^2 - 4\rho\alpha_{jk} w_{jk}\right]^{1/2}}{2\alpha_{jk}} \tag{40}$$

The minus sign in (40) was picked to ensure the proper high- and low-density limits. The α_{jk}'s are given by

$$\alpha_{jk} = 2(\langle G \rangle_{jj} - \langle G \rangle_{jk}) \tag{41}$$

An interesting limit is obtained if the square root in (40) can be expanded, i.e., if

$$\left| \frac{4\rho\alpha_{jk} w_{jk}}{(1 + \alpha_{jk} w_{jk})^2} \right| \ll 1$$

then

$$S_{jk}^{\mathrm{cm}} \to \frac{\rho w_{jk}}{1 + \alpha_{jk} w_{jk}} \tag{42}$$

Note that the α_{jk}'s are now functions of the full Green's function and self-consistent equations must be solved, using (40), (41), (18), and (39) in order to complete the evaluation.

4. DISCUSSION

If a nearest-neighbor approximation is made, the self-consistent results derived here for site averaging in our form of the coherent medium are *identical* to the *bond* averaging equations of Odagaki and Lax and Webman. The bond disorder problem for nearest neighbors is characterized by the distribution function

$$P(w_{jk}) = \rho\delta(w_{jk} - w_0) + (1 - \rho)\delta(w_{jk}) \tag{43}$$

where ρ is the probability a bond between sites j and k is open and w_0 is the nearest-neighbor hopping rate. The excitation is allowed to start anywhere on the lattice, so the T matrix is given by the right-hand side of (30) with all q's set equal to zero. The reason the coherent medium approximation presented here gives the same result for bond and site disorder is that only the terms proportional to the first power of the density are used to construct the coherent medium. These terms are identical in both models. *Differences in the averaging procedure occur, however, in all higher-order terms*. This can be seen by examination of the average of Eq. (30). In the site case, the averages of the t matrices in (30) factor only if all sites involved in the average are different. When the coherent medium approximation is made, correction terms appear in every order after the *second*. In the bond case, the lowest *three* orders of $\langle T \rangle$ vanish since different bonds

(pairs of sites) are independent. One obvious consequence of the equivalence between this low-order site-averaged coherent medium and low-order bond-averaged coherent medium theories is that bond and site percolation probabilities are predicted to be the same.

Another often used approximate method is the continuum approximation. In this approximation, lattice sites are replaced by a continuum of points $R = (r_1, r_2, r_3, \ldots, r_n)$ and averaging is done with the following distribution function:

$$f(R) = V^{-n} \int dr_1 \, dr_2 \ldots dr_n \, f(R) \tag{44}$$

where V is the volume of the system under consideration. Gochanour, Andersen, and Fayer (GAF) have applied the above distribution function to transport in solution. Using diagram techniques, they obtained an exact equation for $\langle G \rangle$ in terms of an expansion in an n-body self-energy. On a lattice, however, an exact equation cannot easily be obtained because of the presence of "excluded volume" terms. These terms arise because, in order to do the average over lattice sites correctly, the indices of all sums must be completely restricted so that no sites in the sums are equal. Once the average is done and the sums are unrestricted, the added terms do not sum up easily. An analogous situation occurs for a solution if the molecules have a finite volume.

Equation (42), which was obtained by expanding the square root in Eq. (40), is similar to the two-body self-energy derived by GAF [Eqs. (83) and (84) in Ref. 7]. The two become identical if we replace α_{jk} by $\langle G \rangle_{jj}$ (i.e., we neglect the off-diagonal elements of $\langle G \rangle$ compared to the diagonal elements) and we replace lattice sums by integrals. This similarity suggests that the two-body solution results are a special case of the coherent medium approximation of Eq. (40). However, although the steps leading to Eq. (42) from (40) are mathematically trivial, it is difficult to say, in general, when they are valid. In spite of this, a few general statements can be made. At *short time* or large u, compared to the hopping rate, only the first few terms in $\langle G \rangle$ and α are important. These are proportional to u^{-1}, so that at very short times $\alpha_{jk} w_{jk} \ll 1/4$ and so Eq. (42) should be valid for all densities. For intermediate and long times, $\alpha_{jk} w_{jk} \gtrsim 1$, so that the density must be small in order that (42) be valid. For very long times, if α_{jk} does not remain finite (i.e., it is proportional to u^{-1}), and the expansion of (40) is valid, then Eq. (42) would predict that the diffusion constant would be zero. If α_{jk} remains finite as $t \to \infty$, then the diffusion constant will be nonzero and the expansion will be valid only for sufficiently small density. Finally, we note that the lattice and solution results differ in that, as pointed out above, the term $\langle G \rangle_{jk}$ in α_{jk} is neglected in the solution case. From the above discussion, this implies that the long-time behavior of lattice and solution may be different. Finally, note that the ATA results

(Eq. (37)) are never diffusive in the long time limit [$D(\mathbf{k} = 0, u = 0) = 0$] regardless of the density or range of interaction and give a percolation edge of 1 for all dimensions.

In the next section, we present numerical calculations which illustrate some of the points mentioned above.

5. NUMERICAL RESULTS

In the following, we present numerical results for two very different models: (a) a two-dimensional *solution* with long-range interactions [the GAF result, Eq. (44)], and (b) two-dimensional lattice (either triangular or square) with nearest-neighbor interactions in the coherent medium approximation. These show the limits of possible behavior. The calculations are for $\langle G(t)\rangle_{00}$ which is related to the probability of being at the origin by

$$\langle p(t)\rangle_0 = \rho\langle G(t)\rangle_{00}.$$

The self-consistent coherent medium equations were solved numerically and the Laplace transform inverted numerically using an algorithm developed by Stehfast.[15] The solution results are the *two-body* approximation of GAF solved in two dimensions using the Forster rate[16]

$$W(R_{ij}) = \frac{1}{\tau}\left(\frac{R_0}{R_{ij}}\right)^6$$

In order to compare to a lattice, the solution density ρ_s was replaced by ρ_L/a^2, where ρ_L is a dimensionless parameter, $0 < \rho_L < 1$, and a is a lattice constant. When this is done

$$\langle G(u)\rangle_{00} \overset{\text{solution}}{=} \frac{1}{w_0}\left[S_1 + S_2\right]^3$$

$$S_1 = \left[r + \left(q^3 + r^2\right)^{1/2}\right]^{1/3}, \qquad S_2 = \left[r - \left(q^3 + r^2\right)^{1/2}\right]^{1/3}$$

$$r = \frac{1}{2\tilde{u}}, \qquad q = \frac{\pi\Gamma(2/3)}{4^{1/3}3\tilde{u}}\rho_L$$

$$\tilde{u} = \frac{u}{w_0}, \qquad w_0 = \frac{1}{\tau}\left(\frac{R_0}{a}\right)^6$$

w_0, the nearest-neighbor hopping rate, also scales the lattice Green's functions. All times in the following calculations are scaled by w_0, $\tilde{t} = tw_0$.

In Fig. 1, results are presented for $\langle G(t)\rangle_{00}$ as a function of $1/\tilde{t}$ for the coherent medium lattices and the two-body approximation to the solution

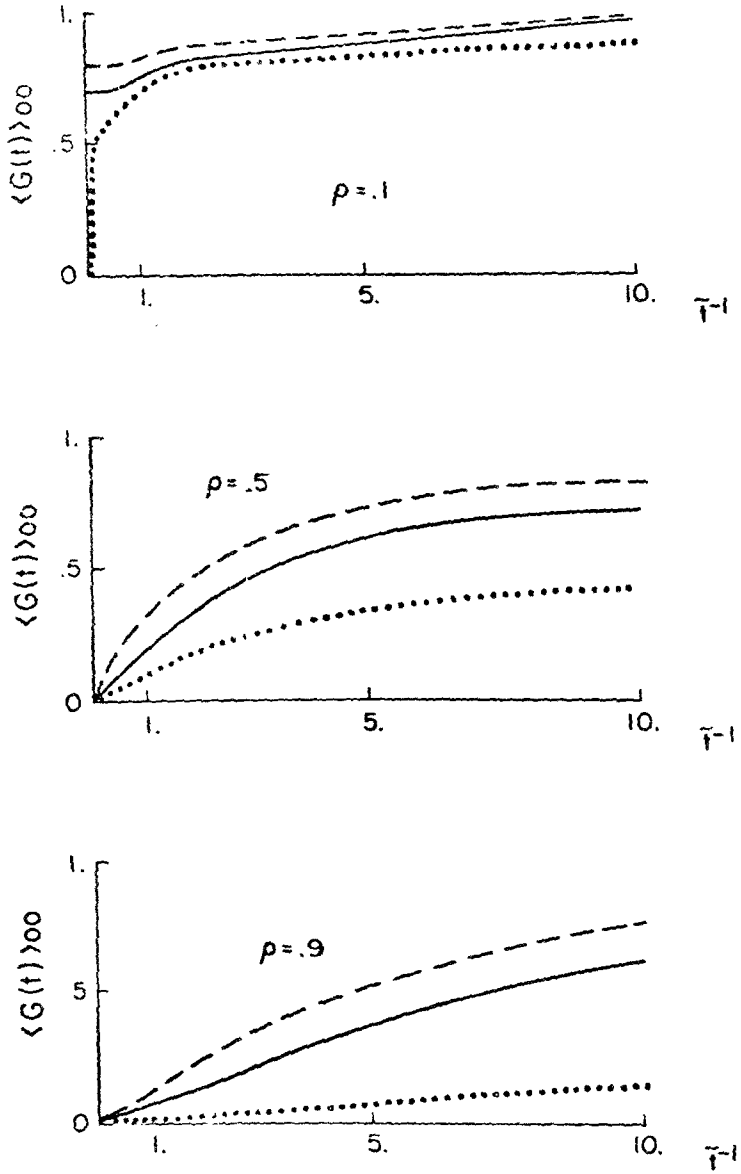

Fig. 1. Coherent medium and solution results for $\langle G(t)\rangle_{00}$ as a function of inverse time and density. Here $\tilde{t}^{-1} = 1/tw_0$ where w_0 is a nearest-neighbor hopping rate. The dotted lines are two-dimensional, two-body solution results of GAF Eq. (45). Solid lines are coherent medium, nearest neighbor, triangular lattice. Dashed lines are coherent medium, nearest-neighbor square lattice.

Table I. Approximate Number of Hops After Which Long-Time Behavior Is Reached for Coherent Medium Nearest-Neighbor Triangular and Square Lattices

ρ	$\tilde{t}$ (triangular)		$\tilde{t}$ (square)	
0.1	10		10	
0.2	50	$\langle G\rangle_{00}$	20	$\langle G\rangle_{00}$
0.3	$>\underline{500}$	const	50	const
0.4	>200		$\underline{\underline{100}}$	
0.5	100			
0.6	100		>400	
0.7	100		100	
0.8	50	$\langle G\rangle_{00} \propto \frac{1}{t}$	100	$\langle G\rangle_{00} \propto \frac{1}{t}$
0.9	50		50	
1	25		25	

for various densities. For the smallest density $\rho = 0.1$, and at short times, both lattices and the solution give similar results. As time gets longer, however, the solution results go to zero and the lattice results go to a nonzero value, because, as noted above, on nearest-neighbor lattices, it is possible for the excitation to be trapped in small clusters. For example, if all of the excitation is trapped in n-body clusters, $\langle G(t=\infty)\rangle_{00}$ would be $1/n$. At $\rho = 0.1$, much of the excitation is trapped in one-body clusters since $\langle G(t=\infty)\rangle_{00} > 0.5$. The solution results are always diffusive and $\langle G(t=\infty)\rangle_{00} = 0$ for all densities. At higher densities, the lattice results also go to zero at $t = \infty$, indicating that all the excitation is in an infinite cluster.

The coherent medium results show a very sharp transition into characteristic long-time behavior. For both lattices, below some critical density ρ_c, and after a certain number of hops, $\langle G\rangle_{00}$ becomes constant within the accuracy of the calculation (10^{-6}). Above this density, $\langle G\rangle_{00}$ becomes proportional to $1/t$ and goes to zero (within the accuracy of the calculation) at $t = \infty$. Table I shows the approximate number of hops needed to reach this long-time regime for various densities.

If the intercept at $t = \infty$, $\langle G(t=\infty)\rangle_{00}$ is plotted vs. density, a straight line results which intercepts the density axis as is shown in Fig. 2. The resulting critical densities (0.33 triangular, 0.5 square) are much closer to the exact bond percolation probabilities (0.347 triangular, 0.5 square)[13] than the exact site percolation probabilities (0.5 triangular, 0.59 square).[13] (Note that this is not always true in the coherent medium approximation since Odagaki and Lax have found the coherent medium percolation critical density, ρ_c, for simple cubic lattices to be 0.33, while the exact ρ_c for bonds is 0.247[13] and the exact ρ_c for sites 0.307.[13])

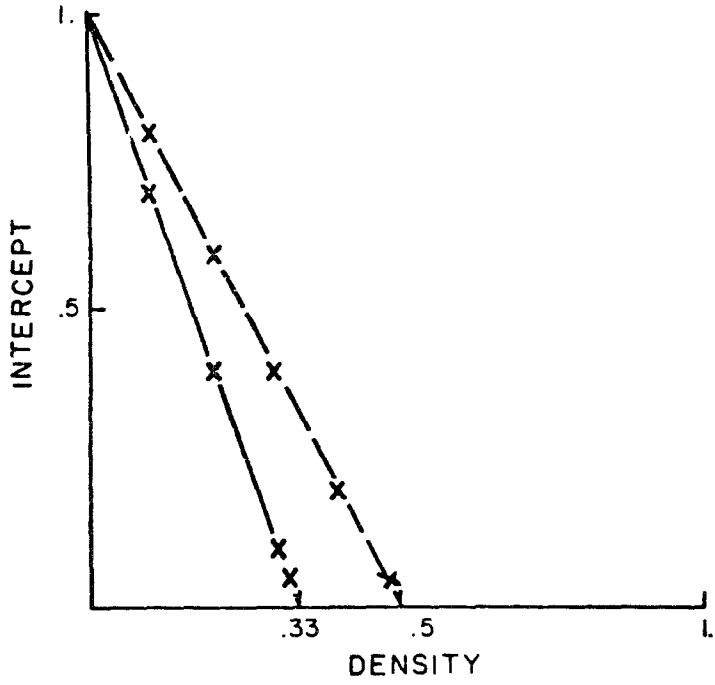

Fig. 2. $\langle G(t=\infty)\rangle_{00}$ for coherent medium, nearest neighbor triangular (solid line) and square (broken line) lattices. Exact critical site densities, ρ_c, for the lattices are 0.5 for the triangular lattice and 0.59 for the square lattice.

The slope of $\langle G\rangle_{00}$ at long times and densities above the percolation edge can be used to define a diffusion constant. In Fig. 3, the inverse of this slope is plotted vs. density. Again a straight line which intercepts the density axis at ρ_c results. The translationally invariant Green's functions at long times are easy to obtain:

$$G_{00}(\rho = 1, t \to \infty) = \frac{1}{4\pi Dt} \qquad \text{(square lattice)}$$

$$G_{00}(\rho = 1, t \to \infty) = \frac{\sqrt{3}}{8\pi Dt} \qquad \text{(triangular lattice)}$$

where D is a diffusion constant. We know that for the $\rho = 1$ case $D = zw_0/4$, where z is the number of nearest neighbors, and by taking the constants into account, we find, using Fig. 3, that the density dependent diffusion constant (for both two-dimensional lattices in the coherent medium approximation) is

$$D(\rho, t=\infty) = \frac{zw_0}{4}\,\frac{(\rho - \rho_c)}{(1-\rho_c)}$$

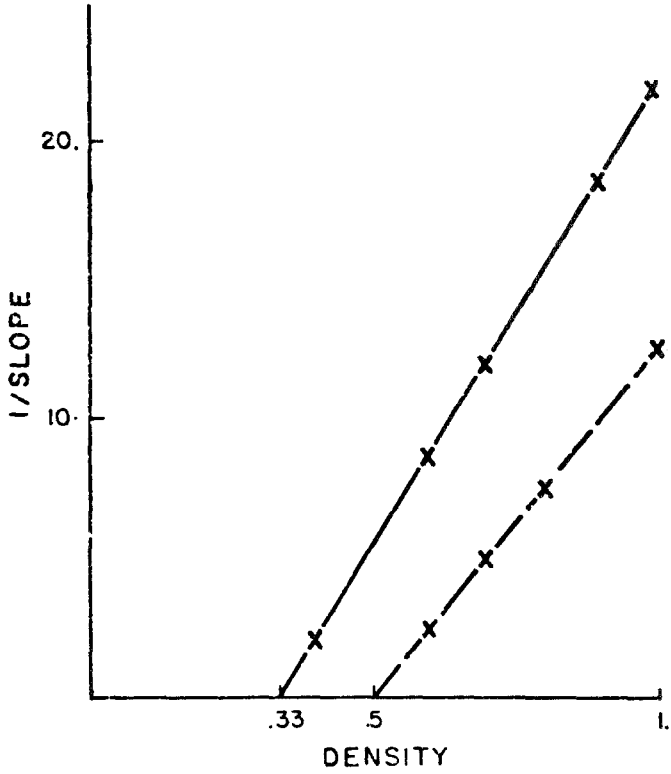

Fig. 3. Plot of 1/slope of $\langle G \rangle_{00}$ vs $1/\tilde{t}$ for long times for coherent medium nearest-neighbor triangular (solid line) and square (broken line) lattice. For $\tilde{t}$ large, $\langle G \rangle_{00} \propto 1/\tilde{t}$ for these lattices above the critical density.

6. CONCLUSION

We have derived a site-averaged coherent medium theory which is identical to the bond-averaged theories of previous workers,[8,9] and shown how these reduce in the low-density, short-time limit to the two-body solution results of GAF. Because of the flexibility in choosing S in Eqs. (21) or (38), many other coherent medium theories are possible. Some of these will describe the site-averaging problem more correctly, especially at long times. Note that there are several features of the exact solution which are incorrectly accounted for by the coherent medium theory presented here. For example, bond and site percolation probabilities should be different. There is no reason to believe that $\langle G(t = \infty) \rangle_{00}$ should be exactly zero at the percolation edge because not all sites are in the infinite cluster until $\rho = 1$.[14] Numerical simulations show that the diffusion constant is not

linear above the percolation edge but is $\alpha(\rho - \rho_c)^{\nu}$ with $\nu \sim 1.1$–1.3 for two-dimensional lattices.[17] Knowledge of the exact onset of long-time behavior is important because, in an experiment, the excitation may decay before it can make the necessary number of hops. We plan in the near future to publish results, using two-point Padé approximants, which will give exact numerical results for Eq. (6).

ACKNOWLEDGMENTS

This paper was presented at the Symposium on Random Walks in the Physical and Biological Sciences, which was held at the National Bureau of Standards from June 28 to July 1, 1982. We would like to thank the Organizing Committee of the Symposium for their invitation. We would also like to thank the National Science Foundation for support of this work.

REFERENCES

1. R. Kopelman, E. M. Monberg, and F. W. Ochs, *Chem. Phys.* **19**:413 (1977); S. D. Colson, S. M. George, T. Keyes, and V. Vaida, *J. Chem. Phys.* **67**:4941 (1977).
2. H. Dubost and R. Charneau, *Chem. Phys.* **12**:407 (1976).
3. D. L. Huber, D. S. Hamilton, and B. Barnett, *Phys. Rev. B* **16**:4642 (1977); and references therein.
4. E. Montroll and G. Weiss, *J. Math. Phys.* **6**:167 (1965); H. Scher and M. Lax, *Phys. Rev. B* **7**:4491 (1973); K. Godzik and J. Jortner, *Chem. Phys. Lett.* **63**:428 (1979).
5. S. W. Haan and R. Zwanzig, *J. Chem. Phys.* **68**:1879 (1978); S. Alexander, J. Bernasconi, W. R. Schneider, and R. Orbach, *Rev. Mod. Phys.* **53**:175 (1981); J. Machta, *Phys. Rev. B* **24**:5260 (1981); W. Y. Ching, D. L. Huber, and B. Barnett, *Phys. Rev. B* **17**:5025 (1978); U. Titulaer and J. Deutch, *J. Chem. Phys.* **77**:472 (1982).
6. J. Klafter and R. Silbey, *J. Chem. Phys.* **72**:843 (1980).
7. C. R. Gochanour, H. C. Andersen, and M. D. Fayer, *J. Chem. Phys.* **70**:4254 (1979).
8. T. Odagaki and M. Lax, *Phys. Rev. B* **24**:5284 (1981).
9. I. Webman, *Phys. Rev. Lett.* **47**:1496 (1981).
10. K. Godzik and J. Jortner, *Chem. Phys.* **38**:227 (1979); A. Blumen, J. Klafter, and R. Silbey, *J. Chem. Phys.* **72**:5320 (1980); D. Huber, *Phys. Rev. B* **20**:2307 5333 (1979).
11. J. Klafter and R. Silbey, *Phil. Mag.* (to be published).
12. T. Odagaki and F. Yonezawa, *Solid State. Commun.* **27**:1203 (1978).
13. V. Shante and S. Kirkpatrick, *Adv. Phys.* **20**:325 (1971).
14. D. Thouless, *Ill Condensed Matter*, (North-Holland, Amsterdam, 1979).
15. H. Stehfast, *Commun. ACM* **13**:47 (1970).
16. T. Forster, *Ann. Phys. (Leipzig)* **2**:55 (1948).
17. P. Li, W. Strieder, *J. Phys. C: Solid State Phys.* **15**:6591 (1982).