Correlated hopping in a disordered medium

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This paper discusses random walks with memory on a percolating network as a model of correlated hopping transport through a disordered system. Correlations can arise from such sources as hard-core and Coulomb repulsions, correlated hops of groups of particles, or lattice-relaxation effects. In general these correlations will result in a difference between the hopping probability for return to the previously visited site and the probability to jump to another nearest neighbor of the currently occupied site. Thus the hopping process possesses a memory of its previous hop. Such a random walk is investigated in this paper for the case of bond percolation on a regular lattice. The frequency-dependent conductivity $\sigma(\omega)$ is calculated using a generalized effective-medium approximation. Results are presented for the linear chain and the hexagonal lattice. New features appear in both the real and the imaginary part of σ. These depend on the strength of the correlations and on the concentration of bonds. As an example, the possibility of a pronounced maximum in the real part of $\sigma(\omega)$ at finite frequencies is found, which is sometimes accompanied by a change of sign in the imaginary part. The results are found to agree qualitatively with experimental data on ionic transport in Na^+-β-alumina, where both disorder and correlations are known to be important.

I. INTRODUCTION

Amorphous solids and other disordered systems often exhibit transport via a hopping mechanism. Examples include hopping transport in amorphous semiconductors, ionic conductivity of superionic solids, carrier recombination in glasses, or excitation migration in a molecular crystal.[1]

Much theoretical work has concentrated on the hopping (or random walk) of a single particle in a disordered environment without considering the effect of interactions or correlations between particles. Other investigations have focused on correlations but neglected disorder. It is the objective of this paper to investigate the case where both disorder and correlations are present. This study is motivated by the attempt to incorporate correlation effects into the dynamic percolation model which was developed as a model for ionic transport in mixed Na^+-$Ba^{2+}\beta''$alumina.[2] To this end it is necessary to study first the case of correlated hopping in a disordered system whose disorder is time independent. This will be done in the present paper. The outcome will be applied to Na^+-β-alumina where correlations are known to play an important role. The extension to the case of dynamic disorder is presented elsewhere.[3]

Disorder will be discussed in the framework of the well-known bond-percolation model on a regular lattice while correlations from sources other than the disorder will be treated in terms of the correlated jump model of Gillis.[4] The essential idea of the model is that quite generally hopping transport can be viewed as correlated if the particle has a memory of its previous hop,[5] i.e., if the probability for a transition to a given site at step n depends on the site that was occupied after step $n-1$. More precisely, it is assumed that the particle returns to its previously occupied site with a transition rate w_b which is different from its transition rate w to all other neighboring sites. The ratio $b=w_b/w$ is a measure of the correlation strength. The case $b=0$ corresponds to completely forbidden immediate reversal, $b=1$ to the uncorrelated random walk, and $b=\infty$ corresponds to a particle which oscillates persistently between two sites.

Generally there can be several distinct physical mechanisms giving rise to such temporal correlations. A well-known example is that of tracer diffusion in a hard-core lattice gas at low vacancy concentrations.[6] In this case the tracer particle is more likely to find a vacancy at its previous site than at any other neighboring site. Consequently the particle performs many correlated forward and backward hops before encountering another vacancy. Coulomb interactions between charged carriers will give rise to a similar effect. On the other hand, lattice-relaxation effects might lead to reduced as well as enhanced probability for return to the previous site. If the lattice-relaxation time associated with a site is longer than the hopping time, then the previously occupied site will still be in a different state when the particle is ready to jump again, and consequently the probability for return to this site will be changed. Another source of correlations is simultaneous hops of several particles. Such correlated hopping is well known to exist in Na^+-β-alumina where the activation energy for correlated hopping of Na^+ ions is lower than that for a single ion hop.[7] In any realistic situation several or all of the different sources for correlations may well be present and relevant. In this paper it is assumed that their net effect can be described as an effective correlation strength b. Because of this approximate character the model has to be restricted to applications where b differs from 1 only by a small amount.

Like for ordered systems the correlations introduced by $b \neq 1$ can be expected to result in pronounced effects on the frequency dependence of the electrical conductivity $\sigma(\omega)$ because both correlations *and* disorder are known to give rise to a strong dependence on frequency each in its own right. It is the objective of this paper to calculate $\sigma(\omega)$ for such correlated random walks in a percolating system. This will be done by developing an effective-medium approach, which allows one to treat the correlations exactly.

As a result it is found in this paper that $\sigma(\omega)$ can exhibit unusual features. For $b > 1$, which will be the case in most applications, the real part $\mathrm{Re}[\sigma(\omega)]$ "flattens off" in some intermediate-frequency regime, and a similar feature appears in the imaginary part. This flattening off leads to an almost linear behavior on a log-log plot allowing for a power-law fit $\mathrm{Re}[\sigma(\omega)] \propto \omega^y$ with $0 < y < 1$ over roughly one to two decades in frequency. For $b < 1$ $Re[\sigma(\omega)]$ can attain a maximum while $\mathrm{Im}[\sigma(\omega)]$ can change sign. Results will be presented for the linear chain and the two-dimensional hexagonal lattice. These lattices are expected to show strong correlation effects because of their low coordination number.

The presentation proceeds as follows. First the formulation of the model containing correlations and disorder is developed. Then an effective-medium-type approximation is derived which approximates the correlated disordered system by a correlated system on a regular lattice. The solution of the correlated effective medium can then be used to solve the regular system. This will be done analytically for the one-dimensional linear chain. The equations for the two-dimensional hexagonal lattice will be solved numerically. Finally, the results will be discussed in terms of qualitative physical arguments, and a brief discussion will relate them to experiment.

II. THE MODEL

Consider the hopping of a single particle in a disordered medium. Usually this problem is approached via a master equation with disordered (random) transition rates for the conditional probability density $P(i,t)$ [or $P(\mathbf{r}_i,t)$] to find the particle at site i at time t if it started from the origin at time $t=0$. As discussed in the Introduction one possibility to describe the effects of correlations is to assume that the particle (random walker) has a memory of its previous step. It is well known[8] that such a Non-Markovian random walk can be mapped onto a Markovian random walk if the memory extends only over a finite number of steps. The trick is to enlarge the state space by introducing internal states of the walker each of which corresponds to a different history. In this case the memory extends only to the previous step, and one is led to consider the probability density $P(i,j,t)$ to find the walker at site i at time t given that it arrived at site i via a direct transition from site j. The different histories of the walker are labeled by the previously occupied site j. The symmetric probability density $P(i,t)$ is then obtained from $P(i,j,t)$ by a summation over all possible histories as

$$P(i,t)=\sum_{j\{i\}} P(i,j,t) \tag{2.1}$$

where the sum runs over all nearest-neighbor sites j of site i. The model will now be defined through an equation for $P(i,j,t)$.

A transition rate w_b is assigned to jumps returning to the site occupied after the previous step, and the rate w is assigned to transitions to any other nearest-neighbor site. Then the ratio $b=w_b/w$ characterizes the strength of the correlations. The case $b=1$ corresponds to the uncorrelated random walk. The conditional probability densities $P(i,j,t)$ must obey the master equation

$$\frac{d}{dt}P(i,j,t)= w_b[P(j,i,t)-P(i,j,t)] + w\sum_{k\neq i}[P(j,k,t)-P(i,j,t)] \tag{2.2}$$

where the sum runs over all nearest neighbors k of site j except for site i. Equation (2.2) is valid for regular lattices.

It is the objective of this paper to study Eq. (2.2) for the case of bond percolation on a regular lattice. This is achieved most easily if one first writes Eq. (2.2) in a more symmetric form. Using Eq. (2.1) one can rewrite Eq. (2.2) on a regular lattice as

$$\frac{d}{dt}P(i,j,t)=(w_b-w)P(j,i,t)+wP(j,t)-\gamma P(i,j,t) \tag{2.3}$$

where $\gamma=w_b+(z-1)w$, and z denotes the coordination number of the lattice. Note that Eq. (2.3) reduces to the master equation for a random walk on a regular lattice if one sets $b=1$ and sums over all sites j which are nearest neighbors of site i. To further symmetrize Eq. (2.3) one differentiates it and sums over j. Then Eq. (2.3) is employed for i and j interchanged to eliminate the term $(d/dt)P(j,i,t)$ and one finds

$$\frac{d^2}{dt^2}P(i,t)+\gamma\frac{d}{dt}P(i,t)=(w_b-w)\gamma P(i,t)-w\sum_{j\{i\}}\frac{d}{dt}P(j,t)-(w_b-w)\gamma\sum_{j\{i\}}P(j,i,t)\ . \tag{2.4}$$

Solving Eq. (2.3) for $P(j,i,t)$ and inserting the result into Eq. (2.4) one obtains a closed second-order equation for $P(i,t)$,

$$\frac{d^2}{dt^2}P(i,t)+(\gamma+w_b-w)\frac{d}{dt}P(i,t)=w\sum_{j\{i\}}\frac{d}{dt}[P(j,t)-P(i,t)]+w\gamma\sum_{j\{i\}}[P(j,t)-P(i,t)]\ , \tag{2.5}$$

where the summations, as before, run over all nearest-neighbor sites j of site i. Equation (2.5) contains the same information as Eq. (2.2) but no longer involves the directional quantities $P(i,j,t)$. Again, upon setting $b=1$, it reduces to the derivative of the ordinary master equation for an uncorrelated random walk on a regular lattice.

Equation (2.5) now lends itself easily to the introduction of disorder. For the case of bond percolation considered here each lattice bond has a probability p of being occupied. The random walker is then restricted to move only over occupied bonds. Equation (2.5) now becomes

$$\frac{d^2}{dt^2}P(i,t)+(\gamma+w_b-w)\frac{d}{dt}P(i,t)=w\sum_{j\{i\}}A_{ij}\frac{d}{dt}[P(j,t)-P(i,t)]+w\gamma\sum_{j\{i\}}A_{ij}[P(j,t)-P(i,t)]\ , \tag{2.6a}$$

where $\gamma=w_b+w(z-1)$ and z is the coordination number of the underlying regular lattice. The symmetric quantities $A_{ij}=A_{ji}$ represent the bond disorder and are defined as

$$A_{ij}=\begin{cases}1 & \text{if the bond } [ij] \text{ is present}\\ 0 & \text{otherwise}\ .\end{cases} \tag{2.6b}$$

The bonds are occupied, and thus accessible to the walkers with probability p. They are unoccupied (blocked) with probability $1-p$. Equation (2.6) represents the final mathematical formulation of the model including both correlations and disorder. It describes a random walk with temporal correlations over two steps on a bond-disordered lattice.

Instead of disordering Eq. (2.5) it is also possible to introduce disorder directly into Eq. (2.2). There are, however, some subtle problems with such an approach which require modifications in the formulation of Eq. (2.2). The problems arise from the fact that a naive introduction of disorder into Eq. (2.2) will lead to an infinite memory in the limit $w_b=0$ at sites with $z_i=1$. The necessary modifications to avoid this inconsistency and the derivations of Eq. (2.6) from a modified first-order master equation with bond disorder are discussed in Ref. 9.

It remains to specify the initial conditions for Eq. (2.6). Because Eq. (2.6) is of second order special attention has to be paid to the condition on $(d/dt)P(i,t)$. The correct choice is

$$P(i,0+)=\delta_{i0} \tag{2.7a}$$

and

$$\frac{d}{dt}P(i,0+)=[w_b+w(z_i-1)]\frac{1}{z_i}\times\sum_{j\{i\}}A_{ij}[P(j,0+)-P(i,0+)]$$
$$=\frac{\gamma}{z}\sum_{j\{i\}}A_{ij}(\delta_{j0}-\delta_{i0})\ , \tag{2.7b}$$

where $P(i,0+)\equiv\lim_{t\to 0}P(i,t)$ from above. Note that γ/z is the average transition rate out of the starting point.

III. CORRELATED EFFECTIVE MEDIUM

In this section an effective-medium approximation is developed to solve Eq. (2.6) with initial conditions (2.7). This will be done by determining a self-consistent correlated effective medium. The kernel or "self-energy" obtained from such a calculation has, however, no direct physical interpretation as it does for the usual uncorrelated effective medium. Instead it is only an intermediate result for the final solution of the correlated random walk on a regular lattice. The exposition will proceed similarly to the uncorrelated case.[10]

One begins by Laplace transforming Eq. (2.6) and inserting the initial conditions from Eq. (2.7). This gives

$$u(u+\gamma+w_b-w)P_i(u)-(u+\gamma+w_b-w)\delta_{i0}-(w_b-w)\frac{1}{z}\sum_{j\{i\}}A_{ij}(\delta_{j0}-\delta_{i0})=w(u+\gamma)\sum_{j\{i\}}A_{ij}[P_j(u)-P_i(u)]\ , \tag{3.1}$$

where the notation $P_i(u)=P(i,u)=\int_0^\infty e^{-ut}P(i,t)dt$ is used for the Laplace transform. Now one introduces the correlated effective medium on the regular reference lattice described by the frequency-dependent kernel $A^0(u)$ via the equation

$$u(u+\gamma+w_b-w)P_i^0(u)-(u+\gamma+w_b-w)\delta_{i0}-(w_b-w)\frac{1}{z}\sum_{j\{i\}}A^0(u)(\delta_{j0}-\delta_{i0})$$
$$=w(u+\gamma)\sum_{j\{i\}}A^0(u)[P_j^0(u)-P_i^0(u)]\ . \tag{3.2}$$

Subtracting Eq. (3.2) from Eq. (3.1) gives

$$u(u+\gamma+w_b-w)[P_i(u)-P_i^0(u)]-(w_b-w)\frac{1}{z}\sum_{j\{i\}}[(A_{ij}-A^0)(\delta_{j0}-\delta_{i0})]$$
$$=w(u+\gamma)\sum_{j\{i\}}\{A_{ij}[P_j(u)-P_i(u)]-A^0(u)[P_j^0(u)-P_i^0(u)]\}\ . \quad (3.3)$$

Adding and subtracting a term $A^0[P_j(u)-P_i(u)]$ this can be rewritten as

$$\left[\frac{u}{wA^0}\left[1+\frac{w_b-w}{u+\gamma}\right]+z\right](P_i-P_i^0)-\sum_{j\{i\}}(P_j-P_j^0)-\frac{w_b-w}{u+\gamma}\frac{1}{wz}\sum_{j\{i\}}\Delta_{ij}(\delta_{j0}-\delta_{i0})=\sum_{j\{i\}}\Delta_{ij}(P_j-P_i)\ , \quad (3.4)$$

where $\Delta_{ij}=(A_{ij}-A^0)/A^0$ and the dependence on u has been suppressed to further shorten the notation.

One now defines the Green's function associated with the reference lattice through the equation

$$\left[\frac{u}{wA^0}\left[1+\frac{w_b-w}{u+\gamma}\right]+z\right]G_{ik}-\sum_{j\{i\}}G_{jk}=-\delta_{ik}\ . \quad (3.5)$$

Multiplication of Eq. (3.4) with G_{ik} and utilization of Eq. (3.5) then gives

$$(P_i-P_i^0)\sum_{j\{i\}}G_{jk}-(P_i-P_i^0)\delta_{ik}-G_{ik}\sum_{j\{i\}}(P_j-P_j^0)-G_{ik}\frac{w_b-w}{u+\gamma}\frac{1}{wz}\sum_{j\{i\}}\Delta_{ij}(\delta_{j0}-\delta_{i0})=G_{ik}\sum_{j\{i\}}\Delta_{ij}(P_j-P_i)$$

which upon summation over i simplifies to

$$(P_k-P_k^0)+\sum_i G_{ik}\frac{w_b-w}{u+\gamma}\frac{1}{wz}\sum_{j\{i\}}\Delta_{ij}(\delta_{j0}-\delta_{i0})$$
$$=\sum_{i,j}G_{ik}\Delta_{ij}(P_j-P_i)\ . \quad (3.6)$$

For bond percolation it is convenient to switch from site related quantities to bond related ones. This is done by writing Eq. (3.6) for a second site l, and then forming the differences $Q_{kl}=P_k-P_l=-Q_{lk}$. In terms of the quantities Q_{kl} one now has

$$Q_{kl}-Q_{kl}^0+\sum_{i,j}(G_{ik}-G_{il})\frac{w_b-w}{u+\gamma}\frac{1}{wz}\Delta_{ij}(\delta_{j0}-\delta_{i0})$$
$$=\sum_{i,j}(G_{ik}-G_{il})\Delta_{ij}Q_{ij}\ .$$

Denoting the bond between sites i and j by $[ij]$, and rewriting the summations as summations over bonds one obtains

$$Q_{kl}=Q_{kl}^0\sum_{[ij]}(G_{ik}-G_{il}-G_{jk}+G_{jl})\Delta_{ij}Q_{ij}$$
$$-\sum_{[ij]}\left[(G_{ik}-G_{il})\frac{w_b-w}{u+\gamma}\frac{1}{wz}-(G_{jk}-G_{jl})\right.$$
$$\left.\times\frac{w_b-w}{u+\gamma}\frac{1}{wz}\right]\Delta_{ij}(\delta_{j0}-\delta_{i0})\ . \quad (3.7)$$

As usual only a finite number of bonds (here only one bond) are allowed to fluctuate while all other bonds are given their effective-medium value.[10] Thus Eq. (3.7) reduces to

$$Q_{kl}=Q_{kl}^0(G_{kk}-G_{kl}-G_{lk}+G_{ll})\Delta_{kl}Q_{kl}$$
$$-\left[(G_{kk}-G_{kl})\frac{w_b-w}{u+\gamma}\frac{1}{wz}-(G_{lk}-G_{ll})\frac{w_b-w}{u+\gamma}\frac{1}{wz}\right]$$
$$\times\Delta_{kl}(\delta_{l0}-\delta_{k0})\ . \quad (3.8)$$

The bond $[kl]$ can be chosen arbitrarily and should be chosen such that it does not touch the starting point of the random walk, i.e., $k\neq 0$, $l\neq 0$. Then Eq. (3.8) is solved to give

$$Q_{kl}=\frac{1}{1-\Delta_{kl}(G_{kk}+G_{ll}-G_{kl}-G_{lk})}Q_{kl}^0\ . \quad (3.9)$$

The solution of Eq. (3.5) is recognized as the Green's function for that lattice if one introduces the new spectral variable

$$\tilde{u}=\frac{u}{wA^0(u)}\left[1+\frac{w_b-w}{u+\gamma}\right] \quad (3.10)$$

instead of u.

The one bond effective-medium approximation now demands a choice of $A^0(u)$ such that it reproduces on average the behavior of the original system, i.e., one requires $\langle Q_{kl}\rangle=\langle Q_{kl}^0\rangle$, where $\langle\ \rangle$ denotes the average over all possible configurations of the bond $[kl]$. Using this condition in Eq. (3.9) yields

$$1=\left\langle\left[1+\Delta_{kl}\left[\frac{2}{z}+\frac{2\tilde{u}}{zG_{ii}(\tilde{u})}\right]\right]^{-1}\right\rangle\ , \quad (3.11)$$

where the symmetry of the Green's function and Eq. (3.5) were used to express $G_{ij}(\tilde{u})$ in terms of $G_{ii}(\tilde{u})$. The average in Eq. (3.11) has to be taken with respect to the prob-

ability density $f(A_{kl})$ which was given in Eq. (2.6) as $f(A_{kl})=p\delta(A_{kl}-1)+(1-p)\delta(A_{kl})$. Performing the average and introducing the notation $p_c=2/z$ for the percolation threshold one finds from Eq. (3.11) the self-consistent equation

$$A^0(u)=\frac{p-p_c-p_c\tilde{u}G(\tilde{u})}{1-p_c-p_c\tilde{u}G(\tilde{u})}$$

with $\tilde{u}$ given by Eq. (3.10), and $G(u)=G_{ii}(u)$. Partially solving for A^0 then leads to the functional equation

$$A^0(u)=\frac{p-p_c-F(u,A^0)}{2(1-p_c)}\times\left[1\pm\left[1+\frac{4(1-p_c)F(u,A^0)}{[F(u,A^0)-p+p_c]^2}\right]^{1/2}\right], \quad (3.12a)$$

where

$$F(u,A^0)=p_c\frac{u}{w}\left[1+\frac{w_b-w}{u+\gamma}\right]\times G\left[\frac{u}{wA^0(u)}\left[1+\frac{w_b-w}{u+\gamma}\right]\right]. \quad (3.12b)$$

This formulation has the advantage that it displays explicitly the two different branches of the solution. The decision of which branch to use is made by enforcing the correct limiting behavior. This requires one to show first how to obtain the frequency-dependent conductivity $\sigma(\omega)$ from the solution of Eq. (3.12). This will be done in the next section.

IV. SOLUTION FOR THE CORRELATED MEDIUM

In order to utilize A^0 for the calculation of $\sigma(\omega)$ one has to solve Eq. (2.5) first. Laplace transforming Eq. (2.5) and using the initial conditions of Eq. (2.7) gives

$$\left[\frac{u}{wA^0(u)}\left[1+\frac{w_b-w}{u+\gamma}\right]+z\right]P^0(i,u)-\left[\frac{1}{wA^0(u)}+\frac{w_b-w}{u+\gamma}\frac{1}{w}\left[\frac{1}{A^0}-1\right]\right]-\frac{w_b-w}{u+\gamma}\frac{1}{wz}\sum_{j\{i\}}\delta_{j0}=\sum_{j\{i\}}P(j,u), \quad (4.1)$$

where the sum runs over all nearest neighbors of site i on the underlying regular lattice. This equation can be solved by Fourier transformation to yield

$$P(\mathbf{k},u)=\frac{\frac{1}{wA^0}+\frac{w_b-w}{u+\gamma}\frac{1}{w}\left[\frac{1}{A^0}-1\right]+\frac{w_b-w}{u+\gamma}\frac{1}{w}p(\mathbf{k})}{\frac{u}{wA^0}\left[1+\frac{w_b-w}{u+\gamma}\right]+z-zp(\mathbf{k})}, \quad (4.2)$$

where $\mathbf{k}=(k_1,\ldots,k_d)$ denotes the wave vector, and $p(\mathbf{k})$ is the characteristic function of the random walk for the lattice under consideration, e.g., $p(\mathbf{k})=1/d\sum_{i=1}^{d}\cos k_i$ for the d-dimensional simple cubic lattices.

From Eq. (4.2) one can calculate the frequency-dependent conductivity $\sigma(\omega)$ in standard fashion via the formulas[11]

$$\sigma(\omega)=\frac{\rho e^2}{k_BT}D(\omega), \quad (4.3a)$$

$$D(\omega)=-\frac{\omega^2}{z}\int_0^\infty\sum_{\mathbf{r}_i,\mathbf{r}_0}(\mathbf{r}_i-\mathbf{r}_0)^2e^{-i\omega t}P(\mathbf{r}_i,t|\mathbf{r})dt, \quad (4.3b)$$

where ρ is the carrier density, e the carrier charge, k_B the Boltzmann constant, T the temperature, and $D(\omega)$ the generalized frequency-dependent diffusion coefficient. $P(\mathbf{r}_i,t|\mathbf{r}_0)=P(i,t)$, the inverse Fourier-Laplace transform of $P(\mathbf{k},u)$, is the probability density to find the particle at site i at time t if it started from the origin $\mathbf{r}_0$ at $t=0$. Using the fact that $p(\mathbf{k})|_{\mathbf{k}=0}=1$ and $\nabla_{\mathbf{k}}p(\mathbf{k})|_{\mathbf{k}=0}=0$ one finds after a straightforward calculation of the second moment from Eq. (4.2)

$$D(u)=p''(0)A^0(u)\frac{w}{z}(b-1+z)\frac{u/w+z}{u/w+z+2b-2}, \quad (4.4)$$

where $p''(0)$ denotes $\nabla_{\mathbf{k}}^2p(\mathbf{k})|_{\mathbf{k}=0}$ and $u=i\omega$.

Equation (4.4) combined with Eq. (4.3a) and the solution of Eq. (3.12) now allows one to calculate the frequency-dependent conductivity. Note that the solution of Eq. (3.12) enters multiplicatively in Eq. (4.4). In order to proceed one has to specify a particular lattice

Green's function for $G(x)$, and to solve Eq. (3.12). This will be done in the next section for two particular cases, the one-dimensional chain, and the two-dimensional hexagonal lattice.

V. RESULTS

Correlation effects are expected to be most pronounced for lattices of low coordination number z. Thus it is interesting to consider the cases $z=2$ (linear chain), and $z=3$ (hexagonal lattice). The latter is particularly important for applications to β- and β''-alumina where conduction occurs in two-dimensional hexagonal lattices. From now on the frequencies will be normalized by setting $w=1$.

In one dimension Eq. (3.12) can be solved exactly. The functional form of the Green's function at the origin in this case is given by

$$G(x)=-[x(x+4)]^{-1/2}$$

and one finds

$$D(u)=\left\{p''(0)(b+1)(u+2)\Big/\left[2(u+2b)u\left[1+\frac{b-1}{u+b+1}\right]\right]\right\}$$
$$\times\left[u\left[1+\frac{b-1}{u+b+1}\right]+2(1-p)^2-(1-p)\left\{\left[u\left[1+\frac{b-1}{u+b+1}\right]+2\right]^2+4p(p-2)\right\}^{1/2}\right] \tag{5.1}$$

which is proportional to the conductivity via Eq. (4.3a) It is instructive to expand the result for low and high frequency. In the high-frequency limit, $\omega\to\infty$, one has

$$D(u)=C\left[p+2p(p-b)\frac{1}{u}+2p[(p-1)(p-b-1)+2b(b-1)+2(p-1)(1-b)]\frac{1}{u^2}+\cdots\right], \tag{5.2}$$

where $C=\frac{1}{2}p''(0)(b+1)$. Similarly for $\omega\to 0$

$$D(u)=C\left\{\frac{2}{b+1}\frac{p(2-p)}{4(p-1)^2}u+\frac{p(2-p)}{4(1-p)^2(b+1)^2}\left[b\left[1-\frac{2}{(p-1)^2}\right]-1\right]u^2+\cdots\right\}. \tag{5.3}$$

The low-frequency expansion, Eq. (5.3), implies that $D(0)=0$ and $\mathrm{Re}D(\omega)>0$, $\mathrm{Im}D(\omega)>0$ for $\omega\gtrsim 0$. On the other hand, the high-frequency expansion, Eq. (5.2), shows that for certain values of the parameters p and $b<1$ the imaginary part, $\mathrm{Im}D(\omega)$, can become negative, and $\mathrm{Re}D(\omega)$ can approach its limiting value Cp from above. By continuity this implies that $\mathrm{Im}D(\omega)$ will have at least one zero, and $\mathrm{Re}D(\omega)$ will have at least one maximum. More precisely, one finds that $\mathrm{Im}D(\omega)$ must have zero if

$$b<p \tag{5.4}$$

and $\mathrm{Re}D(\omega)$ must have a maximum if

$$b<\tfrac{1}{2}(p+1)\,. \tag{5.5}$$

The different possible behaviors of $D(\omega)$ are summarized in a "phase diagram" in Fig. 1. In the figure a (dashed) line has also been drawn to separate the regions of enhanced ($b>1$) from those of reduced ($b<1$) reversal. Although $D(\omega)$ remains monotonous for $b<1$ this does not imply that it will not exhibit new features. In fact one finds that for $b>1$ the real part flattens off at intermediate frequencies of the order of b. This can be seen in

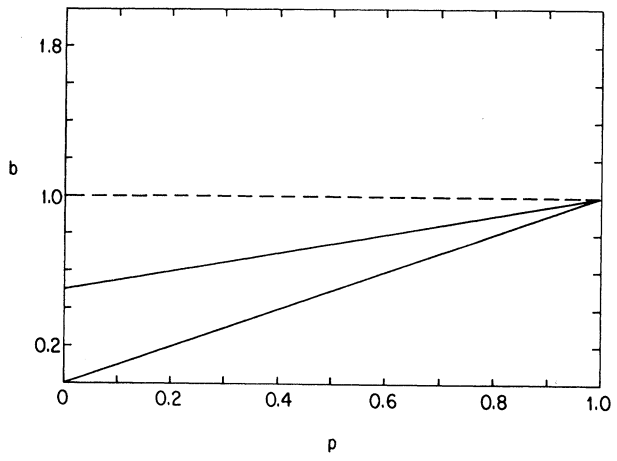

FIG. 1. "Phase diagram" for the linear chain. Below the line from 0 to 1 the imaginary part of $D(\omega)$ has a zero. Below the line from $\frac{1}{2}$ to 1 the real part of $D(\omega)$ has a maximum. The dashed line separates regions of reduced reversals (above) from regions of enhanced reversals (below).

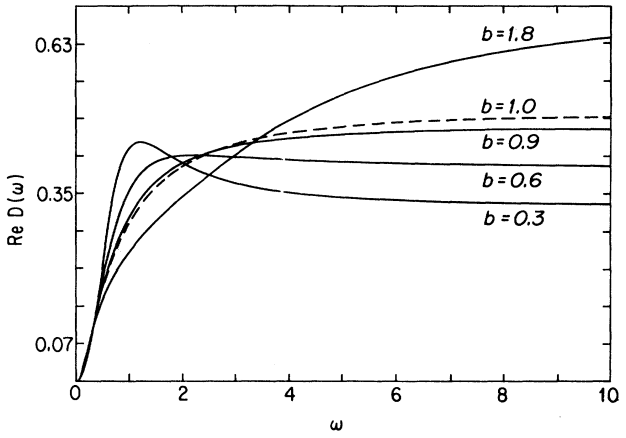

FIG. 2. Re$D(\omega)$ vs ω for the linear chain with $p=0.5$ and $b=0.3,0.6,0.9,1,1.8$.

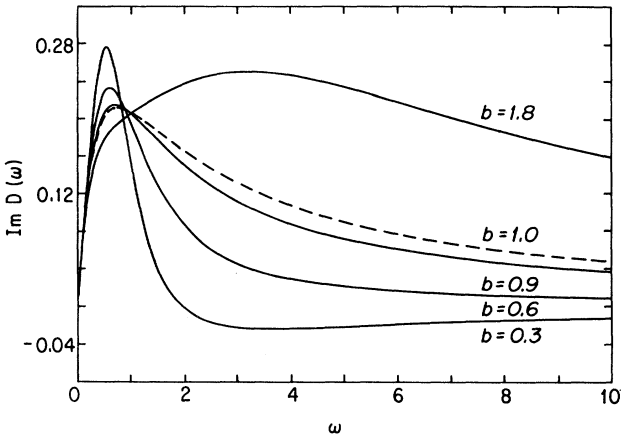

FIG. 3. Im$D(\omega)$ vs ω for the linear chain with $p=0.5$ and $b=0.3,0.6,0.9,1,1.8$.

Figs. 2 and 3 where the real and imaginary parts for $p=0.5$ and a range of b values, $b=0.3,0.6,0.9,1.8$ are displayed. These values have been chosen to provide an example for each of the four regions in the phase diagram.

For the two-dimensional hexagonal lattice the Green's function at the origin is given by

$$G(x)=-\frac{2(3+x)}{\pi(2+x)^{3/2}(6+x)^{1/2}}K\left[\frac{16(x+3)}{(x+2)^3(x+6)}\right],$$

where $K(m)$ denotes the complete elliptical integral of the first kind,

$$K(m)=\int_0^{\pi/2}(1-m\sin^2\phi)^{-1/2}d\phi\ .$$

For this case Eq. (3.12) can no longer be solved exactly. Instead one has to resort to a numerical solution. This is done iteratively. The iteration is stopped if the maximal relative change between two consecutive iterations over the predefined frequency range falls below 10^{-9}. The result is inserted into Eq. (4.4). The primary difference to the one-dimensional case is the appearance of a percolation threshold. This is not affected by memory correlations. It follows that $D(0)$ must vanish below $p_c=\frac{2}{3}$, while $D(0)$ is different from zero above the percolation threshold. This is consistent with Eq. (3.12) if one employs the + sign above and the − sign below p_c.

The results for the frequency dependence of $D(\omega)$ are not changed qualitatively compared to the one-dimensional case. The main difference appears above the percolation threshold in that the dc conductivity can rise above the high-frequency value if $b<1$, i.e., for the case of reduced reversals. This had to be expected as it is known to hold also for $p=1$, i.e., on the regular lattice. In Figs. 4 and 5 the real and imaginary part of $D(\omega)$ for two concentrations p (one above and one below p_c) in the frequency regime between $\omega=0$ and 10 have been displayed. For each value of $p=0.5$ and 0.9 three different curves corresponding to $b=0.5,1.0,2.0$ are shown where the uncorrelated case, $b=1.0$, is represent-

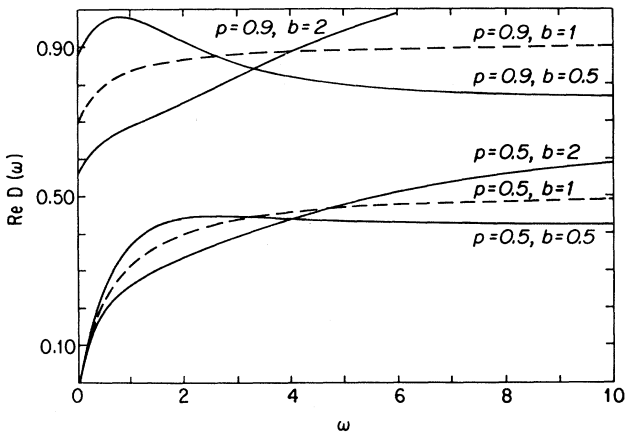

FIG. 4. Re$D(\omega)$ vs ω for the hexagonal lattice with $p=0.5,0.9$ and $b=0.5,1,2$.

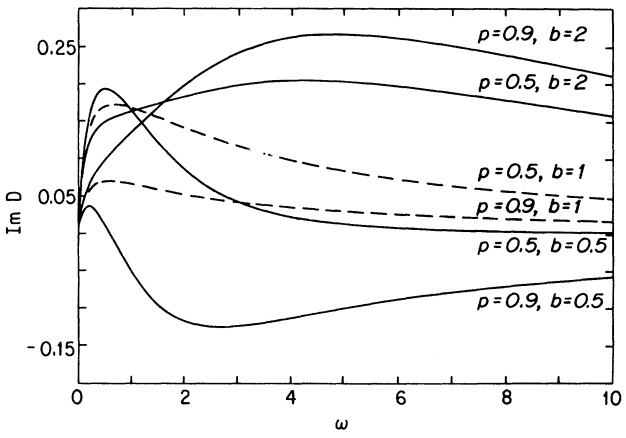

FIG. 5. Im$D(\omega)$ vs ω for the hexagonal lattice with $p=0.5,0.9$ and $b=0.5,1,2$.

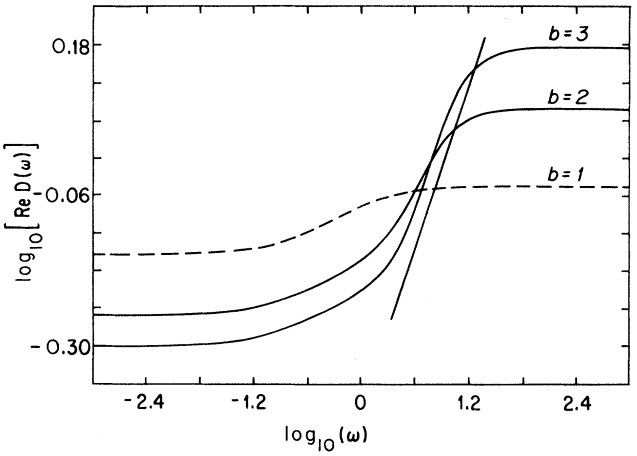

FIG. 6. $\log_{10}[\mathrm{Re}D(\omega)]$ vs $\log_{10}(\omega)$ for the hexagonal lattice with $p=0.9$ and $b=1,2,3$. The straight line has a slope of ~ 0.5.

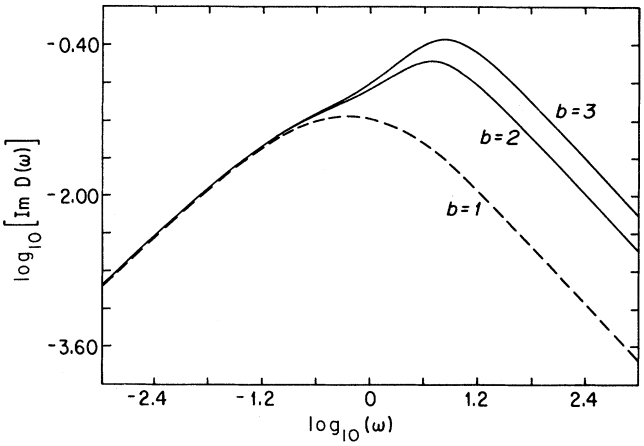

FIG. 7. $\log_{10}[\mathrm{Im}D(\omega)]$ vs $\log_{10}(\omega)$ for the hexagonal lattice with $p=0.9$ and $b=1,2,3$.

ed by the dashed line. Figures 6 and 7 present the solutions for $p=0.9$ and $b=1,2,3$ over a wide frequency range spanning six orders of magnitude on a log-log plot. Again the dashed line corresponds to the uncorrelated case with $b=1.0$, and $p=0.9$. Let me now turn to a discussion of these results.

VI. DISCUSSION

At high frequencies the particles experience only the conductance of a single bond which, as in every hopping model, is assumed to be constant. Consequently there will be no effects from the existence of a percolation threshold, and the conductivity must approach a limiting value which for the uncorrelated case is well known[10] to be proportional to the elementary jump rate w, the mean square displacement of a single step, and the concentration p. If correlations are present then the conductance of the bond that was just passed is increased or decreased by a factor b. Thus the limiting high-frequency value has to be increased for enhanced reversal, $b>1$, respectively, decreased for reduced reversal, $b<1$. This is indeed borne out by the solutions as can be seen from Figs. 2, 4, and 6.

At low frequencies the difference between concentrations p above and below p_c becomes important because the walker explores a much larger region. Consider first the case $p>p_c$. In this case the charge carriers can always get through the network and the dc conductivity is nonzero. For the uncorrelated case ($b=1.0$), the conductivity is well known to be proportional to $(p-p_c)/(1-p_c)$ within the effective-medium approximation (EMA). For $b\neq 1$ the same proportionality can be expected to hold, however, now with an additional b-dependent correlation factor. To estimate whether the correlation factor will lead to an increased or decreased value for the dc conductivity it is instructive to consider the effect of $b\neq 1$ for the linear chain in the limits $b\to 0$, respectively, $b\to\infty$. In both cases the random walk becomes deterministic. In the first case the particle will move with constant velocity to the right or to the left depending upon its initial velocity, in the second the particle oscillates between two sites. Thus for $b<1$ the dc transport through the system will be enhanced, for $b>1$ it will be reduced. This remains true for higher dimensions and can thus be expected to hold also for the disordered case if $p>p_c$. Again this reasoning is confirmed by the numerical solution.

The case $p<p_c$, however, will be different. This originates from the fact that now there is no connected path through the system, and the dc conductivity must be zero. On time scales short compared to the time necessary to explore the finite clusters the correlations will have the same effect as above p_c. On longer times scales, however, restricted reversals will tend to decrease the overall mobility of the particle because they make it more difficult to exit from dead ends or singly connected regions of the cluster. On the other hand, for $b>1$ the walker oscillates more rapidly, and escapes more easily from singly connected regions. These considerations suggest that the conductivity at very low frequencies is increased for $b>1$, and decreased for $b<1$. Such a behavior is indeed found numerically although it is a more subtle effect.

The fact that the low-frequency conductivity below p_c will be decreased for $b<1$, respectively, increased for $b>1$ can also be found mathematically from Eq. (5.3) for the one-dimensional case. Equation (5.3) shows that the coefficient of ω^3 becomes larger for $b>1$ and smaller for $b<1$. This carries over to the hexagonal lattice for $p<p_c$ as verified by the numerical solution. From the preceding discussion it follows by continuity that for $p>p_c$ $\mathrm{Re}D(\omega,b=1)$ and $\mathrm{Re}D(\omega,b\neq 1)$ must have at least one point of intersection. For $p<p_c$ there will be either no point of intersection or an even number of them.

The intermediate-frequency regime can also be discussed qualitatively by considering the limiting cases for b. For $b\gg 1$ a second frequency scale enters into the problem. In this case the motion of the particle consists of many correlated forward-backward jumps before on the average after b jumps a new nearest neighbor is

reached. The correlation factor b determines the oscillation frequency. Thus one may view the oscillating particle as delocalized over two sites. The bond between these two sites may in turn be viewed as performing a random walk with a rate reduced by a factor $1/b$. Consequently there must be a low-frequency regime in which the conductivity is reduced. This fact is now combined with the discussions of the preceding paragraphs. It was shown there that, for $p < p_c$, $\mathrm{Re}D(\omega, b > 1)$ is increased for very low frequencies. One concludes that there are two points of intersection with $\mathrm{Re}D(\omega, b = 1)$ in this case. For $p > p_c$, on the other hand, $\mathrm{Re}D(\omega, b > 1)$ should remain smaller than $\mathrm{Re}D(\omega, b = 1)$ down to $\omega = 0$. Consider now the case $b \ll 1$. In this case it is not possible to identify b as an oscillation frequency, but obviously the particle is most likely to be pushed away from its previously occupied site and will thus explore its environment more efficiently in some low-frequency range. Again if $p > p_c$ this remains true down to $\omega = 0$, while for $p < p_c$ it only holds down to a crossover frequency corresponding to the time needed to explore all the finite clusters.

Thus one arrives at the following picture: Below p_c one has $\mathrm{Re}D(\omega, b < 1) < \mathrm{Re}D(\omega, b = 1)$ for low frequencies as well as for high frequencies, and $\mathrm{Re}D(\omega, b < 1) > \mathrm{Re}D(\omega, b = 1)$ at intermediate frequencies. The reversed inequalities hold for $b > 1$, and there are always two points of intersection. In the case $p > p_c$ one has $\mathrm{Re}D(\omega, b < 1) > \mathrm{Re}D(\omega, b = 1)$ at low frequencies, and $\mathrm{Re}D(\omega, b < 1) < \mathrm{Re}D(\omega, b = 1)$ at high frequencies with an additional crossover at intermediate frequencies. Again the reverse is true for $b > 1$, and the two curves intersect only in one point.

Let me conclude the discussion with a suggestive similarity between the behavior of the present model and some experimental results for β-alumina. It was the objective of this work to study the combined effects of disorder and correlations on hopping transport in a simple setting. The motivation arose from the problem of ion transport in materials such as β-alumina where both disorder and correlations are known to be important. In fact the theoretical model reproduces certain low-frequency features of the experiment. This is found when one plots $\sigma(\omega)$ on a log-log plot. Figures 6 and 7 present such plots for the case $p = 0.9$ and $b = 1, 2, 3$ over a frequency range spinning six decades. The parameter values could be well realized in Na^+-β-alumina where the disorder results from roughly 9% of the interstitial oxygen. The interesting point is that $\mathrm{Re}D(\omega)$ shows power-law behavior over roughly one to two decades in frequency. A straight line with slope ~ 0.5 has been drawn in Fig. 6 to illustrate this point. The experimental studies at room temperature have shown similar low-frequency behavior with similar power laws over a comparable frequency range.[12] Of course these results are relevant only if it is possible to relate the correlation parameter b of the model to the microscopic conduction mechanism of Na^+-β-alumina. This was not attempted here. The results show, however, that correlations in general can give rise to apparent power laws in the frequency-dependent conductivity for hopping transport in a disordered environment.

In summary, this paper has investigated the case of correlated hopping transport in disordered systems. The problem has been approached as that of a correlated random walk with two-step memory on a bond-percolation lattice. The problem was formulated in terms of an infinite system of randomly coupled second-order differential equations which resembles the master equation for an ordinary random walk. These equations were then solved using a generalized effective-medium approximation within which the correlations could be treated exactly. The frequency-dependent conductivity was calculated for the case of bond percolation on the linear chain and the hexagonal lattice. The real part of $\sigma(\omega)$ was found to exhibit unusual behavior. In particular $\mathrm{Re}\sigma(\omega)$ can exhibit a maximum for reduced reversal to the previous site ($b < 1$). The imaginary part can change sign in this parameter regime. For enhanced reversals ($b > 1$) the real part remains a monotonous function of frequency but shows a new crossover behavior which may appear as a power law over more than a decade in frequency. As a general conclusion it is found that the low-frequency behavior of $\sigma(\omega)$ is mainly determined by correlations resulting from the disorder, while at high frequencies the memory correlations become dominant.

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