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Site-diagonal T-matrix expansion for anisotropic transport and percolation on bond-disordered lattices

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A study is made of the dynamical behavior of an electron or exciton undergoing anisotropic hopping on a d-dimensional bond-disordered lattice. Starting with a master equation for the site probabilities, an exact equation of motion is obtained for the probability currents that flow along the bonds connecting nearest-neighbor sites. Unlike the original master equation, the equation of motion which couples the microscopic currents contains the randomly distributed hopping rates in a form which is strictly site diagonal. The simplification that results leads to a new and exact expansion for the diffusion tensor in powers of an appropriately defined single-bond t matrix. From the lowest term of this expansion, a frequency-dependent effective-medium theory for anisotropic solids is constructed. The theory is then used to study the vanishing transport anisotropy that occurs for an anisotropic random walk on an isotropically percolating lattice near the critical point.

I. INTRODUCTION

Considerable progress has been made towards understanding the macroscopic transport properties of disordered systems in terms of relevant microscopic properties of the disordered environment.[1–19] Of particular use in this regard has been a large number of implementations of what are variously termed self-consistent, coherent-potential, or effective-medium theories.[8–16] These approaches offer a relatively simple but approximate means for calculating conductivities and diffusion constants in terms of the microscopic constituents of a particular disordered system. They have been applied with considerable success to a wide range of problems including the hopping conduction of charge carriers in amorphous solids,[10] exciton transport in mixed molecular crystals,[7] and disordered "random-resistor" networks.[9,14,16] In the latter problem particularly, they have been extensively applied in calculations of the dc conductivity for bond- and site-disordered percolating networks. The approach has even been phenomenologically extended to treat dc properties of anisotropic resistor networks,[16] where it has worked surprisingly well.

Indeed, the overall quantitative success of effective-medium theories is sometimes surprising in view of the relatively intuitive and phenomenological methods with which they are commonly derived. A typical approach consists of the following steps: (1) assume that the totally averaged system is well described by a nearest-neighbor network of "effective" (sometimes frequency-dependent) constituents (resistors, hopping rates, etc.), (2) replace one or more of these effective constituents with physical ones drawn from the original distribution characterizing the system, (3) calculate some relevant physical quantity for the effective network in the presence of the "defect" introduced in the second step, and finally, (4) average the solution over the original distribution and equate it to the corresponding quantity calculated for the homogeneous effective network. The result is an implicit equation for the effective constituent or bond introduced in step (1).

Such procedures obviously incorporate much of the correct underlying physics. On the other hand it is widely recognized that even when the original network contains only nearest-neighbor elements, the configuration-averaged system will not be characterized by a *single* nearest-neighbor bond. Indeed, there will generally be a translationally invariant set of such effective bonds connecting every site in the network.[20] While quantities such as the conductivity or the diffusion constant are apparently somewhat insensitive to this structure, the oversimplification associated with a strictly nearest-neighbor effective medium is certainly related to the breakdown of these theories in the region of critical points. Perhaps the most serious drawback of phenomenological derivations of this kind, however, is that they usually offer no guide to the calculation of *systematic* corrections to the effective-medium results.

The present paper addresses these concerns as they relate to the problem of a particle executing an *anisotropic* random walk on a d-dimensional bond-disordered lattice. The paper has two basic purposes. The first is to show how a hierarchy of effective-medium theories for the frequency-dependent diffusion tensor may be obtained in the form of a general and exact expansion in powers of an appropriate t-matrix. The second is to use the theory and expansion which results to study several classes of anisotropic percolation relevant to disordered solids.

The analytical approach used in the paper is an extension of one introduced recently by Kundu, Parris, and Phillips,[19] who considered a special case of the random-hopping model in two dimensions. The emphasis of that paper was on the development of equations of motion for the probability current, rather than for the site probabilities themselves.[21] The work presented here proceeds largely along the same lines. There are important differences, however, particularly regarding the division of the problem into perturbed and unperturbed parts. The current formulation facilitates a t-matrix resummation and thus yields a slightly different form for the final expansion. Perhaps more important for the purpose of this study, however, is the extension that the present work provides to higher dimensions and to the treatment of highly anisotropic solids.

The paper is laid out as follows. In the next section we start with an appropriate master equation and obtain an exact equation of motion for the probability currents which flow along the bonds connecting nearest-neighbor sites of the lattice. In contrast to the original master equation for the site probabilities, the randomly distributed rates appear in the form of a site-diagonal perturbation in the equations of motion which couple the microscopic currents. This leads to a simplification in the corresponding Dyson equation for the propagators of the current, and facilitates a standard t-matrix resummation using known techniques. In a manner similar to that of Ref. 19, a nonstandard but exact relationship (similar to one originally derived by van Kampen for the mean-square displacement of linear chains[22]) is used to obtain an exact expansion for the frequency-dependent diffusion tensor appropriate for anisotropic solids. To lowest order the expansion provides expressions which generalize isotropic results obtained previously.[11,12] The zero-frequency limit extends results obtained by Bernasconi[16] for the random-resistor network, and the general expression allows the calculation of frequency corrections that are important to the diffusion problem. In Sec. III, the theory is applied to two different classes of anisotropic percolation. For the problem of an anisotropic random walk on an isotropically percolating lattice, the theory predicts vanishing anisotropy at the critical point in both two and three dimensions. Such behavior has been predicted on other grounds and observed in simulations.[23] The present treatment is the first that the author is aware of which considers the vanishing anisotropy of the frequency-dependent parts of the diffusion tensor as well. The theory is also used to study the crossover between two and three dimensional behavior as a function of the microscopic anisotropy. The last section contains a summary and discussion of the main results of the paper as they pertain to hopping transport in quasi-low-dimensional systems.

II. MODEL AND APPROACH

To obtain an expansion for the diffusion tensor associated with an anisotropic disordered solid, we follow the basic approach of Kundu, Parris, and Phillips,[19] generalized so as to incorporate higher dimensions and the possibility of an anisotropic distribution of hopping rates. Thus, a particle executing a nearest-neighbor random walk on a d-dimensional bond-disordered cubic lattice can be described by the master equation

$$\dot{p}_{\mathbf{n}}(t)=\sum_{\nu=1}^{d} W_{\mathbf{n}}^{\nu}[p_{\mathbf{n}-\hat{\nu}}-p_{\mathbf{n}}]+W_{\mathbf{n}+\hat{\nu}}^{\nu}[p_{\mathbf{n}+\hat{\nu}}-p_{\mathbf{n}}] \quad (2.1)$$

for the probability $p_{\mathbf{n}}(t)$ of finding the diffusing particle at site $\mathbf{n}=(n_1,n_2,\ldots,n_d)$ of the lattice at time t. In (2.1), $\hat{\nu}$ represents a unit d vector pointing along the positive ν-coordinate axis from the $\mathbf{n}$th site to its neighbor along that direction, and $W_{\mathbf{n}}^{\nu}$ is the hopping rate from site $\mathbf{n}$ to its neighbor at $\mathbf{n}-\hat{\nu}$. In standard treatments the $W_{\mathbf{n}}^{\nu}$ are taken to be independent random variables governed by a single rate distribution function $\rho(w)$. In the present approach a different distribution function $\rho_\nu(w)$ is associated with each axis of the crystal.

The goal of the calculation is to determine information about the moments associated with the solutions to (2.1), averaged over all configurations of the randomly distributed rates. The second moments are of particular importance, since it is from these that one obtains the diffusion tensor and frequency corrections which describe the approach to diffusion. It is on the second moments that we concentrate in the present paper. To that end, a time-dependent diffusion tensor is introduced through the relation

$$2D_{\nu\nu}(t)\equiv\frac{d}{dt}\langle R_\nu^2(t)\rangle \quad (\nu=1,\ldots,d)\,, \quad (2.2)$$

where angular brackets denote configuration averages taken with respect to the entire ensemble of fluctuating jump rates, and $R_\nu^2(t)$ is the mean-square displacement of the particle along the ν-axis. If the transport is ultimately diffusive, then the mean-square displacement becomes linear at long times and $D_{\nu\nu}(t)$ approaches a constant. (For simplicity of notation, all distances along a given axis are assumed to be measured in units of the appropriate lattice constant.)

If we write the original master equation (2.1) in matrix form, i.e., $|\dot{p}\rangle=W|p\rangle$, then the spatially fluctuating rates $W_{\mathbf{n}}^{\nu}$ appear both as diagonal and off-diagonal elements in the site representation of the transition matrix W. It is the off-diagonal structure of W which complicates the task of obtaining a systematic expansion for (2.2) in powers of the disorder. As demonstrated in Ref. 19, however, this difficulty can be largely circumvented by starting out with a transformation from the site probabilities $p_{\mathbf{n}}(t)$, to the *probability currents* or fluxes

$$I_{\mathbf{n}}^{\nu}(t)=W_{\mathbf{n}}^{\nu}[p_{\mathbf{n}}-p_{\mathbf{n}-\hat{\nu}}] \quad (\nu=1,\ldots,d)\,, \quad (2.3)$$

which flow along the bonds connecting each site to its neighbors. The probability currents (2.3) can then be related to the time-dependent diffusion tensor defined in (2.1) by making use of the identity

$$\frac{d}{dt}\langle R_\nu^2\rangle=\langle R_\nu\rangle-2\sum_{\mathbf{n}} n_\nu\langle W_{\mathbf{n}}^{\nu}[p_{\mathbf{n}}-p_{\mathbf{n}-\hat{\nu}}]\rangle\,, \quad (2.4)$$

in which n_ν is the νth component of the position vector $\mathbf{n}$. Equation (2.4) is readily proved and has appeared in different forms elsewhere. A form of it was originally derived for linear chains by van Kampen.[22] It was later generalized to include higher-dimensional site[18]- and bond[19]-disordered lattices, for which it assumes the form appearing in Eq. (2.4). In the present context it may be made even more useful by introducing the Fourier-Laplace transform of the local current along each direction through the relation

$$J^{\nu}(\mathbf{k},z)=\sum_{\mathbf{n}}\int_0^{\infty}dt\,I_{\mathbf{n}}^{\nu}(t)e^{-zt}e^{i\mathbf{k}\cdot\mathbf{n}}\quad(\nu=1,\ldots,d)\ ,\qquad(2.5)$$

in which $\mathbf{k}=(k_1,k_2,\ldots,k_d)$ is a reciprocal-lattice d vector and z is the Laplace variable conjugate to time. This allows us to define a frequency-dependent diffusion tensor of the form

$$\begin{aligned}D_{\nu\nu}(z)&\equiv zL_z\{D_{\nu\nu}(t)\}\\&=iz\frac{\partial}{\partial k_\nu}\langle J^{\nu}(\mathbf{k},z)\rangle\bigg|_{\mathbf{k}=0}\end{aligned}\qquad(2.6)$$

in which $L_z\{f(t)\}$ denotes the Laplace transform of a function $f(t)$, and $D_{\nu\nu}(z)$ has been defined so that its value at $z=0$ is equal to the infinite-time limit of the time-dependent diffusion tensor defined in (2.2). The second equality in (2.6) is obtained from (2.2)–(2.5) by assuming an initial condition in which the particle starts each walk at the origin; thus the average displacement $\langle R_\nu\rangle$ appearing in (2.4) vanishes. Note however, that, with the symmetry exhibited by the jump rates displayed in (2.1), the averaging process makes this initial condition equivalent to having used the equilibrium distribution. Thus, it is the equilibrium properties that are obtained from an evaluation of (2.6).

The chief result of the transformation introduced in (2.3) is that the original equations of motion may now be recast so that the disorder takes the form of a strictly site-diagonal perturbation. To see this we generalize a procedure introduced in Ref. 19 for isotropic systems. Substituting the definition (2.3) of the current $I_{\mathbf{n}}^{\nu}(t)$ into the original master equation (2.1), taking Laplace transforms, and using (2.5), we obtain the expression

$$\begin{aligned}&z\sum_{\mathbf{n}}[P_{\mathbf{n}}-P_{\mathbf{n}-\hat{\nu}}]e^{i\mathbf{k}\cdot\mathbf{n}}\\&\quad=(1-e^{ik_\nu})-\sum_{\mu}(1-e^{ik_\nu})(1-e^{-ik_\mu})J^{\mu}(\mathbf{k},z)\ ,\end{aligned}\qquad(2.7)$$

where $P_{\mathbf{n}}(z)$ is the Laplace transform of $p_{\mathbf{n}}(t)$, and the first term on the right-hand side of the equation arises from the initial condition $p_{\mathbf{n}}(0)=\delta_{\mathbf{n},0}$. The quantity on the left-hand side of (2.7) may be rewritten using the identity

$$\begin{aligned}&z\sum_{\mathbf{n}}[P_{\mathbf{n}}-P_{\mathbf{n}-\hat{\nu}}]e^{i\mathbf{k}\cdot\mathbf{n}}\\&\quad=z_\nu J^{\mu}(\mathbf{k},z)-z\int d\mathbf{k}'V^{\nu}(\mathbf{k}-\mathbf{k}',z)J^{\nu}(\mathbf{k}',z)\ ,\end{aligned}\qquad(2.8)$$

in which

$$V^{\nu}(\mathbf{k})=(2\pi)^{-d}\sum_{\mathbf{n}}[(1/C_\nu)-(1/W_{\mathbf{n}}^{\nu})]e^{i\mathbf{k}\cdot\mathbf{n}}\ .\qquad(2.9)$$

In (2.8) and (2.9), the quantity $z_\nu=z/C_\nu$ is a scaled Laplace variable, integrations over wave vector are to be understood as running over the first Brillouin zone, and the quantities C_ν, which depend upon the crystal axis and possibly the frequency, define a uniform but generally anisotropic reference system about which the fluctuating jump rates along each axis are measured. At this stage they are arbitrary, however, because (2.8) is an identity for any value of the C_ν. This is readily verified by substituting (2.4), (2.5), and (2.9) into (2.8) and performing the resultant integral over $\mathbf{k}'$. The delta functions that appear cause the C_ν dependence to drop out entirely, allowing one to recover the left-hand side of the expression. Replacing the left-hand side of (2.7) with the right-hand side of (2.8), we then obtain the desired equation of motion for the currents $J^{\mu}(\mathbf{k},z)$. These can be compactly written in operator matrix notation as

$$[Z+H-zV]J=j\qquad(2.10)$$

in which J and j are column d vectors whose νth components are $J^{\nu}(\mathbf{k},z)$ and $1-e^{ik_\nu}$, respectively; the diagonal operator Z has components $Z_{\mathbf{kk}'}^{\nu\mu}=z_\nu\delta_{\nu\mu}\delta(\mathbf{k}-\mathbf{k}')$, and the operator H is given by

$$H_{\mathbf{kk}'}^{\mu\nu}=(1-e^{ik_\mu})(1-e^{-ik_\nu})\delta(\mathbf{k}-\mathbf{k}')\ .$$

The operator V appearing in (2.10) has elements $V_{\mathbf{kk}'}^{\nu\mu}=V^{\nu}(\mathbf{k}-\mathbf{k}')\delta_{\nu\mu}$ given by (2.9). Its inverse Fourier transform

$$\begin{aligned}V_{\mathbf{nm}}^{\mu\nu}&=[(1/C_\nu)-(1/W_{\mathbf{n}}^{\nu})]\delta_{\mathbf{nm}}\delta_{\mu\nu}\\&\equiv V_{\mathbf{n}}^{\nu}\delta_{\mathbf{nm}}\delta_{\mu\nu}\end{aligned}\qquad(2.11)$$

demonstrates the point emphasized earlier; the operator V, which now contains all of the disorder, is strictly diagonal in the site representation. Observe that it is diagonal in the directional indices as well. Indeed, *both* the perturbation V and the currents $I_{\mathbf{n}}^{\nu}$ exhibit this *bond diagonality*. It is this common symmetry which motivates the choice of the latter as a natural set of variables for the bond-disorder problem.

To proceed we now define the operator $G=z(Z+H-zV)^{-1}$ and make the following observation. Equation (2.6) shows that a calculation of the diffusion tensor requires the derivative with respect to wave vector of the quantity $z\langle J\rangle=\langle G\rangle j$. As a result of averaging, however, the operator $\langle G\rangle$ is diagonal in $\mathbf{k}$ space. Let us denote its diagonal part by $D_{\nu\nu}(\mathbf{k},z)$, i.e., let us write $\langle G\rangle_{\mathbf{kk}'}^{\nu\nu}=D_{\nu\nu}(\mathbf{k},z)\delta(\mathbf{k}-\mathbf{k}')$ and use the fact that the elements $1-e^{ik_\nu}$ of the vector j vanish as $\mathbf{k}\rightarrow0$ to obtain the result

$$\begin{aligned}D_{\nu\nu}(z)&=\left\{i\frac{\partial}{\partial k_\nu}\langle Gj\rangle_{\mathbf{k}}^{\nu}\right\}\bigg|_{\mathbf{k}=0}\\&=D_{\nu\nu}(\mathbf{k},z)\,|_{\mathbf{k}=0}\ .\end{aligned}\qquad(2.12)$$

In obtaining (2.12) we have also used the fact that all but the diagonal terms of the implied matrix multiplication inside the average have disappeared because of the vanishing of the components of j. Equation (2.12) demonstrates the point of immediate interest—the diffusion tensor may be obtained solely from a knowledge of the diagonal part of the current propagator. It suffices, therefore, to focus the analysis on the properties of $\langle G\rangle$. We wish to now cast it in a form more amenable to solution. Up to this point, the calculation has essentially been a generalization of the approach taken by Kundu, Parris, and Phillips[19] to higher-dimensional anisotropic systems. At this point, however, we deviate from the approach taken earlier by choosing as an unperturbed propagator the quantity $g=z(Z+H)^{-1}$, which represents uniform motion with diffusion tensor $D_{\nu\nu}(z)=C_\nu(z)$. The main difference between this choice and that of Ref. 19 is that the unperturbed propagator used in the earlier work includes a part which depends upon average properties of the perturbation. Such an inclusion is not undesirable—however, it does complicate the task of resumming the perturbation series and so in the present approach a simpler choice is made. This leads immediately to an expansion of the Dyson form

$$\langle G\rangle=\langle g+gVG\rangle=\langle g+gVg+gVgVg+\cdots\rangle\ , \tag{2.13}$$

for which the elements of the unperturbed Green's function g are given explicitly by

$$g_{\mathbf{k}\mathbf{k}'}^{\mu\nu}(z)=C_\mu\left[\delta_{\mu\nu}-C_\nu\frac{[1-\exp(-ik_\mu)][1-\exp(ik_\nu)]}{z+\sum\limits_\lambda 2C_\lambda(1-\cos k_\lambda)}\right]\delta(\mathbf{k}-\mathbf{k}')\ . \tag{2.14}$$

We have succeeded therefore in casting the problem into a standard one that involves both normal and perturbed components, and we have identified a representation in which the perturbation is diagonal and uncorrelated, viz., the bond representation labeled by the set $\{n,\nu\}$. This latter fact makes it possible to perform a t-matrix resummation[24] by summing internal indices over repeated scatterings from the same bond. To this end we introduce the single-bond t matrix

$$t_{\mathrm{nm}}^{\mu\nu}(z)=V_{\mathrm{n}}^{\nu}[1-g_0^\nu V_{\mathrm{n}}^\nu]^{-1}\delta_{\mathrm{nm}}\delta_{\mu\nu}\ , \tag{2.15}$$

and a restricted propagator p, defined in terms of its matrix elements $p_{\mathbf{k}\mathbf{k}'}^{\mu\nu}=g_{\mathbf{k}\mathbf{k}'}^{\mu\nu}-g_0^\nu\delta_{\mu\nu}\delta(\mathbf{k}-\mathbf{k}')$. These definitions along with that of the self-propagator

$$g_0^\nu=(2\pi)^{-d}\int\int d\mathbf{k}\,d\mathbf{k}'g_{\mathbf{k}\mathbf{k}'}^{\nu\nu}\ , \tag{2.16}$$

which appears in both (2.15) and (2.16), leads to the desired expansion in its final form

$$D_{\nu\nu}(\mathbf{k},z)\delta(\mathbf{k}-\mathbf{k}')\\
=[g+g\langle t\rangle g+g\langle tpt\rangle g+g\langle tptpt\rangle g+\cdots]\Big|_{\mathbf{k},\mathbf{k}'}^{\nu,\nu}\ . \tag{2.17}$$

Equation (2.17) forms the basis for the analysis which follows.

III. A SELF-CONSISTENT EXPANSION

Equation (2.17) with the definitions (2.14)–(2.16) constitute one of the main results of the present paper. The expansion, which is exact for any value of the C_ν, provides a systematic means of obtaining information about the frequency-dependent diffusion tensor for anisotropic systems. Naturally, the choice of the C_ν will vary according to the application. For a nearly pure solid possessing a relatively small fraction of defective bonds it is natural to use the perfect crystal as a uniform reference system. Thus C_ν will equal the pure-crystal hopping rate for jumps along the νth direction. The two lowest terms in the expansion (2.17) provide a solution for this case which is exact to $O(q)$ in the concentration q of defective bonds. It is also possible to sum selected terms from higher orders in the expansion to obtain the exact contribution to $O(q^2)$. This approach has been used recently by Parris, Phillips, and Kundu[25] to investigate higher-order corrections to effective-medium results, and yields an accurate prediction, $p_c=0.256$, for the transport threshold of the three-dimensional bond-percolation model.

In a strongly disordered system, however, the diffusion tensor itself represents the best average system about which to measure the fluctuating rates–formally choosing $C_\nu(z)=D_{\nu\nu}(z)$ we obtain from (2.17) an exact self-consistent condition for determining the frequency-dependent diffusion tensor, viz.,

$$\langle T\rangle\equiv[\langle t\rangle+\langle tpt\rangle+\langle tptpt\rangle+\cdots]=0\ . \tag{3.1}$$

This condition follows from (2.17) and the fact that $g_{kk'}^{\nu\mu}(z)\rightarrow C_\nu\delta_{\nu\mu}\delta(\mathbf{k}-\mathbf{k}')$ as $\mathbf{k}\rightarrow 0$. To use (3.1) it must be truncated at some order m (possibly after some additional partial resummation) and solved to find those values of the $C_\nu(z)$ which make the resultant approximation to the total scattering matrix $\langle T\rangle$ vanish. By assumption, then, these values will correspond to the actual values of the diffusion tensor. Thus the condition (3.1) represents a hierarchy of self-consistent equations, each member of which corresponds to a consideration of successively higher orders of the t matrix.

In what follows, we will be primarily concerned with investigating general features that emerge as a result of microscopic transport anisotropy. Therefore, we defer to a later study a detailed investigation of the higher-order corrections and, instead, concentrate on the self-consistent theory that results from truncating (3.1) after the first term; that is, we investigate the behavior of the frequency-dependent diffusion tensor that arises as a solution to the CPA-like (CPA denotes coherent potential approximation) condition[26]

$$\langle t\rangle^{\nu\nu}=0\quad(\nu=1,\ldots,d) \tag{3.2}$$

in which the quantities C_ν appearing in the definitions (2.14)–(2.16) are presumed to represent the exact components of the diffusion tensor $D_{\nu\nu}(z)$.

The important observation at this point, particularly for anisotropic solids, is that the diagonal components of the average t matrix are not generally independent—each one depends implicitly on the other components, and on the actual components of the diffusion tensor, through the quantity g_0^ν appearing in the definition (2.15). To cast these expressions in a more suggestive form let us define a frequency-dependent "dimensionality" for each direction through the relation

$$\begin{aligned} d_\nu^{-1}(z) &\equiv [1-C_\nu^{-1}(z) g_0^\nu(z)] \\ &= (2\pi)^{-d} \int d\mathbf{k} \frac{2(1-\cos k_\nu)}{z_\nu + \sum_\lambda 2\eta_{\lambda\nu}(1-\cos k_\lambda)} \end{aligned}$$

$$(\nu=1,\ldots,d) , \quad (3.3)$$

which depends upon the quantities $\eta_{\mu\nu}(z) \equiv D_{\mu\mu}(z)/D_{\nu\nu}(z)$ that characterize the *macroscopic* (and generally frequency-dependent) anisotropy of the disordered medium. With this definition and (2.15), Eq. (3.2), which expresses the vanishing of the t matrix can, after some slight manipulation, be written

$$\left\langle \frac{W_{\mathrm{n}}^\nu - D_{\nu\nu}(z)}{W_{\mathrm{n}}^\nu + [d_\nu(z)-1] D_{\nu\nu}(z)} \right\rangle = 0 \quad (\nu=1,\ldots,d) . \quad (3.4)$$

Thus, combining (3.3) and (3.4) we obtain a set of $2d$ coupled equations from which the effective-medium dimensionality $d_\nu(z)$ and the diffusion tensor $D_{\nu\nu}(z)$ may be calculated. Of course, if the rate distribution function $\rho_\nu(w)$ is independent of the crystal axes, then the system will be isotropic on the average, the d_ν will reduce at $z=0$ to the Euclidean dimension, and the $\eta_{\nu\mu}$ will all equal 1. In this limit (3.4), which expresses the vanishing of the $\langle t \rangle$ matrix, reduces to a single equation identical to the frequency-dependent effective-medium theories obtained elsewhere.[11,12] In the general case, however, the distribution functions along different axes are different and the $\eta_{\nu\mu}$ will be different from 1. In this latter situation Eqs. (3.3) and (3.4) must be solved simultaneously.

IV. APPLICATIONS

A. Anisotropic walks on isotropically percolating lattices

To illustrate the general approach, we first consider a three-dimensional lattice described by the distribution function

$$\rho_\nu(W) = p\delta(W-W_\nu) + (1-p)\delta(W) . \quad (4.1)$$

This corresponds to an anisotropic bond-percolation model wherein hops along different directions proceed with different rates W_ν, but the fraction p of available bonds in each direction is identical (as in normal percolation). If we now fix the rates for two of the directions (x and y say), and vary or reduce the rate W_z associated with the z direction, then the corresponding curve of D_{xx} versus p will exhibit a crossover from three-dimensional to two-dimensional percolative behavior as $W_z \to 0$. With the distribution (4.1), however, the *connectivity* remains that of a three-dimensional percolating structure until W_z is identically zero. Thus, only in this limit does the critical concentration collapse from the three-dimensional value to the two-dimensional one, $p_c = \frac{1}{2}$.

We examine the dc behavior first. Figure 1 shows the solution of (3.3) and (3.4) for the dc components of the diffusion tensor corresponding to several different values of the *microscopic* anisotropy ratio $\zeta = W_z/W_x$. In Fig. 2, the degree of macroscopic anisotropy $\eta = D_{zz}/D_{xx}$ associated with the curves depicted in Fig. 1 is also shown. To obtain these figures the analytical solution to (3.4) for this distribution $D_{\nu\nu} = W_\nu(pd_\nu - 1)/(d_\nu - 1)$, was used to obtain an expression for the ratio η as function of the set $\{d_x, d_y, d_z\}$. Substitution of the resulting expression into (3.3) then allows d_x or d_z to be determined by numerical integration. Note that the value of p_c predicted by the theory is the effective-medium value for three-dimensions, $p_c = \frac{1}{3}$. This is, of course, a result of truncating the expansion (3.1) at lowest order.

As the microscopic anisotropy is increased the curve tends toward the two-dimensional effective-medium limit, which is indicated by the dashed line. Ultimately, when $\zeta = 0$, the correct two-dimensional critical concentration is recovered. Even when the microscopic anisotropy is finite, however, the theory predicts that the macroscopic anisotropy will vanish as the critical point is approached from above. This behavior can be clearly seen in Fig. 2, and has been observed in simulations.[23] It can be understood as follows. In an ordered lattice the macroscopic diffusion tensor directly reflects the microscopic anisotropy; hence $\eta = \zeta$ when $p=1$. As p de-

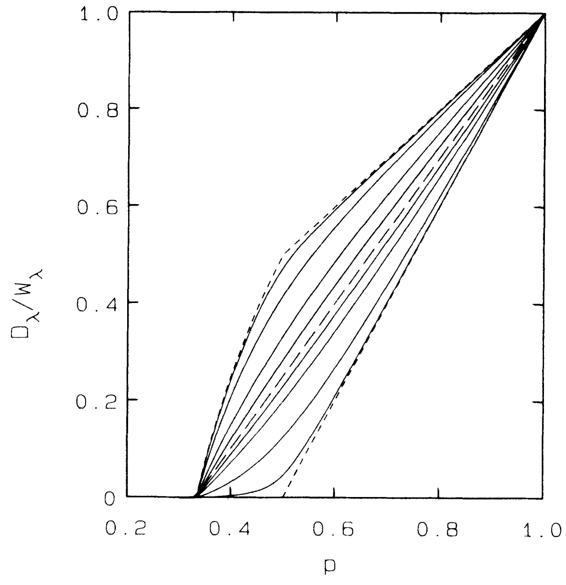

FIG. 1. Normalized components of the diffusion tensor for a three-dimensional lattice with unbroken bond concentration p. The center curve with long dashes shows the isotropic result. Curves lying below the isotropic one correspond to the x component D_{xx}/W_x, those which lie above to the z component D_{zz}/W_z. Moving outward from the isotropic curve are curves corresponding to microscopic anisotropies $\zeta = W_z/W_x = 0.7$, 0.4, 0.1, 0.01, and 0, respectively.

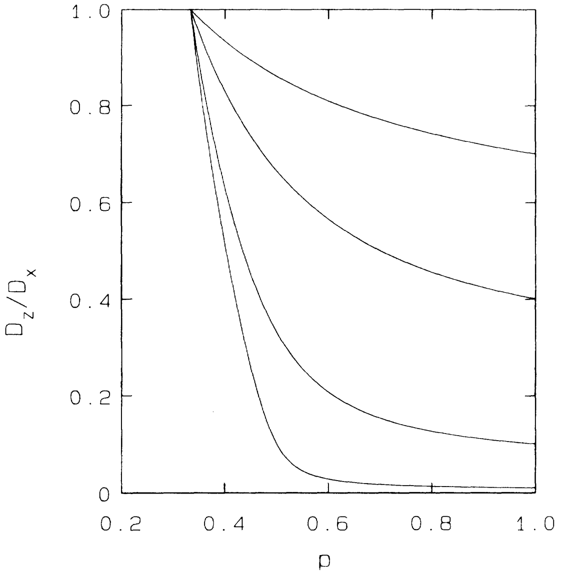

FIG. 2. Macroscopic anisotropy ratio $\eta=D_{zz}/D_{xx}$ as a function of unbroken bonds p for the curves depicted in Fig. 1. The value of each curve at $p=1$ indicates the microscopic anisotropy; $\zeta=0.7$, 0.4, 0.1, and 0.01.

creases, however, motion along a given direction becomes more difficult and depends more critically upon the possibility of hops alongs orthogonal directions. The motion along the slower z direction is helped more by hops along the faster directions than it would be if those hops occurred with frequency W_z. On the other hand, motion along the faster directions is helped less as a result of hops along the z direction than it would be if those hops occurred with frequency W_x. The net effect is clearly to reduce the anisotropy exhibited at the macroscopic level. (This would also seem to be a rather general argument not limited to the present example.) Ultimately, the theory predicts that the system becomes isotropic in the limit, with the diffusion constant in each direction vanishing in the same manner:

$$D_{xx}\sim D_{zz}\sim\tfrac{3}{2}(p-p_c)\frac{3W_xW_yW_z}{W_xW_y+W_xW_z+W_yW_z}\quad p\to p_c$$

$$=\tfrac{3}{2}(p-p_c)\langle 1/W\rangle^{-1}\,, \tag{4.2}$$

where the average in the second line of (4.2) is over the rates associated with the three directions along which the particle can move. The result (4.2) is readily established by expanding (3.3) and (3.4) for small η and small values of $p-p_c$. It is interesting to note that, aside from the factor of $p-p_c$, the form of (4.2) is identical to that associated with a *one-dimensional* disordered system in which the rates take the values W_x, W_y, and W_z at random. This gives an indication of the tortuous but essentially one-dimensional path followed by the particle near the critical point, and reiterates the interdependency of motion along the different directions. (Such behavior is difficult to recognize in the standard isotropic analysis.) If we introduce an exponent λ to describe the vanishing of the anisotropy, i.e., we write $\eta-1\sim(p-p_c)^{\lambda}$, we find that at this order the theory predicts $\lambda=1$. Simple arguments would seem to suggest that λ should be related to the exponent t that describes the vanishing of the diffusion constant (and is generally speaking greater than one) by the relation $\lambda=2-t$.

Before discussing the frequency corrections let us discuss another interesting feature of Fig. 1, namely the noticeable kink that appears at $p=\frac{1}{2}$ in the z component of the diffusion tensor when ζ is reduced to zero. This feature can be understood by viewing the vanishing of ζ as a process in which W_x and W_y are going to infinity with W_z fixed, rather than one in which W_z is going to zero with W_x and W_y fixed. We have scaled the components of the diffusion tensor by the hopping rates, so the figures apply to both cases. In this limit, as $p\to\frac{1}{2}$ the x-y plane independently undergoes a two-dimensional percolation transition to a macroscopically "superconducting" state. As a consequence, motion along the z direction is "shorted-out" and immediately becomes motionally averaged. Thus for $p>\frac{1}{2}$ we obtain the exact result, $D_{zz}=\langle W_z\rangle$. The kink, therefore, is merely a signature of a transition taking place in a perpendicular plane.

Let us now consider the leading frequency corrections to the zero-frequency behavior discussed above. Such corrections can be obtained from the small-z properties of the effective dimensionality (3.3). By expanding (3.3) and (3.4) about $z=0$, we obtain the following results. At low frequencies, for $p>p_c$ we may write $D_{\nu\nu}(z)=D_0^{\nu}+D_1^{\nu}z+D_2^{\nu}z^{3/2}$. The value of D_0^{ν} is determined from the zero-frequency limit of (3.3) and (3.4) and has already been discussed. The coefficients D_1^{ν} and D_2^{ν} can then be written

$$D_1^{\nu}=-\frac{d_{0,\nu}^2(1-p)W_\nu}{d_{1,\nu}(d_{0,\nu}-1)^2}\,, \tag{4.3}$$

$$D_2^{\nu}=-\frac{d_{0,\nu}^2(1-p)W_\nu}{d_{2,\nu}(d_{0,\nu}-1)^2}\,, \tag{4.4}$$

where $d_{0,\nu}$, $d_{1,\nu}$, and $d_{2,\nu}$ come from an expansion of the effective dimensionality about $z=0$;

$$\frac{1}{d_\nu}=\frac{1}{d_{0,\nu}}+\frac{z}{d_{1,\nu}}+\frac{z^{3/2}}{d_{2,\nu}}+O(z^2)\,. \tag{4.5}$$

The zero-frequency limit of (3.3) defines $d_{0,\nu}$. The values of $d_{1,\nu}$ and $d_{2,\nu}$ may be obtained explicitly for this problem. We find e.g., that for the x component we may write $d_{1,x}=\Gamma_1^x/\Omega$ and $d_{2,x}=\Gamma_2^x/\Omega$, where

$$\Gamma_1^x=-A_x+b_y[(A_x+A_y)M_{xy}+A_xM_{yz}]$$
$$+b_z[(A_x+A_z)M_{zx}+A_xM_{yz}]$$
$$+b_yb_z(A_x+A_y+A_z)(M_{zx}M_{xy}+M_{zx}M_{yz}+M_{xy}M_{yz})\,, \tag{4.6}$$

$$\Gamma_2^x = A[1+b_y(2M_{xy}+M_{yz})+b_z(2M_{zx}+M_{yz}) + 3b_yb_z(M_{zx}M_{xy}+M_{zx}M_{yz}+M_{xy}M_{yz})] , \quad (4.7)$$

$$\Omega = 1+b_x(M_{xy}+M_{zx})+b_y(M_{xy}+M_{yz})+b_z(M_{yz}+M_{zx}) + (b_xb_y+b_yb_z+b_zb_x)(M_{xy}M_{yz}+M_{xy}M_{zx}+M_{yx}M_{zx}), \quad (4.8)$$

$$b_\nu = \frac{d_{0,\nu}^2(1-p)W_\nu}{D_0^\nu(d_{0,\nu}-1)^2} , \quad (4.9)$$

$$A = \frac{1}{12\pi}\frac{1}{(D_0^xD_0^yD_0^z)^{1/2}} , \quad (4.10)$$

and the quantities A_ν and $M_{\nu\mu}$ are defined in terms of the integrals

$$A_\nu = (2\pi)^{-3}\int dk^3 \frac{2D_0^\nu(1-\cos k_\nu)}{\left[\sum_\lambda 2D_0^\lambda(1-\cos k_\lambda)\right]^2} , \quad (4.11)$$

$$M_{\nu\mu} = (2\pi)^{-3}\int dk^3 \frac{2D_0^\mu(1-\cos k_\mu)2D_0^\nu(1-\cos k_\nu)}{\left[\sum_\lambda 2D_0^\lambda(1-\cos k_\lambda)\right]^2} . \quad (4.12)$$

The expressions for the y and z components may be obtained from those for the x components given above by a cyclic permutation of the indices x, y, and z. Note that the frequency corrections are entirely determined by the zero-frequency behavior of the diffusion tensor and effective dimensionality. Equations (4.6)–(4.12), which describe the frequency corrections, while useful, are somewhat complicated. Their behavior near the critical point is relatively simple, however. A straightforward analysis of (4.11) and (4.12) near the isotropic limit reveals that the frequency corrections become isotropic at the critical point, tending as $p \to p_c$ towards the values

$$D_1^\nu \sim \tfrac{1}{6}M_0(p-p_c)^{-1} \quad (4.13)$$

and

$$D_2^\nu \sim -(\tfrac{3}{2})^{1/2}(1/12\pi)\langle 1/W\rangle^{1/2}(p-p_c)^{-3/2} , \quad (4.14)$$

in which M_0 is given by (4.12) with all D_ν^0 set equal to 1 (for which it reduces to a Watson integral[27]) and the average of $1/W$ appearing in (4.14) has the same meaning as in (4.2). Writing $\lambda(z)$ to describe the vanishing of the anisotropy of the diffusion tensor at frequency z, the theory predicts that to $O(z^{3/2})$, $\lambda(z)=\lambda=1$. Note, that in the critical region the second frequency correction depends explicitly upon the microscopic anisotropy, as does the zero-frequency value (4.2); the first frequency correction, on the other hand, is independent of the microscopic rates and is in fact identical to the value associated with a completely isotropic system. The reasons for this difference are not immediately apparent. It will be noted, however, that a frequency correction of $O(z)$ in the diffusion tensor gives rise to a time-independent correction to the mean-square displacement.

A similar approach can be taken for the two-dimensional square lattice. In Figs. 3 and 4, respective-

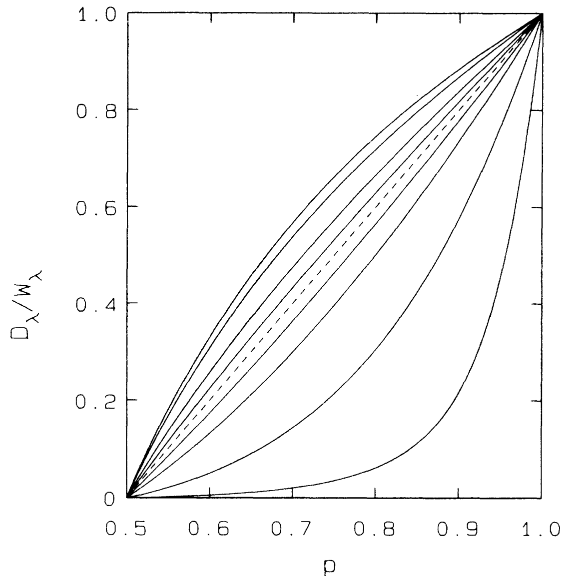

FIG. 3. Normalized components of the diffusion tensor for a two-dimensional lattice with unbroken bond concentration p. The dashed curve shows the isotropic result. Curves lying below the isotropic one correspond to the x component D_{xx}/W_x, those which lie above to the y component D_{yy}/W_y. Moving outward from the isotropic curve are curves corresponding to microscopic anisotropies $\zeta = W_y/W_x = 0.7$, 0.4, 0.1, and 0.01, respectively.

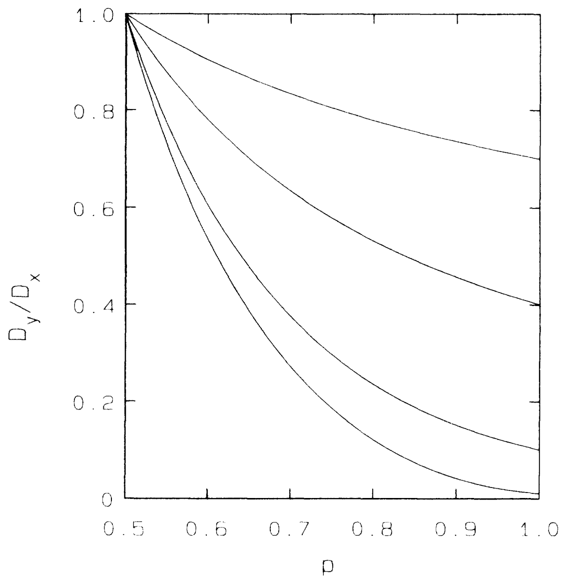

FIG. 4. Macroscopic anisotropy ratio $\eta = D_{yy}/D_{xx}$ as a function of unbroken bonds p for the curves depicted in Fig. 3. The value of each curve at $p=1$ indicates the microscopic anisotropy; $\zeta = 0.7$, 0.4, 0.1, and 0.01.

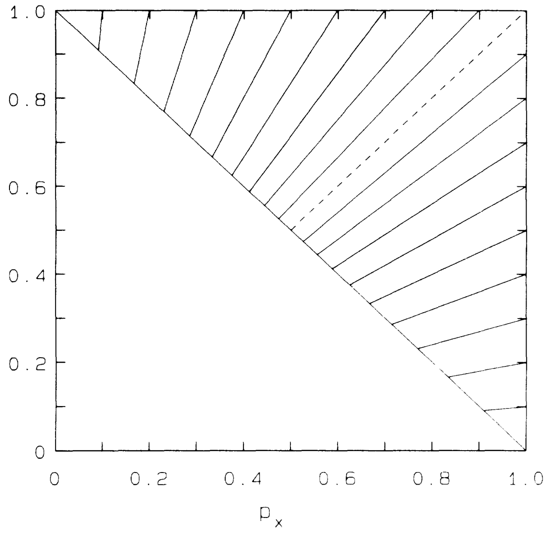

FIG. 5. Phase diagram showing region of macroscopically diffusive transport (upper right-hand corner) and subdiffusive transport (lower left-hand corner), for a two-dimensional lattice with a fraction p_x of allowed hopping rates in the x direction and a fraction p_y of hopping rates in the y direction. The line of critical points is exact. The radial lines in the diffusive region are lines of constant anisotropy ratio $D_{yy}/D_{xx}=\text{const}$. The dashed curve is the isotropic case.

ly, the diffusion tensor and macroscopic anisotropy are plotted as a function of the concentration for a two-dimensional system corresponding to the distribution function (4.1). Again the system becomes isotropic at the critical point. For low frequencies we may write the components of the diffusion tensor in two dimensions in the form $D_{\nu\nu}=D_0^\nu+D_1^\nu z\ln z$, which near the critical point exhibits the isotropic behavior

$$D_0^\nu \sim \tfrac{1}{2}(p-p_c)\langle 1/W\rangle^{-1} ,$$

$$D_1^\nu \sim (1/2\pi)(p-p_c)^{-1} .$$

Again we see that the zero-frequency result depends explicitly upon the microscopic anisotropy, whereas the first frequency correction does not.

B. Isotropic walks on anisotropically percolating lattices

Finally, consider a slightly different form of anisotropic percolation characterized by the distribution $\rho_\nu(W)=p_\nu\delta(W-w)+(1-p_\nu)\delta(W)$. With this choice the hopping rate associated with allowed bonds is the same for all directions, but bonds along different axes occur with different probabilities p_ν. For simplicity consider the square lattice. The solution of Eqs. (8) and (9) for this distribution produces the two-parameter phase diagram shown in Fig. 5. The line of critical points $p_x=1-p_y$ is exact.[28] Also shown are the predicted isoanisotropes, the lines of constant $\eta=D_{yy}/D_{xx}$. The system does not become isotropic at the critical points as it did in the previous example. However, the anisotropy is clearly reduced from that which is evident at the microscopic level.

V. SUMMARY

A theoretical description of hopping transport in anisotropic disordered systems has been developed and used to study the incoherent dynamics of particles moving in anisotropic percolating environments. The general approach outlined in the paper is adaptable to a wide class of distribution functions and should prove useful in analyzing anisotropic materials, such as organic and inorganic molecular crystals. One conclusion that can be drawn from the treatment of percolating lattices presented in the paper is that highly anisotropic materials are not always well modeled by systems of physically reduced dimensionality. Indeed it would appear that for strongly disordered solids the interdependency of motion along each direction can lead to a substantial reduction of the macroscopic anisotropy relative to that which characterizes the microscopic environment. The present work raises the possibility of questions concerning the interpretation of a number of exciton transport measurements made on substitutionally disordered mixed molecular crystals.[29] Such measurements have been interpreted in terms of percolation models in both two and three dimensions. It seems likely that if percolation concepts are really appropriate for these systems, then, given the anisotropy of the pure materials, the actual situation may be better characterized by an anisotropic percolation model. Hence, any extraction of critical exponents from the data should somehow take into account the possibility of increased curvature outside the critical region as a result of anisotropy (see, e.g., Fig. 1). In such circumstances, the condition of validity for a lower-dimensional analysis is that the mean time between jumps along the slow (i.e., neglected) dimension be much longer than the natural lifetime of the excitation.

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