

# Correlated dynamic percolation: Many bond effective-medium theory

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We study the diffusion (and conductivity) associated with the random walk of noninteracting particles on a disordered lattice characterized by bond disorder, temporal rearrangement, and spatial correlations. This paper extends previous works on dynamic bond percolation processes to situations where spatial correlations in the rearrangement process are important. Many bond effective-medium theory is used to obtain the effective diffusion coefficient  $D_{\text{eff}}(\omega)$  in such systems. The resulting  $D_{\text{eff}}(\omega)$  depends on the frequency through combinations of the form  $\omega - i/\tau_j$  where  $\tau_j$  are characteristic relaxation times associated with the rearrangement process. We analyze in detail a model combining single bond renewal with a two bond exchange process. The resulting DC ( $\omega = 0$ ) diffusion coefficient shows a new percolation threshold for the bond exchange model (in the absence of single bond renewal which eliminates the threshold altogether), and a crossover between the different limiting behaviors is seen as the different kinds of renewal process are switched on and off. Implications for ionic transport in polymeric ionic conductors are discussed.

## I. INTRODUCTION

There has recently been some interest in transport process in dynamically evolving disordered systems.<sup>1-13</sup> The work done by Druger *et al.*<sup>3-8</sup> was motivated by the applicability of such models to carrier motions in polymeric ionic conductors where experimental results show strong coupling between the ionic mobilities and the polymer segmental motion. Works of other groups were related to diffusion in mixed particle systems<sup>2,13</sup> and to carrier mobility in water in oil microemulsions.<sup>1,10-12</sup>

Druger, Ratner, and Nitzan (DRN) have recently considered a bond percolation model in which the entire environment is fluctuating so that spatial correlations are disregarded. This was achieved by reassigning the bond probabilities at random intervals determined by some renewal time distribution. Harrison and Zwanzig<sup>9</sup> (HZ) have considered a different model where the (spatially and temporally uncorrelated) dynamics of a single bond is used as an input. Remarkably the exact solution of the DRN model is identical to the HZ solution in the effective-medium approximation (EMA). This result, for a Poisson distribution of renewal times, is

$$D(\omega, \lambda) = D_0(\omega - i\lambda), \quad (1)$$

where  $\lambda = 1/\tau$  is the inverse mean renewal time in the DRN model or the characteristic rate of switching between the open and close bond configurations in the HZ model;  $D_0(\omega)$  is the frequency dependent diffusion coefficient in the static disorder case and  $D(\omega, \lambda)$  is the corresponding coefficient in the dynamically disordered system. In the DC ( $\omega = 0$ ) limit Eq. (1) yields

$$D(0, \lambda) = \frac{\langle r^2 \rangle_{0, \text{ren}}}{2 d \tau}, \quad (2)$$

where  $\langle r^2 \rangle_{0, \text{ren}}$  is the mean square displacement in the static network during one renewal interval of the corresponding dynamic network, averaged over the renewal time distribu-

tion, and where  $d$  is the Euclidean dimensionality of the (assumed isotropic) system.

Similar results were obtained, using somewhat more heuristic scaling arguments, by Grest *et al.*,<sup>10</sup> who have considered the implications of the result (2) near the static percolation threshold. More generalized treatments in this spirit were given by Kerstein and Edwards<sup>11</sup> and by Bug and Gefen.<sup>12</sup> The latter authors have studied the implication of an assumption which relates the cluster rearrangement time to its size with an undetermined scaling exponent. A similar idea has been recently examined in a different framework by Hilfer and Orbach.<sup>13</sup>

The simplicity of the result (1) makes it a potentially very useful tool, in particular because it generalizes all available analytical results for the static bond percolation problem<sup>14-17</sup> to the dynamic percolation regime. It is clear, however, that Eq. (1) cannot hold under all circumstances, since it relies on the assumption that the network rearrangement (or "renewal") occurs on a single timescale  $\tau$  without spatial correlations. It is of interest to explore other simple models where this arrangement is inherently characterized by more than one timescale and by spatial correlations.

The purpose of the present paper is to generalize the HZ effective medium theory<sup>9</sup> in this direction. First (Sec. II), we generalize the usual model of random network, with bonds either open for transfer or blocked, to the case where a bond has many states (rather than two), each corresponds to a different hopping rate of the walker. The probability for a bond to be in a particular state evolves in time according to a characteristic rate matrix. It is natural to consider such a model in view of the complexity of realistic fluctuating disordered systems. For example, an ion moving through a conducting polymer network will experience different transition rates, in fact a continuous spectrum of rates, depending on the instantaneous network configurations.

Second, we develop a general many bond EMA formalism for the dynamic percolation (Sec. III). Many bond

EMA's have already been formulated for static random networks<sup>17-19</sup> and have been used to improve the single bond EMA and to accommodate correlations in the bond network (such as those that exist in site percolation<sup>19</sup>). The dynamic many bond EMA can be used to study models with spatial (bond-bond) correlations in the network rearrangement processes, where the correlations are assumed to be localized within repeating lattice units (clusters). Although this assumption is not generally valid, solution of such models may also serve to estimate the corrections to Eq. (1) in more general cases.

Our specific model with local correlations, the two bond exchange process, is studied in detail in Sec. IV. In contrast to the uncorrelated dynamics which leads to Eq. (1) and which implies that no percolation threshold exists in the DC ( $\omega = 0$ ) limit, locally correlated rearrangement processes only shift the threshold to lower  $p$  (bond probability) values. This is intuitively clear as such processes are insufficient to insure connectivity in the system. The complete dependence on  $p$  and on  $\omega$  and the crossover from one type of behavior to another (within the EMA) as we switch on and off the uncorrelated and the locally correlated rearrangement processes are discussed in Sec. IV. One surprising result associated with the two bond exchange model is the occurrence of a very shallow minimum in  $\text{Re}[D(\omega)]$  at low frequencies and above the static percolation threshold.

The HZ formalism,<sup>9</sup> which is the basis of the present work, starts with a stochastic master equation for the walker probability  $P_i(t)$  to be at site  $i$  at time  $t$ , which can be written in the vector form

$$\frac{d}{dt} \mathbf{P} = -\mathbf{W} \cdot \mathbf{P} \equiv -\sum_{\alpha} \sigma_{\alpha}(t) \mathbf{V}_{\alpha} \cdot \mathbf{P}, \quad (3)$$

where  $\alpha$  corresponds to a bond ( $ij$ ) between the nearest-neighbor sites  $i$  and  $j$  characterized by a time dependent hopping rate  $\sigma_{\alpha}(t)$  (which is assumed to be a stochastic variable) and where

$$\mathbf{V}_{\alpha} = (|i\rangle - |j\rangle)(\langle i| - \langle j|), \quad (4)$$

$$\mathbf{P} = \sum_i P_i |i\rangle. \quad (5)$$

Each bond is assumed to have two possible states with corresponding hopping rates  $\sigma_{\alpha} = \sigma_a$  or  $\sigma_{\alpha} = \sigma_b$  (HZ take  $\sigma_a = 0$ ,  $\sigma_b = 1$ ). The probability  $\phi_{\alpha}(\sigma, t)$ , that the hopping rate associated with bond  $\alpha$  at time  $t$  is  $\sigma$ , is assumed to evolve in time according to

$$\frac{\partial}{\partial t} \begin{bmatrix} \phi_{\alpha}(\sigma_a, t) \\ \phi_{\alpha}(\sigma_b, t) \end{bmatrix} = \frac{1}{\tau} \begin{pmatrix} -p & q \\ p & -q \end{pmatrix} \begin{bmatrix} \phi_{\alpha}(\sigma_a, t) \\ \phi_{\alpha}(\sigma_b, t) \end{bmatrix} \quad (6)$$

or, in a more compact notation

$$\frac{\partial}{\partial t} \phi_{\alpha}(\sigma_{\alpha}, t) = \Omega_{\alpha} \phi_{\alpha}(\sigma_{\alpha}, t), \quad (7)$$

where the operator  $\Omega_{\alpha}$  is defined by Eq. (6).  $p$  and  $q$  are the equilibrium values of  $\phi_{\alpha}(\sigma_b)$  and  $\phi_{\alpha}(\sigma_a)$ , respectively,  $p + q = 1$ . The joint probability distribution  $f(\mathbf{P}, \boldsymbol{\sigma}, t)$  to find the walker distributed according to  $\mathbf{P}$  and the bonds in the collective state  $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \dots, \sigma_{\alpha}, \dots)$  at time  $t$ , satisfies the Liouville master equation

$$\frac{\partial}{\partial t} f = \frac{\partial}{\partial \mathbf{P}} \cdot (\mathbf{W} \cdot \mathbf{P} f) + \Omega f, \quad (8)$$

where, since all the bonds fluctuate independently

$$\Omega = \sum_{\alpha} \Omega_{\alpha}. \quad (9)$$

To avoid confusion, vector and matrix notations are used for quantities in the site space (such as  $\mathbf{P}$  and  $\mathbf{W}$ ), while the operator  $\Omega$  which operates in the bond state variables  $\boldsymbol{\sigma}$  is written as a scalar, but should not be confused as such.

Equation (8), which is still exact within the model, is the starting point of the HZ treatment. Our present generalization considers many states for each bond (Sec. II), and many bond clusters as basic lattice entities (Sec. III). In both situations, the general forms of Eqs. (3)–(9) is conserved so that more general EMAs can be carried out. Section IV is devoted to the two bond exchange model, which is a special case of the formalism of Sec. III.

## II. MANY BOND STATES

Our starting point is again Eqs. (3)–(5), however each bond can be in many possible states, each corresponds to a different walker jump rate  $\sigma$ . The probability  $\phi_{\alpha}(\sigma, t)$  that the bond  $\alpha$  is in state  $\sigma$  at time  $t$  is taken to evolve in time according to the master equation.

$$\frac{\partial}{\partial t} \phi_{\alpha}(\sigma, t) = \sum_{\sigma'} \Omega_{\alpha}(\sigma, \sigma') \phi_{\alpha}(\sigma', t) \equiv \Omega_{\alpha} \phi_{\alpha}(\sigma, t), \quad (10)$$

where the sum is over all possible  $\sigma$  values. Repeating the HZ procedure leads again to Eq. (8) for the joint probability distribution  $f(\mathbf{P}, \boldsymbol{\sigma}, t)$  with  $\mathbf{W}$  and  $\Omega$  defined in Eqs. (3) and (9). Defining the partial average of  $\mathbf{P}$

$$\mathbf{P}(\boldsymbol{\sigma}, t) = \int d\mathbf{P} \mathbf{P} f(\mathbf{P}, \boldsymbol{\sigma}, t) \quad (11)$$

leads to

$$\frac{\partial}{\partial t} \mathbf{P}(\boldsymbol{\sigma}, t) = -\mathbf{W} \cdot \mathbf{P}(\boldsymbol{\sigma}, t) + \Omega \mathbf{P}(\boldsymbol{\sigma}, t). \quad (12)$$

The initial condition for  $f(\mathbf{P}, \boldsymbol{\sigma}, t)$  is taken to be

$$f(\mathbf{P}, \boldsymbol{\sigma}, t=0) = \delta(\mathbf{P} - \mathbf{P}_0) \rho(\boldsymbol{\sigma}), \quad (13)$$

where

$$\mathbf{P}(\boldsymbol{\sigma}, t=0) = \mathbf{P}_0 \rho(\boldsymbol{\sigma}) \quad (14)$$

with  $\rho(\boldsymbol{\sigma})$ , the equilibrium distribution for collective bond state, given by

$$\rho(\boldsymbol{\sigma}) = \prod_{\alpha} \rho_{\alpha}(\sigma_{\alpha}), \quad (15)$$

where  $\rho_{\alpha}(\sigma_{\alpha})$  is the equilibrium solution of Eq. (10), namely

$$\sum_{\sigma'} \Omega_{\alpha}(\sigma, \sigma') \rho_{\alpha}(\sigma') = 0. \quad (16)$$

(We may further assume the existence of the detailed balance condition but this is not needed in the following procedure.) Taking the Laplace transform ( $t \rightarrow z$ ) of Eq. (12) leads to

$$\mathbf{P}(\boldsymbol{\sigma}, z) = \mathbf{g}(\boldsymbol{\sigma}, z) \cdot \mathbf{P}_0, \quad (17)$$

where  $\mathbf{g}(\boldsymbol{\sigma}, z)$ , the partially averaged Green's operator, is formally given by

$$\mathbf{g}(\boldsymbol{\sigma}, z) = [z\mathbf{1} + \mathbf{W}(\boldsymbol{\sigma}) - \Omega\mathbf{1}]^{-1}\rho(\boldsymbol{\sigma}). \quad (18)$$

( $\Omega\mathbf{1}$  is a direct product of a unit operator in the site space, and the operator  $\Omega$  which operates in the space of the bonds.) The important quantity is the full average of  $\mathbf{P}$

$$\langle \mathbf{P}(z) \rangle = \sum_{\boldsymbol{\sigma}} \mathbf{P}(\boldsymbol{\sigma}, z) \equiv \mathbf{g}(z) \cdot \mathbf{P}_0, \quad (19)$$

where  $\mathbf{g}(z)$ , the fully averaged Green's operator, is

$$\mathbf{g}(z) = \sum_{\boldsymbol{\sigma}} \mathbf{g}(\boldsymbol{\sigma}, z) \quad (20)$$

and can be written in the form

$$\mathbf{g}(z) = [z\mathbf{1} + \mathbf{W}_m(z)]^{-1}, \quad (21)$$

where

$$\mathbf{W}_m(z) = \psi(z) \sum_{\alpha} \mathbf{V}_{\alpha} \quad (22)$$

while the effective medium rate  $\psi(z)$  is not yet determined.

Exact solution for  $\psi(z)$  is difficult and therefore the EMA is used. First one notices that an effective medium characterized by  $\mathbf{W} = \mathbf{W}_m$  and  $\Omega = 0$  will automatically yield Eq. (21). Then, in the (single bond) EMA, one introduces a second medium consisting of one fluctuating bond imbedded in an effective medium, explicitly written as

$$\mathbf{W} = \psi(z) \sum_{\alpha \neq 1} \mathbf{V}_{\alpha} + \sigma_1 \mathbf{V}_1 = \mathbf{W}_m + [\sigma_1 - \psi(z)] \mathbf{V}_1 \quad (23)$$

$$\Omega = \Omega_1. \quad (24)$$

The effective rate is then determined self-consistently by using Eqs. (23) and (24) in Eq. (18) for  $\mathbf{g}(\boldsymbol{\sigma}, z)$  and performing a trivial summation in Eq. (20) [using also Eq. (15)], which leads to the (effective-medium) condition

$$[z\mathbf{1} + \mathbf{W}_m(z)]^{-1} = \sum_{\sigma_1} \Gamma_{\sigma_1} \quad (25)$$

with

$$\Gamma_{\sigma_1} = [z\mathbf{1} + \mathbf{W}_m + (\sigma_1 - \psi)\mathbf{V}_1 - \Omega_1\mathbf{1}]^{-1}\rho_1(\sigma_1), \quad (26)$$

where the sum stands over all the possible states of a single bond.

From now on we suppress the bond index 1 and rewrite Eq. (26) in the form

$$[z\mathbf{1} + \mathbf{W}_m + (\sigma - \psi)\mathbf{V}] \cdot \Gamma_{\sigma} - \sum_{\sigma'} \Omega(\sigma, \sigma') \Gamma_{\sigma'} = \rho(\sigma)\mathbf{1}. \quad (27)$$

Reduction of this equation may be achieved by using the left eigenvectors of the  $\sigma$  space operator  $\Omega$  ( $= \Omega_1$ )

$$\sum_{\sigma'} C_{\sigma'}^{(l)} \Omega(\sigma', \sigma) = -\lambda_l C_{\sigma}^{(l)}; \quad \lambda_l \geq 0. \quad (28)$$

In particular the eigenvalue  $\lambda_0 = 0$  corresponds to the eigenvector  $C_{\sigma}^{(0)} = 1$  for all  $\sigma$ . Summing Eq. (27) over all  $\sigma$  (after a trivial multiplication by  $C_{\sigma}^{(0)}$ ) and using Eq. (25) and the identity

$$\sum_{\sigma} \rho(\sigma) = 1, \text{ yields } \sum_{\sigma} (\sigma - \psi) \mathbf{V} \cdot \Gamma_{\sigma} = 0. \quad (29)$$

Multiplying Eq. (27) with any other  $C_{\sigma}^{(l)}$  and summing over  $\sigma$  similarly yields

$$\sum_{\sigma} C_{\sigma}^{(l)} [(z + \lambda_l)\mathbf{1} + \mathbf{W}_m + (\sigma - \psi)\mathbf{V}] \cdot \Gamma_{\sigma} = 0 \quad (l \neq 0), \quad (30)$$

where, in addition to Eq. (28), we have used the orthogonality relation between left and right eigenvectors of different eigenvalues

$$\sum_{\sigma} C_{\sigma}^{(l)} \rho(\sigma) = 0 \quad (l \neq 0). \quad (31)$$

Equations (29) and (30) are equivalent to Eqs. (22) and (23) of HZ.<sup>9</sup>

Next we multiply Eq. (30) from the left by  $\mathbf{V} \cdot \mathbf{H}^{(l)}$  where

$$\mathbf{H}^{(l)} = [(z + \lambda_l)\mathbf{1} + \mathbf{W}_m]^{-1} \quad (32)$$

and use the fact that

$$\mathbf{V} \cdot \mathbf{H}^{(l)} \cdot \mathbf{V} = h_l \mathbf{V} \quad (33)$$

where  $h_l$  is a scalar. This leads to

$$\sum_{\sigma} C_{\sigma}^{(l)} [1 + (\sigma - \psi)h_l] \mathbf{V} \cdot \Gamma_{\sigma} = 0 \quad (l \neq 0). \quad (34)$$

Equations (29) and (34) have a nontrivial solution (such that  $\mathbf{V} \cdot \Gamma_{\sigma}$  are not all equal to zero) provided that the determinant of the coefficients of  $\mathbf{V} \cdot \Gamma_{\sigma}$  in these equations vanishes. This is the required equation for the effective medium rate  $\psi(z)$ . While we shall not attempt to solve this equation for a specific model, we note that the result for  $\psi(z)$  depends on  $z$  only through the quantities  $h_l$  which in turn depend on  $z$  through the combinations  $z + \lambda_l$ . It is seen that unlike in the DRN model or in the original HZ model which are characterized by a single environmental relaxation rate  $\lambda$ , the diffusion coefficient depends, in this case, on all the relaxation rates  $\lambda_l$  (eigenvalues of the  $\sigma$  space operator  $\Omega_{\alpha}$ ) and cannot be obtained from a simple analytical continuation of the frequency dependent diffusion coefficient for the static medium case. It can be however evaluated by solving the secular equation associated with Eqs. (29) and (34). A similar procedure will be used when we next deal with the evolution in time of clusters of bonds for which a particular model will be discussed.

### III. CORRELATED BOND FLUCTUATIONS BY MANY BOND EMA

As discussed in Sec. I, a shortcoming of both the DRN and the HZ models is the neglect of spatial correlations between the on/off switching of the bonds. In some physical situations, e.g., in systems where the potential barriers for hopping fluctuate randomly due to random motion of an underlying lattice characterized by short range correlations, this may be a realistic assumption. However, in most physical applications of dynamic percolation models, the physical picture is that of moving barriers or, equivalently, moving transport channels. Thus, when a particle A is moving on a network together with other particles B, the network as seen by A is disordered, with sites containing B unavailable,

and the positions of these blocked sites changes in time as the B particles move. If the number of B particles is conserved, this time evolution of the site availability is obviously correlated in space, with one site opening as a neighboring site becomes blocked. A similar situation exist for an ion moving through a polymer network where opening and blocking of pathways result from polymer segmental motion.

A simple two dimensional model that take such spatial correlations into account is depicted in Fig. 1. Here the  $2d$  square network is made of correlated pairs of bonds. Such a pair (e.g.,  $\alpha$  and  $\beta$  in Fig. 1) can be in four different states: both open, both blocked or (two possibilities of) one open and one blocked. Correlated dynamics is introduced by postulating a rate process which switches between the two latter states as indicated by the arrows in Fig. 1. Physically this amounts to a double sided gate where one side is open when the other is closed and vice versa. It mimicks a picture of a polymer segment which, while fluctuating between two configurations, can block one transport channel or the other.

More generally, we consider a lattice which can be separated into identical finite network units (clusters) of  $n$  bonds ( $n = 2$  in Fig. 1). Denote by  $\sigma_\nu$  the vector  $(\sigma_{\nu 1}, \sigma_{\nu 2}, \dots, \sigma_{\nu n})$  whose elements denote the state of the bonds within the cluster  $\nu$  (each bond can have several states as in the previous section). The probability  $f_\nu(\sigma_\nu, t)$  to find the bond configuration  $\sigma_\nu$  in the cluster  $\nu$  evolves in time according to

$$\frac{\partial}{\partial t} f_\nu(\sigma_\nu, t) = \sum_{\sigma'_\nu} \Omega_\nu(\sigma_\nu; \sigma'_\nu) f_\nu(\sigma'_\nu, t) \equiv \Omega_\nu f(\sigma_\nu, t). \tag{35}$$

Thus, the different network units are assumed to evolve independently. If the cluster is large enough so that the average residence time of the walker within a single cluster is large relative to all characteristic timescales associated with the cluster rearrangement process, this assumption is of no consequence. The state of the whole bond network is given by

$$f(\sigma, t) = \prod_\nu f_\nu(\sigma_\nu, t) \tag{36}$$

with the time evolution

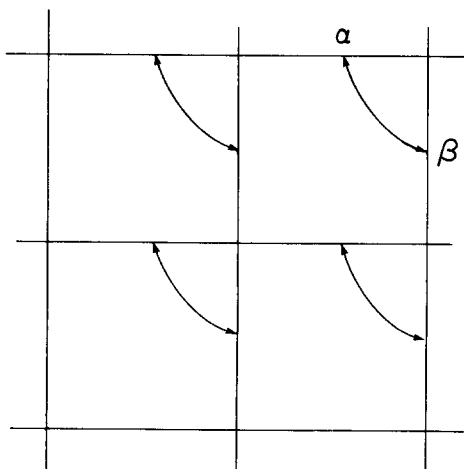


FIG. 1. A schematic representation of the two bond exchange model. The arrows denote the allowed exchange processes.

$$\frac{\partial}{\partial t} f(\sigma, t) = \Omega f(\sigma, t); \quad \Omega = \sum_\nu \Omega_\nu. \tag{37}$$

The random walk itself is described by Eqs. (3)–(5).

Applying the HZ formalism result again with Eqs. (8), (11)–(22); the only difference from previous sections is the new definition of the bond evolution operator  $\Omega$ . The EMA is invoked now by introducing a medium consisting of one fluctuating cluster ( $\nu = 1$ ) imbedded in an effective medium

$$\mathbf{W} = \psi(z) \sum_{\nu \neq 1} \sum_{\alpha=1}^n \mathbf{V}_{\nu\alpha} + \sum_{\alpha=1}^n \sigma_{1\alpha} \mathbf{V}_{1\alpha} \tag{38}$$

(the first index refers to the clusters and the second is the bond index within a cluster) and

$$\Omega = \Omega_1. \tag{39}$$

$\sigma_{1\alpha}$  is an element of the vector  $\sigma_1$  which describes the state of the fluctuating cluster  $\nu = 1$ . We can write Eq. (38) in terms of the effective medium matrix  $\mathbf{W}_m$  Eq. (22)

$$\mathbf{W} = \mathbf{W}_m + \sum_{\alpha=1}^n (\sigma_{1\alpha} - \psi) \mathbf{V}_{1\alpha}. \tag{40}$$

Using Eqs. (39) and (40) in  $\mathbf{g}(\sigma, z)$  [of Eq. (18)] and performing a trivial summation in Eq. (20) leads to the effective-medium condition

$$[z\mathbf{1} + \mathbf{W}_m]^{-1} = \sum_{\sigma_1} \Gamma_{\sigma_1}, \tag{41}$$

where the sum is over all possible values of the vector  $\sigma_1$ , namely over all possible configurations of cluster  $\nu = 1$ , and  $\Gamma_{\sigma_1}$  is

$$\Gamma_{\sigma_1} = \left[ z\mathbf{1} + \mathbf{W}_m + \sum_{\alpha=1}^n (\sigma_{1\alpha} - \psi) \mathbf{V}_{1\alpha} - \Omega_1 \mathbf{1} \right]^{-1} \rho_1(\sigma_1). \tag{42}$$

This equation is very similar to Eq. (26). Note however the differences: in Eq. (26)  $\rho_1(\sigma_1)$  was the equilibrium probability that the bond 1 is in state  $\sigma_1$ . Here  $\rho_1(\sigma_1)$  is the equilibrium probability that the network cluster 1 is in state  $\sigma_1$ , namely that the  $n$  bonds belonging to that cluster are in states  $\{\sigma_{1\alpha}\}, \alpha = 1, \dots, n$ . In Eq. (26) the operator  $\Omega_1$  operates in the space of state of bond 1 while here it operates in the space of states of all bonds belonging to cluster 1. The solutions of Eqs. (41) and (42) proceeds along the same lines as in the previous section. We drop the cluster index 1 and rewrite Eq. (42) in the form

$$\left[ z\mathbf{1} + \mathbf{W}_m + \sum_{\alpha=1}^n (\sigma_\alpha - \psi) \mathbf{V}_\alpha \right] \cdot \Gamma_\sigma - \sum_{\sigma'} \Omega(\sigma, \sigma') \Gamma_{\sigma'} = \rho(\sigma) \mathbf{1}. \tag{43}$$

Then we multiply by the element  $C_\sigma^{(l)}$  of the  $l$ th left eigenvector of the operator  $\Omega$ , which corresponds to eigenvalue  $-\lambda_l$  [ $\lambda_l \geq 0$ ; cf. Eq. (28)] and sum over all  $\sigma$ . Using also Eq. (41), the identity

$$\sum_\sigma \rho(\sigma) = 1, \tag{44}$$

and (an equivalent form of) the orthogonality relation (31) we get

$$\sum_{\sigma} \left[ \sum_{\alpha=1}^n (\sigma_{\alpha} - \psi) \mathbf{V}_{\alpha} \right] \cdot \Gamma_{\sigma} = 0 \quad (45)$$

and, for  $\lambda_l = 0$

$$\sum_{\sigma} C_{\sigma}^{(l)} \left[ (z + \lambda_l) \mathbf{1} + \mathbf{W}_m + \sum_{\alpha=1}^n (\sigma_{\alpha} - \psi) \mathbf{V}_{\alpha} \right] \cdot \Gamma_{\sigma} = 0. \quad (46)$$

Equation (45) corresponds to the zero eigenvalue of  $\Omega$  [cf. Eq. (28)]. If  $N$  is the number of different vectors  $\sigma$  [and hence the order of the matrix  $\Omega(\sigma, \sigma')$ ], then there are  $N - 1$  equations (46) corresponding to  $\lambda_l > 0$ , and  $N$  equations altogether (when each bond has only two states  $N = 2^n$ ).

In order to extract from Eqs. (45) and (46) an equation for the effective medium rate  $\psi(z)$  we multiply Eq. (45) from the left by  $\langle q | - \langle r |$ , where  $\beta = (qr)$  in any bond within the cluster under consideration. Denoting

$$\Gamma_{\sigma}^{\alpha} \equiv (\langle i | - \langle j |) \cdot \Gamma_{\sigma} \quad (47)$$

[ $\Gamma_{\sigma}^{\alpha}$  is a left vector in the site space and  $\alpha = (ij)$  is the bond index] leads to

$$\sum_{\sigma} \sum_{\alpha=1}^n (\sigma_{\alpha} - \psi) \Delta_{\beta\alpha} \Gamma_{\sigma}^{\alpha} = 0 \quad (48)$$

with

$$\Delta_{\beta\alpha} = \delta_{qi} + \delta_{rj} - \delta_{qj} - \delta_{ri}. \quad (49)$$

Similarly, multiplying Eq. (46) from the left by  $(\langle q | - \langle r |) \cdot \mathbf{H}^{(l)}$  where

$$\mathbf{H}^{(l)} = [(z + \lambda_l) \mathbf{1} + \mathbf{W}_m]^{-1} \quad (50)$$

yields

$$\sum_{\sigma} C_{\sigma}^{(l)} \left[ \Gamma_{\sigma}^{\beta} + \sum_{\alpha=1}^n (\sigma_{\alpha} - \psi) K_{\beta\alpha}^{(l)} \Gamma_{\sigma}^{\alpha} \right] = 0, \quad (l \neq 0), \quad (51)$$

where

$$K_{\beta\alpha}^{(l)} = H_{qi}^{(l)} + H_{rj}^{(l)} - H_{qj}^{(l)} - H_{ri}^{(l)}. \quad (52)$$

Equations (48) and (51) form a closed set of equations for the unknowns  $\Gamma_{\sigma}^{\alpha}$ . There are  $n \cdot N$  unknowns (where  $n$  is the number of bonds in the characteristic cluster and  $N$  is the order of  $\Omega$ ). The number of available equations is the same because we have a set of  $N$  equations for each of the  $n$  possible choices of the bond  $\beta = (qr)$ .

To set a non trivial solution for  $\Gamma_{\sigma}^{\alpha}$  the determinant of the coefficients in Eqs. (48) and (51) should vanish. The resulting equation is the EMA equation for  $\psi(z)$ . This equation contains matrix elements of  $\mathbf{H}^{(l)}$ . These however can be written explicitly in terms of the desired  $\psi$ . Since  $H^{(l)}$  has the Green's operator form, we find (see also Appendix A)

$$\mathbf{H}_{ij}^{(l)} = -\frac{G_{ij}(\epsilon_l)}{\psi}, \quad (53)$$

where  $G_{ij}(\epsilon)$  is the lattice Green's function, defined by<sup>17</sup>

$$(C_{nn} + \epsilon) G_{ik} - \sum_{j \in \{i\}} G_{jk} = -\delta_{ik}, \quad (54)$$

where  $\{i\}$  denotes the group of sites which are nearest-neighbors to  $i$  and where  $C_{nn}$  is the number of these nearest-neighbors.  $\epsilon_l$  is given by

$$\epsilon_l = \frac{z + \lambda_l}{\psi}. \quad (55)$$

Explicit expressions for  $G_{ij}$  are available for simple lattices [see Eq. (A9) for a simple cubic lattice and Refs. 17 and 20].

In the single bond EMA the cluster is made of one bond and Eqs. (48) and (51) reduce to

$$\sum_{\sigma} (\sigma - \psi) \Gamma_{\sigma}^{\beta} = 0 \quad (56)$$

$$\sum_{\sigma} C_{\sigma}^{(l)} [1 + (\sigma - \psi) h_l] \Gamma_{\sigma}^{\beta} = 0, \quad (57)$$

where

$$h_l = K_{\beta\beta}^{(l)} = 2(H_{qq}^{(l)} - H_{rr}^{(l)}). \quad (58)$$

Equations (56) and (57) are identical to Eqs. (29) and (34), so the many-states single-bond EMA is recovered as a special case.

For the sake of completeness we discuss the HZ model, defined by Eq. (6), in detail. When each bond can have only  $\sigma = 0, 1$  Eqs. (56) and (57) reduce to

$$\psi \Gamma_0 - (1 - \psi) \Gamma_1 = 0, \quad (59a)$$

$$p(1 - \psi h) \Gamma_0 - q[1 + (1 - \psi) h] \Gamma_1 = 0. \quad (59b)$$

To get Eq. (59b) from Eq. (57) we first find  $C_{\sigma}(\sigma = 0, 1)$ , the coefficients of the left eigenvector of the bond evolution operator with non-zero eigenvalue (which is  $1/\tau$ ), from

$$(C_0, C_1) \begin{pmatrix} -p/\tau & q/\tau \\ p/\tau & -q/\tau \end{pmatrix} = -\frac{1}{\tau} (C_0, C_1), \quad (60)$$

namely  $C_0 = p$ ,  $C_1 = -q$ . Equations (59a) and (59b) are identical to Eqs. (22) and (26) of HZ.<sup>9</sup> We have thus recovered the HZ result as a special case of our formalism. The condition for Eqs. (59a) and (59b) to have nontrivial solution is

$$p(1 - \psi)(1 - h\psi) - q\psi(1 + h - h\psi) = 0. \quad (61)$$

Using, for any nearest-neighbors  $i, j$  [cf. Eq. (A11)]

$$G_{ij} - G_{ii} = \frac{1 - \epsilon g}{C_{nn}}, \quad (62)$$

where

$$g \equiv -G_{ii} \quad (63)$$

we get [using Eqs. (53) and (58)]

$$h = K_{\alpha\alpha} = \frac{p_c}{\psi} [1 - \epsilon g(\epsilon)] \quad (64)$$

with [cf. Eq. (55)]

$$\epsilon = \frac{z + (1/\tau)}{\psi} \quad (65)$$

and with

$$p_c = \frac{2}{C_{nn}}, \quad (66)$$

the EMA percolation threshold. Together with Eq. (61), this finally leads to the result (expressed in units of the walker bare hopping rate)

$$\psi = \frac{p - p_c + p_c \epsilon g(\epsilon)}{1 - p_c + p_c \epsilon g(\epsilon)}. \quad (67)$$

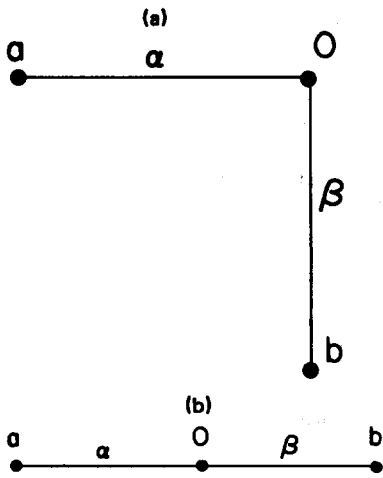


FIG. 2. Sites and bond labels for a specific connected pair in the two bond exchange model. (a) shows the actual model discussed in Sec. IV. (b) shows an alternative model that leads to a slightly different dynamics.

formed from two nearest-neighbor bonds. In the independent bond fluctuation (HZ) model this calculation leads to an improved EMA. For dynamic percolation processes this theory enable us to treat correlated bond fluctuations of the kind depicted in Fig. 1.

IV. CORRELATED TWO BOND MODEL

We consider a particular situation where the lattice is constructed from distinct identical two bond clusters, as the pairs connected by arrows in Fig. 1. We focus on one such cluster, Fig. 2(a), which contains the sites  $o, a$ , and  $b$  and the bonds  $\alpha$  and  $\beta$ . Each of these bonds can be in two states,  $\sigma_\mu = 0,1$  ( $\mu = \alpha, \beta$ ). The bond dynamics is assumed to occur independently within each cluster and is described by

$$\frac{\partial}{\partial \tau} f(\sigma_\alpha, \sigma_\beta, t) = \sum_{\sigma'_\alpha=0,1} \sum_{\sigma'_\beta=0,1} \Omega(\sigma_\alpha, \sigma_\beta; \sigma'_\alpha, \sigma'_\beta) \times f(\sigma'_\alpha, \sigma'_\beta, t) \tag{68}$$

The limit  $1/\tau = 0$ , namely  $\epsilon = z/\psi$  in Eq. (67), is the standard frequency dependent (with  $z = i\omega$ ) EMA result [see, e.g., Eq. (109) of Ref. (17)]. For  $z + 1/\tau \rightarrow 0$  ( $\epsilon \rightarrow 0$ ), the static percolation DC result<sup>21</sup>  $\psi = p - p_c / (1 - p_c)$  ( $p > p_c$ ) is recovered, while for  $z + 1/\tau \rightarrow \infty$  [ $\epsilon \rightarrow \infty$  and therefore  $eg(\epsilon) \rightarrow 1$ ] we get  $\psi = p$ , which is the expected exact result.

We now turn to the two bond EMA where the cluster is

so that the operator  $\Omega$  forms a  $4 \times 4$  matrix. In particular we shall consider the following explicit form of the bond evolution

$$\frac{\partial}{\partial t} \begin{pmatrix} f(0,0) \\ f(1,0) \\ f(0,1) \\ f(1,1) \end{pmatrix} = \begin{pmatrix} -2p/\tau & q/\tau & q/\tau & 0 \\ p/\tau & -(1/\tau + 1/\theta) & 1/\theta & q/\tau \\ p/\tau & 1/\theta & -(1/\tau + 1/\theta) & q/\tau \\ 0 & p/\tau & p/\tau & -2q/\tau \end{pmatrix} \begin{pmatrix} f(0,0) \\ f(1,0) \\ f(0,1) \\ f(1,1) \end{pmatrix}, \tag{69}$$

where  $p + q = 1$ . For  $\theta^{-1} = 0$  the evolution equation (69) is just the independent single bond on-off switching process considered by HZ. For  $\tau^{-1} = 0$  this equation describes the bond rotation depicted in Fig. 1. The equilibrium solution [ $\Omega \rho(\sigma_1, \sigma_2) = 0$ ] of Eq. (69) is  $\rho(0,0) = q^2$ ,  $\rho(1,1) = p^2$  and  $\rho(1,0) = \rho(0,1) = pq$ , corresponding to a random bond structure with probability  $p$  for an open bond and  $q = 1 - p$  for a blocked one. The left eigenvector and the corresponding eigenvalues of the matrix  $\Omega$  are

$$\mathbf{c}^{(0)} = (1, 1, 1, 1); \quad \lambda_0 = 0, \tag{70a}$$

$$\mathbf{c}^{(1)} = (-2p, q - p, q - p, 2q); \quad \lambda_1 = \frac{1}{\tau}, \tag{70b}$$

$$\mathbf{c}^{(2)} = (0, 1, -1, 0); \quad \lambda_2 = \frac{1}{\tau} + \frac{2}{\theta}, \tag{70c}$$

$$\mathbf{c}^{(3)} = (-p^2, pq, pq, -q^2); \quad \lambda_3 = \frac{2}{\tau}. \tag{70d}$$

In accord with Eq. (69) we shall use the notation  $(C_{00}^{(l)}, C_{10}^{(l)}, C_{01}^{(l)}, C_{11}^{(l)})$  for the elements of the vector  $\mathbf{c}^{(l)}$ .

With the vectors  $\mathbf{c}^{(l)}$  and the eigenvalues  $\lambda_l$  explicitly known and with the appropriate matrix elements  $H_{ij}^{(l)}$  assumed known [cf. Eqs. (53)–(55)] we can write Eqs. (48) and (51) explicitly for the present case. As discussed after Eq. (52) there are altogether eight equations for the eight unknowns  $\Gamma_{\sigma_1\sigma_2}^\mu$  ( $\mu = \alpha, \beta$ ;  $\sigma_1\sigma_2 = 00, 10, 01, 11$ ), however, by symmetry we have

$$\Gamma_{\sigma\sigma}^\alpha = \Gamma_{\sigma\sigma}^\beta; \quad \sigma = 0,1, \tag{71}$$

$$\Gamma_{01}^\alpha = \Gamma_{10}^\beta; \quad \Gamma_{10}^\alpha = \Gamma_{01}^\beta$$

so only four equations for (say)  $\Gamma_{\sigma_1\sigma_2}^\alpha$  ( $\sigma_1\sigma_2 = 00, 10, 01, 11$ ) are needed. These are obtained in Appendix B. We get (with the superscript  $\alpha$  on  $\Gamma$  omitted)

$$\begin{pmatrix} -\psi & 1-\psi & -\psi & 1-\psi \\ 2p(-1+a_1\psi) & (q-p)[1+a_1(1-\psi)] & (q-p)(1-a_1\psi) & 2q[1+a_1(1-\psi)] \\ 0 & 1+a_2(1-\psi) & -1+a_2\psi & 0 \\ p^2(-1+a_3\psi) & pq(1+a_3(1-\psi)) & pq(1-a_3\psi) & -q^2[1+a_3(1-\psi)] \end{pmatrix} \begin{pmatrix} \Gamma_{00} \\ \Gamma_{10} \\ \Gamma_{01} \\ \Gamma_{11} \end{pmatrix} = 0 \tag{72}$$

or compactly

$$M \cdot \Gamma = 0 \quad (73)$$

with  $M$  being the matrix in Eq. (72) and where

$$a_l = 3H_{oo}^{(l)} - 4H_{oa}^{(l)} + H_{ab}^{(l)}; \quad l = 1, 3, \quad (74)$$

$$a_2 = H_{oo}^{(2)} - H_{ab}^{(2)}. \quad (75)$$

The effective medium hopping rate  $\psi(z)$  is obtained from the requirement

$$\det(M) = 0. \quad (76)$$

This equation has more than one solution and the correct solution is identified as the one which approaches the correct limit [the single bond EMA result, Eq. (67)] for  $\theta^{-1} \rightarrow 0$ . The resulting implicit equation for  $\psi(z)$  is given by Eqs. (B13) and (B14), and the solution for this equation was obtained numerically. Noting, however, that the single bond EMA result is linear in the bond probability  $p$  [cf. Eq. (67)] and can be regarded as a first order expansion near  $p = 1$  (i.e., in powers of  $q = 1 - p$ ), we search for a similar approximate solution by expanding  $\psi(z)$  up to the first order in  $q$ . This will enable us to study the dynamical bond exchange effect within the same accuracy as the single bond EMA solution. For the  $2d$  square lattice this yields<sup>22</sup>

$$\psi = 1 - \frac{2q}{B(\epsilon_1) - B(\epsilon_2) + 1 + \epsilon_1 g(\epsilon_1)}, \quad (77)$$

where

$$B(\epsilon) = g(\epsilon) + G_{ab}(\epsilon) \quad (77a)$$

$$\epsilon_1 = \frac{z + (1/\tau)}{\psi}; \quad \epsilon_2 = \frac{z + (1/\tau) + (2/\theta)}{\psi} \quad (77b)$$

and where  $g(\epsilon)$  and  $G_{ab}(\epsilon)$ , defined by Eqs. (54) and (63), are explicitly given by [cf. Eq. (A9) with  $d = 2$ ,  $g = -G(0,0)$ ,  $G_{ab} = G(1,1)$ ]

$$g(\epsilon) = \frac{1}{2} \int_0^\infty dt \exp\left(-2t - \frac{1}{2}\epsilon t\right) I_0^2(t), \quad (78a)$$

$$G_{ab}(\epsilon) = -\frac{1}{2} \int_0^\infty dt \exp\left(-2t - \frac{1}{2}\epsilon t\right) I_1^2(t), \quad (78b)$$

where  $I_m(t)$  is the modified Bessel function of order  $m$ . Note that Eq. (78b) holds for the particular geometry of Fig. 2(a). Note also that in Eq. (77): (a) all timescales, namely  $\tau$ ,  $\theta$ ,  $\psi^{-1}$  and  $z^{-1}$ , are expressed in units of the walker bare hopping time (which was omitted from the beginning for convenience), and (b) the eigenvalue  $2/\tau$ , which appears in the complete solution [Eq. (B13)], does not appear here. The following limits can now be examined:—For  $\theta^{-1} \rightarrow 0$  (bond exchange kinetics frozen) we have  $\epsilon_1 = \epsilon_2 = \epsilon$ . Eq. (77) reduces to the HZ result Eq. (67) with  $p_c = 1/2$ , the threshold for a square lattice.—For  $z + \tau^{-1} \rightarrow \infty$  ( $\epsilon_1, \epsilon_2 \rightarrow \infty$ , hence  $B(\epsilon_1), B(\epsilon_2) \rightarrow 0$  and  $\epsilon_1 g(\epsilon_1) \rightarrow 1$ ) we have that, for any value of  $\theta$ ,  $\psi = p$ , which is the expected exact result.—For  $\theta^{-1} \rightarrow \infty$  ( $\epsilon_2 \rightarrow \infty$ ) Eq. (77) takes the form

$$\psi = 1 - \frac{2q}{B(\epsilon_1) + 1 + \epsilon_1 g(\epsilon_1)}. \quad (79)$$

Consider now the case  $z + \tau^{-1} \rightarrow 0$  while  $\theta^{-1} > 0$ . This is the DC limit in the absence of bond renewal but with a bond

exchange process of the type shown in Fig. 1. Using<sup>19</sup>  $B(\epsilon = 0) = 1/\pi$  and  $\epsilon g(\epsilon) \rightarrow 0$  for  $\epsilon \rightarrow 0$  in Eq. (77) yields

$$\psi = 1 - \frac{2q}{1 + 1/\pi - B(2/\theta\psi)}; \quad p > \frac{1}{2} - \frac{1}{2\pi}. \quad (80)$$

This equation implies a threshold at  $p_c = 1/2(1 - 1/\pi) \approx 0.341$  for any  $\theta^{-1} > 0$ . Thus the DC percolation threshold is lower in the presence of bond exchange, as intuitively expected. In the limit  $\theta^{-1} \rightarrow \infty$ , i.e., infinitely fast bond exchange, Eq. (80) reduces to

$$\psi = 1 - \frac{2q}{1 + 1/\pi}; \quad p > \frac{1}{2} - \frac{1}{2\pi} \quad (81)$$

from which the threshold is more readily seen. Eq. (81) describes also the DC conductivity of a static network for which each pair of bonds [Fig. 2(a)] has the probabilities  $2pq$  for bond transition rates  $(1/2, 1/2)$ ,  $p^2$  for  $(1,1)$  and  $q^2$  for  $(0,0)$ , since infinitely fast bond exchange implies a time averaging of the bond rates.

Our results for the  $(2d)$  square lattice for  $\omega = 0$  are summarized in Figs. 3–5. These figures (except Fig. 5) are based on the numerical solution to Eq. (77), while in Fig. 5 we compare them to solutions to Eq. (B13), which includes small corrections (valid far enough from the threshold) due to second order (two bond) EMA. Figure 3 shows the dependence of the effective medium hopping rate  $\psi$  on the fraction of available bonds  $p$  for  $z = \tau^{-1} = 0$  and for different values of the bond exchange rate  $\theta^{-1}$ . For  $\theta^{-1} = 0$   $\psi$  is (almost) a linear line going to zero at  $p_{c2} = 0.5$ . Deviations from linearity (seen in Fig. 5) are barely observed on this plot. For  $\theta^{-1} > 0$   $\psi$  vanishes at  $p_{c1} \approx 0.34$ , however, if  $\theta^{-1}$  is much smaller than one, deviations from the regular EMA result are considerable only for  $p < p_{c2}$ . As  $p$  approaches the  $p_{c2}$  threshold we see a crossover behavior towards  $p_{c1}$ . For  $\theta^{-1} \rightarrow \infty$  the  $\psi(p)$  function again becomes (approximately) linear. A similar crossover behavior to  $p_{c0} = 0$  occurs when the independent bond renewal process is switched on,  $\tau^{-1} > 0$ . The full DC behavior is seen in Fig. 4.

The higher order (in  $q = 1 - p$ ) corrections improve the results far enough from the percolation threshold (Fig.

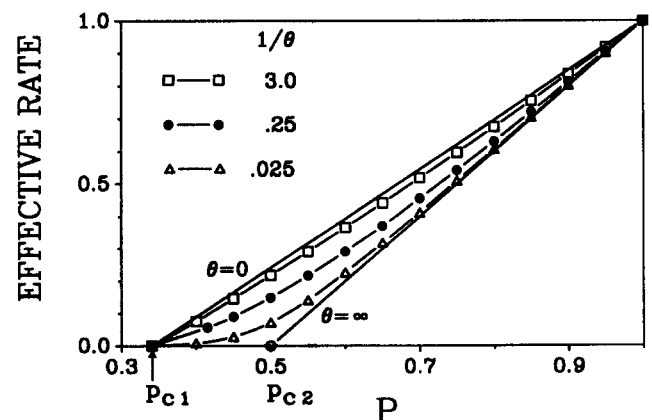


FIG. 3. DC effective-medium rate for the bond exchange process alone, for different values of exchange rate  $1/\theta$ .  $\tau^{-1} = 0$  in all cases. The results are obtained from a numerical solution to Eq. (77). All rates are in units of the primitive bond hopping rate.

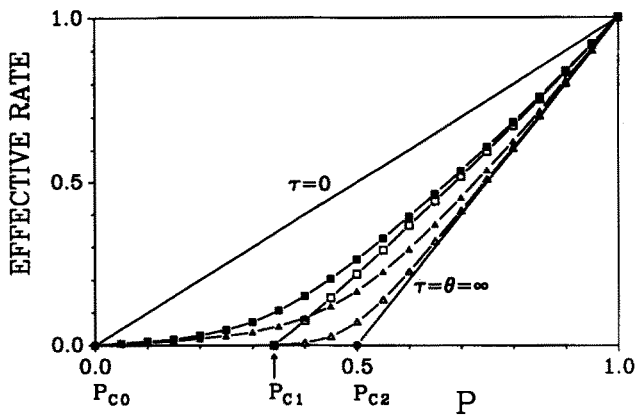


FIG. 4. DC effective-medium rate for the combined process, renewal and exchange, obtained from Eq. (77). Filled squares:  $1/\tau = 0.1, 1/\theta = 3.0$ ; filled triangles:  $1/\tau = 0.1, 1/\theta = 0.025$ ; open squares:  $1/\tau = 0, 1/\theta = 3.0$ ; open triangles:  $1/\tau = 0, 1/\theta = 0.025$ . The lines marked by open squares and open triangles are the same as in Fig. 3.

5). From Eqs. (B13) and (B15) we get in the static, DC limit ( $\tau^{-1} = \theta^{-1} = z = 0$ )

$$\psi \approx 1 - 2q - \delta q^2 + O(q^3); \quad \delta = \pi(1 - 2/\pi)^3 \approx 0.151. \tag{82}$$

The very small curvature of  $\psi(q)$  implied by Eq. (82) (and seen in Fig. 5) can be actually seen in numerical simulations above the percolation threshold.<sup>21</sup> The corrections are larger in the semistatic,  $\theta^{-1} \rightarrow \infty$  limit, where, from Eqs. (B13) and (B16), we similarly find

$$\psi \approx 1 - \frac{2q}{1 + 1/\pi} - \eta q^2 + O(q^3);$$

$$\eta = \pi \left( \frac{1 - 1/\pi}{1 + 1/\pi} \right)^3 \approx 0.434. \tag{83}$$

However, as is well known, the lowest order (or the single bond) EMA result sparsiously gives the exact threshold for the static  $2d$  square lattice bond percolation, so the second order (two bond) EMA result near  $p_{c2}$  is actually worse than the first order one. It is therefore not obvious that the full

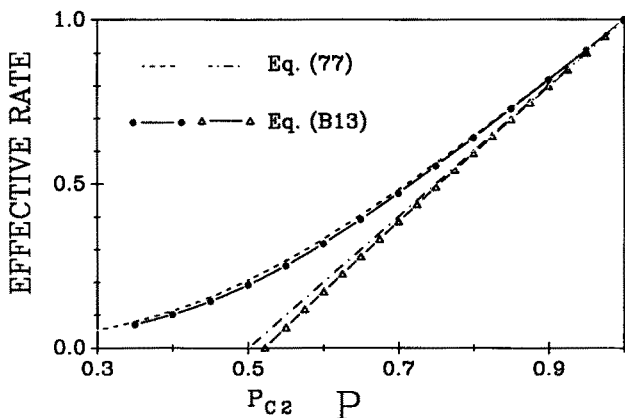


FIG. 5. Comparison between the full two bond EMA results [Eq. (B13)] and the  $O(q)$  results [Eq. (77)] for the DC effective-medium rate. The triangles and the dashed-dotted line correspond to the static case ( $1/\tau = 1/\theta = 0$ ), and the circles and the dashed line are for the dynamic case with  $1/\tau = 0.1, 1/\theta = 0.25$ .

two bond EMA result, Eq. (B13), is better for all  $p$  values, then its linearized form even in the dynamic situations. The qualitative behavior in both cases is the same.

The frequency dependence of  $\text{Re } D(\omega)$  [ $= \text{Re } \psi(i\omega)$  in our reduced units], the real part of the diffusion coefficient, is displayed in Figs. 6–8 for different values of  $p, \theta,$  and  $\tau$ . Comparing (for a given  $p$ ) the dependence associated with different values of  $\theta$  and  $\tau$  (Figs. 6 and 7), we see that the large  $\omega$  behavior ( $\omega \gg \theta^{-1}, \tau^{-1}$ ) is identical, while the small  $\omega$  limit is largely that characterized by the DC behavior (see, however, Fig. 8). The transition from the small to the large  $\omega$  behavior is sensitive to the particular system. An unexpected result obtained for the two bond exchange model (in the EMA) is a very shallow minimum seen at low frequencies (Fig. 8). Although this result is based on the solution to Eq. (77) and not to Eq. (B13), we have found that the minimum vanishes very slowly as  $p \rightarrow 1$  and persists even for  $q = 1 - p = 10^{-3}$  where the  $q^2$  corrections should be negligible (compared to the minimum depth which is  $\sim 10^{-4}$ ). The minimum does not disappear for  $\theta^{-1} \rightarrow \infty$ , suggesting that it exists also in the static correlated bond model obtained in this limit, at least in the EMA. The minimum smears out and disappears, however, as  $\tau^{-1}$  increases from 0. We note that an apparently general argument due to Kimball and Adams<sup>23</sup> suggests that this is perhaps an artifact of the EMA. Hilfer and Orbach<sup>13</sup> have suggested that a similar effect may occur in some other correlated dynamics situations, although below the percolation threshold.

The results discussed above are for a square lattice and are based on the repeating two bond clusters of the kind shown in Fig. 2(a). Obviously other lattices in  $2d$  can also be built from (various kinds of) two bond clusters. A simple alternative for the square lattice is shown in Fig. 2(b). In this case [by Eq. (A9)]

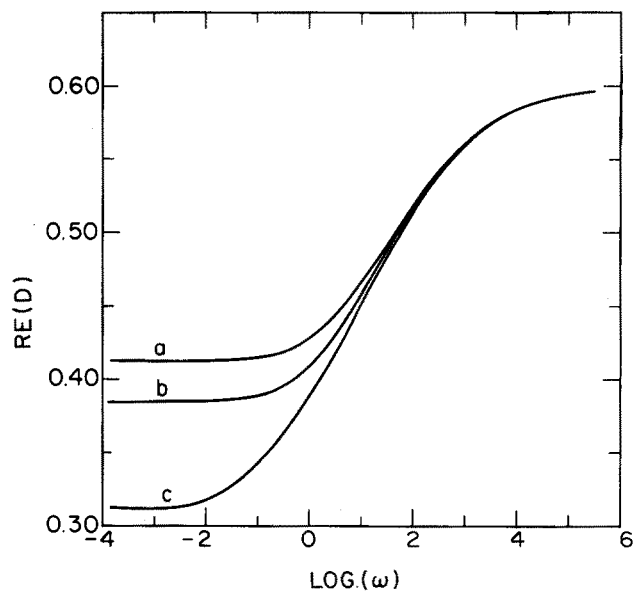


FIG. 6. The real part of the AC diffusion coefficient plotted against the frequency for  $p = 0.6$  and for different values of the renewal and exchange rate parameters. (a)  $1/\theta = 0.5, 1/\tau = 0.5$ ; (b)  $1/\theta = 0, 1/\tau = 0.5$ ; (c)  $1/\theta = 0.5, 1/\tau = 0$ . Note that in these dimensionless units  $\psi(i\omega)$  and  $D(\omega)$  are the same.



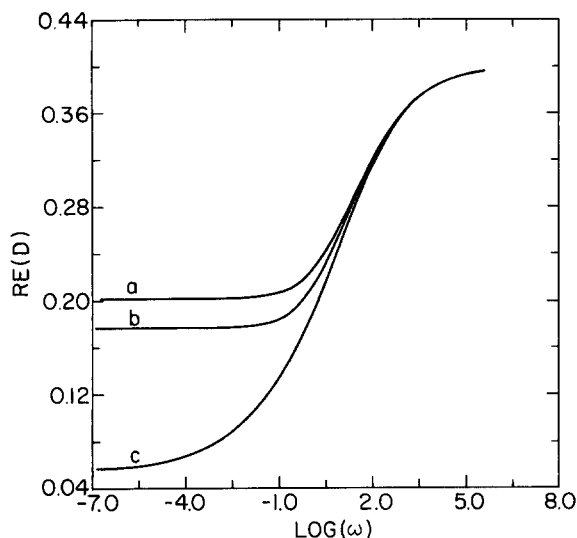


FIG. 7. Same as Fig. 6 but for  $p = 0.4$ .

$$G_{ab}(\epsilon) = -\frac{1}{2} \int_0^\infty dt \exp\left(-2t - \frac{1}{2}\epsilon t\right) I_2(t) I_0(t). \tag{84}$$

This leads to<sup>19</sup>  $B(\epsilon = 0) = 1 - 2/\pi$  so that, by the same analysis as above,  $p_{c1} = 1/\pi \approx 0.318$  for this case. The qualitative behavior depicted in Figs. 3–7 is unchanged.

Finally, we note that the  $n$  bond EMAs discussed in Sec. III–IV give successively better approximations (as  $n$  increases) to the disordered transport problem both in the static and in the dynamic situations. Thus, the result (1) for the HZ model is obtained in the single bond EMA. The formalism described above implies that the  $\omega$  dependence of the exact  $D(\omega)$  for the HZ model enters through infinite num-

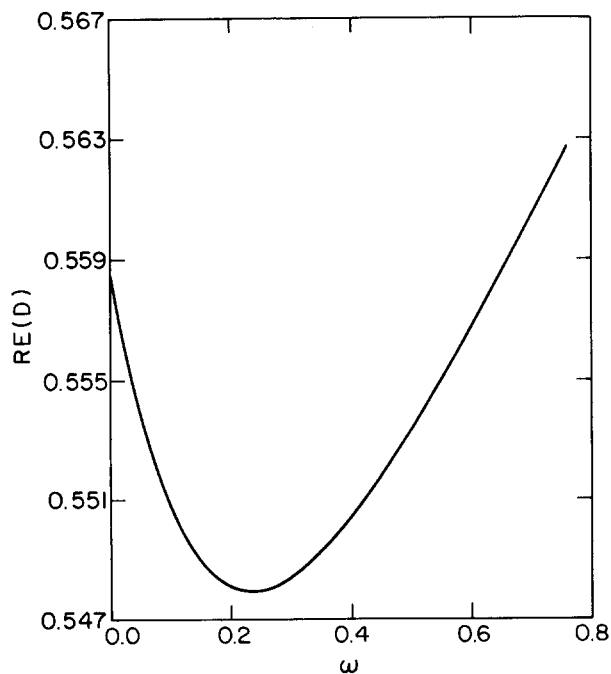


FIG. 8. The real part of the AC diffusion coefficient [obtained from Eq. (77)] at low frequencies, for  $p = 0.75$ ,  $1/\theta = 0.5$ ,  $1/\tau = 0$ .

ber of terms  $\omega - i\lambda_m$  where  $\lambda_m = m/\tau$  ( $m = 1, 2, \dots$ ) are the eigenvalues of the infinite order transition matrix.<sup>24</sup> Yet, for  $p$  close to 1 as well as for large  $\omega$  and/or  $\tau^{-1}$ , Eq. (1) should be an adequate approximation.

**V. CONCLUSIONS**

In this paper we have examined within an effective medium theory the implications of bond renewal and bond exchange dynamics on the diffusion of a particle in a random bond network. Bond exchange leads to a new percolation threshold  $p_{c1}$  whose position depends on the particular exchange process. The behavior of the diffusion coefficient as a function of the bond probability  $p$  for different values of the dynamical timescales  $\tau$ ,  $\theta$ , and  $\omega^{-1}$  is governed by the three thresholds  $p_{c0} = 0$ ,  $p_{c1}$ , and  $p_{c2}$  ( $p_{c2}$  being the usual percolation threshold for the static lattice), as seen in Figs. 3 and 4. In particular, a crossover from  $p_{c2}$  to  $p_{c1}$  occurs when the  $\theta$  process is switched on, and a crossover to  $p_{c0}$  occurs when the  $\tau$  process is switched on or when  $\omega$  becomes different from zero.

When we have more than one time scale for lattice rearrangement, the result (1) is no longer valid. Even when the single bond rearrangement is characterized by one time scale (as in the HZ model) the exact diffusion coefficient depends on an infinite spectrum of relaxation times. However, we have seen in Secs. II and III that the diffusion rate still depends on  $\omega$  and on these relaxation times  $\{\tau_j\}$  through combinations of the form  $\omega - i/\tau_j$ . Thus, if all the (single bond) relaxation times are roughly similar and if correlations in the network dynamics are relatively small, we may use Eq. (1) with one characteristic time  $\tau$  to get a rough estimate of the diffusion coefficient.

Finally, we note that application of the present theory to problems such as ionic diffusion in polymeric ionic conductors is still limited by our lack of knowledge of microscopic parameters such as  $\theta$  and  $\tau$ , and by questions concerning the effect of carrier–carrier interactions. A way to circumvent the first problem is offered by our recent calculation of the viscoelasticity associated with a renewing random network.<sup>25</sup> This calculation makes it possible to relate lattice renewal rates to observed mechanical properties.

**ACKNOWLEDGMENT**

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**APPENDIX A**

Here we derive the simple relation Eq. (53) that exist between the matrix elements of  $\mathbf{H}$ , defined in Eq. (50), and the lattice Green’s functions, defined by Eq. (54). We start from the definition

$$\mathbf{H} \cdot \mathbf{H}^{-1} = 1 \tag{A1}$$

or

$$\sum_k H_{ik} H_{kj}^{-1} = \delta_{ij}. \tag{A2}$$

By Eq. (50) (with the subscript  $l$  omitted)

$$H_{kj}^{-1} \equiv \langle k | \mathbf{H}^{-1} | j \rangle = (z + \lambda) \delta_{kj} + \langle k | \mathbf{W}_m | j \rangle. \quad (\text{A3})$$

Using the definition of the effective-medium matrix  $\mathbf{W}_m$  given by Eqs. (22) and (4) we have

$$\langle k | \mathbf{W}_m | j \rangle = \psi(z) (C_{nn} \delta_{kj} - \Delta_{kj}), \quad (\text{A4})$$

where  $C_{nn}$  is the number of nearest-neighbors and

$$\Delta_{kj} = \begin{cases} 1 & \text{if } k, j \text{ are nearest-neighbors} \\ 0 & \text{otherwise} \end{cases} \quad (\text{A5})$$

so from Eq. (A2) we get

$$[z + \lambda + C_{nn} \psi(z)] H_{ij} - \psi(z) \sum_{k \in \{j\}} H_{ik} = \delta_{ij}, \quad (\text{A6})$$

where  $\{j\}$  denotes the class of sites which are nearest-neighbors to  $j$ . The last equation can be rewritten as

$$(C_{nn} + \epsilon) G_{ij} - \sum_{k \in \{i\}} G_{kj} = -\delta_{ij} \quad (\text{A7})$$

with

$$G_{ij} = -\psi H_{ij}; \quad \epsilon = \frac{z + \lambda}{\psi}, \quad (\text{A8})$$

where use was made of the symmetry relation  $H_{ij} = H_{ji}$ . Equation (A8) is the desired relation. The elements  $G_{ij}$  which satisfy Eq. (A7) are the lattice Green's functions.<sup>17,20</sup> For a simple cubic lattice in  $d$  dimensions the solution of Eq. (A7) is<sup>17</sup>

$$G_{ij} = G(m_1, m_2, \dots, m_d) = -\frac{1}{2} \int_0^\infty \exp\left[-\frac{1}{2} t(2d + \epsilon)\right] \prod_{i=1}^d I_{m_i}(t) dt, \quad (\text{A9})$$

where  $m_k$  is the (bond number) separation along the principal axis  $k$  and  $I_m(t)$  is the modified Bessel function of order  $m$ .

A simple relation between the nearest-neighbors Green's function  $G_{ij}(i, j \text{ are nearest-neighbors})$  and  $G_{ii}$ , the Green's function at the origin, results from Eq. (A9) by writing this equation for  $i = j$

$$(C_{nn} + \epsilon) G_{ii} - \sum_{k \in \{i\}} G_{ki} = -1 \quad (\text{A10})$$

or, since all nearest-neighbor Green's functions are identical by the rotational symmetry of the lattice,

$$G_{ij} - G_{ii} = \frac{1 + \epsilon G_{ii}}{C_{nn}}; \quad i, j \text{ nearest neighbors.} \quad (\text{A11})$$

### APPENDIX B

To arrive at Eq. (72) we first apply Eqs. (48) and (51) to a two bond cluster (i.e., two bonds with one site in common) with two states for each bond,  $\sigma = 0, 1$ . Sites and bonds are labeled as in Figs. 2(a) or 2(b), although we do not refer at first to a particular lattice or geometry. Rewrite Eqs. (48) and (51) with indexes  $\alpha'$  and  $\beta'$  (instead of  $\alpha$  and  $\beta$ ); For  $\beta' = \alpha$  Eq. (48) reads

$$\sum_{\sigma_\alpha \sigma_\beta} [2(\sigma_\alpha - \psi) \Gamma_{\sigma_\alpha \sigma_\beta}^\alpha + (\sigma_\beta - \psi) \Gamma_{\sigma_\alpha \sigma_\beta}^\beta] = 0 \quad (\text{B1})$$

and for  $\beta' = \beta$  we find

$$\sum_{\sigma_\alpha \sigma_\beta} [(\sigma_\alpha - \psi) \Gamma_{\sigma_\alpha \sigma_\beta}^\alpha + 2(\sigma_\beta - \psi) \Gamma_{\sigma_\alpha \sigma_\beta}^\beta] = 0. \quad (\text{B2})$$

By taking linear combinations of Eqs. (B1) and (B2) we get

$$\sum_{\sigma_\alpha \sigma_\beta} (\sigma_\alpha - \psi) \Gamma_{\sigma_\alpha \sigma_\beta}^\alpha = 0 \quad (\text{B3})$$

$$\sum_{\sigma_\alpha \sigma_\beta} (\sigma_\beta - \psi) \Gamma_{\sigma_\alpha \sigma_\beta}^\beta = 0. \quad (\text{B4})$$

Similarly, from Eq. (51) we get

$$\sum_{\sigma_\alpha \sigma_\beta} C_{\sigma_\alpha \sigma_\beta}^{(l)} [\Gamma_{\sigma_\alpha \sigma_\beta}^\alpha + (\sigma_\alpha - \psi) K_{\alpha\alpha}^{(l)} \Gamma_{\sigma_\alpha \sigma_\beta}^\alpha + (\sigma_\beta - \psi) K_{\alpha\beta}^{(l)} \Gamma_{\sigma_\alpha \sigma_\beta}^\beta] = 0; \quad l = 1, 2, 3 \quad (\text{B5})$$

$$\sum_{\sigma_\alpha \sigma_\beta} C_{\sigma_\alpha \sigma_\beta}^{(l)} [\Gamma_{\sigma_\alpha \sigma_\beta}^\beta + (\sigma_\alpha - \psi) K_{\beta\alpha}^{(l)} \Gamma_{\sigma_\alpha \sigma_\beta}^\alpha + (\sigma_\beta - \psi) K_{\beta\beta}^{(l)} \Gamma_{\sigma_\alpha \sigma_\beta}^\beta] = 0; \quad l = 1, 2, 3 \quad (\text{B6})$$

where, by Eq. (52)

$$K_{\alpha\alpha}^{(l)} = K_{\beta\beta}^{(l)} = 2(H_{ii}^{(l)} - H_{ij}^{(l)}) \\ K_{\alpha\beta}^{(l)} = K_{\beta\alpha}^{(l)} = H_{ab}^{(l)} + H_{ii}^{(l)} - 2H_{ij}^{(l)}; \\ i, j \text{ nearest neighbors.} \quad (\text{B7})$$

We can perform the summation in Eqs. (B3), (B4), (B5), and (B6) for the bond values  $\sigma = 0, 1$  to get explicit equations. The eight equations for  $\Gamma_{\sigma\sigma'}^\delta$  [two from (B3) and (B4) with three types from (B5) and (B6) for three nonzero eigenvalues of  $\Omega(\sigma_\alpha, \sigma_\beta; \sigma'_\alpha, \sigma'_\beta)$ ] can be reduced to four equations if one of the following symmetries holds

$$C_{10}^{(l)} = C_{01}^{(l)} \quad (\text{B8a})$$

or

$$C_{00}^{(l)} = C_{11}^{(l)} = 0 \quad \text{and} \quad C_{10}^{(l)} = -C_{01}^{(l)} \quad (\text{B8b})$$

for any  $l$ . Since we are interested only in the physically correct solution for the effective-medium rate  $\psi(z)$ , it is possible to reduce the number of unacceptable solutions by taking the special choice

$$\Gamma_{\sigma\sigma}^\alpha = \Gamma_{\sigma\sigma}^\beta; \quad \sigma = 0, 1 \quad (\text{B9a})$$

and

$$\Gamma_{01}^\alpha = \Gamma_{10}^\beta \quad \text{and} \quad \Gamma_{10}^\alpha = \Gamma_{01}^\beta. \quad (\text{B9b})$$

The choice of Eq. (B9a) seems to follow only from the rotational symmetry of the underlying (square) lattice, while Eq. (B9b) follows from the dynamical symmetry between the two bonds. More relevant to our purpose is the fact that with the choices of (B9a) and (B9b) and with the assumption that Eqs. (B8a) and (B8b) hold, Eq. (B3) becomes identical to Eq. (B4), and the three types of Eq. (B5) become identical to the corresponding types (same  $l$ ) of Eq. (B6). Therefore, we are left with a set of four independent equations for four unknowns, either  $\Gamma_{\sigma_\alpha \sigma_\beta}^\alpha$  or  $\Gamma_{\sigma_\alpha \sigma_\beta}^\beta$  ( $\sigma_\alpha \sigma_\beta = 00, 01, 10, 11$ ).

Indeed, for the model of Sec. IV, we see from Eq. (70) that for  $l = 1, 3$  the relation (B8a) is obeyed, and for  $l = 2$  Eq. (B8b) applies. Using the coefficients from Eq. (70) we write explicitly four equations for  $\Gamma_{\sigma_\alpha \sigma_\beta}^\alpha$ . This leads to Eq. (72) with the coefficients  $a_l$ , given in Eqs. (74) and (75), found by

$$\begin{aligned} a_l &= K_{\alpha\alpha}^{(l)} + K_{\alpha\beta}^{(l)}; \quad l = 1, 3 \\ a_2 &= K_{\alpha\alpha}^{(2)} - K_{\alpha\beta}^{(2)} \end{aligned} \quad (\text{B10})$$

with the  $K$  elements given by Eq. (B7). Using the relations (53) and (A11) we can have explicit forms for these coefficients

$$\begin{aligned} a_l &\equiv \frac{b_l}{\psi}; \quad b_2 = B(\epsilon_2); \\ b_l &= 2p_c [1 - \epsilon_l g(\epsilon_l)] - B(\epsilon_l); \quad l = 1, 3 \end{aligned} \quad (\text{B11})$$

where  $g(\epsilon)$ ,  $B(\epsilon)$ ,  $\epsilon_1$ , and  $\epsilon_2$  are defined by Eqs. (63), (77a) and (77b)

$$\epsilon_3 = \frac{z + (2/\tau)}{\psi} \quad (\text{B12})$$

and  $p_c = 2/C_{nn}$  is the static (EMA) percolation threshold of the lattice under consideration. This analysis can apply only to lattices which can be built from identical (up to rotation) two bond clusters. From Eq. (76), which is the requirement that the determinant of the coefficients of  $\Gamma_{\sigma_\alpha\sigma_\beta}^\alpha$  should vanish, we get<sup>22</sup> an implicit quadratic equation for the effective-medium rate  $\psi(z)$ :

$$X_2(\psi)\psi^2 + X_1(\psi)\psi + X_0(\psi) = 0 \quad (\text{B13})$$

where

$$X_2 = 2[1 - b_1][1 - b_2][1 - b_3], \quad (\text{B14a})$$

$$\begin{aligned} X_1 &= 2p[b_2 - 1][1 - b_1] + b_3[4b_2b_1 - 3b_1 \\ &\quad - 3b_2 + 2] + b_2 + b_1 - 2b_2b_1, \end{aligned} \quad (\text{B14b})$$

$$\begin{aligned} X_0 &= p^2[2b_3 - b_2 - b_1] + 2p[b_2b_1 - b_3] \\ &\quad + b_3[b_1 + b_2 - 2b_1b_2]; \end{aligned} \quad (\text{B14c})$$

only the + sign solution of Eq. (B13) should be taken (since the minus one is not physical). In the static, DC limit ( $1/\theta = 1/\tau = z = 0$ ) we denote  $B(\epsilon = 0) = B_0$  ( $B_0 = 1/\pi$ ,  $1 - 2/\pi$  for the configurations of Figs. 2(a) and 2(b), respectively) and, for a square lattice ( $p_c = 1/2$ ), we get

$$X_2 = 2B_0^2(1 - B_0), \quad (\text{B15a})$$

$$X_1 = B_0\{2p(B_0 - 1) + 4B_0^2 - 6B_0 + 3\}, \quad (\text{B15b})$$

$$\begin{aligned} X_0 &= p^2(1 - 2B_0) - 2p(1 - B_0)^2 - 2B_0^3 \\ &\quad + 4B_0^2 - 3B_0 + 1 \end{aligned} \quad (\text{B15c})$$

whereas in the fast bond interchange, DC limit ( $\theta \rightarrow 0$ ,  $1/\tau = z = 0$ ) it is

$$X_2 = 2B_0^2, \quad (\text{B16a})$$

$$X_1 = B_0\{3(1 - B_0) - 2p\}, \quad (\text{B16b})$$

$$X_0 = (1 - B_0)\{(1 - p)^2 - B_0\}. \quad (\text{B16c})$$

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