Tracer diffusion of interacting particles on incomplete lattices: Effective medium approximation

Marvin Silverberg[a] and Mark A. Ratner
Department of Chemistry, Northwestern University, Evanston, Illinois 60208

Rony Granek
School of Chemistry, Sackler Faculty of Sciences, Tel-Aviv University, Tel Aviv 69978 Israel

Abraham Nitzan[b]
Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

Dynamic percolation theory is adapted to obtain diffusion coefficients for particles with blocking interactions on incomplete lattices, within an effective medium approximation (EMA). The substrate lattices have static bond disorder. The motion of a tracer particle among identical background particles is regarded as particle motion in a fluctuating random environment superimposed on the statically disordered lattice; the fluctuations results from the motion of the background particles. Several schemes for incorporating the effect of the background particles are discussed, all relating their motion in different ways to the macroscopic diffusion. Comparisons with Monte Carlo simulations are performed for two-dimensional simple square and three-dimensional simple cubic lattices. In the range where single bond EMA is thought to be reliable, good agreement with the simulation is achieved.

I. INTRODUCTION

The diffusion of classical particles on disordered lattices is used as a model system to gain insight into a variety of physical systems. Examples are vacancy diffusion in highly disordered solids,[1] ionic diffusion and conduction in solid ionic conductors[2] and in polymer conductors[3] and electronic conductivity in disordered materials.[4] Although an extensive literature exists on the diffusion of particles in such systems,[5] comparatively few studies directly address the issue of particle interactions.[6,7] Of the few calculations done on interacting particle systems, most are simulation studies. These are often very costly and furthermore are hard to apply near singularities of the transport phenomena (e.g., percolation thresholds). In this paper we advance an approximate analytical method, based on the effective medium approximation (EMA) for the tracer diffusion of interacting particles on disordered lattices modeled as random bond networks.

The interactions considered in this paper are of the blocking or excluded volume type, allowing only single particle occupancy of any site. The formalism can be extended to longer range interactions. We have also carried out Monte Carlo simulations for several particle densities and for a series of lattices of varying degrees of incompleteness in order to test the approximate analytical results. Good agreement was found between the EMA and the simulation results sufficiently above the percolation threshold. Our computational resources did not permit thorough investigation of the immediate vicinity of the threshold, however we expect EMA to yield poor results in this region.

The formalism presented below is based on the EMA

approach to dynamic bond percolation (DBP) theory. The latter has been advanced by Druger, Ratner, and Nitzan[3] (DRN) and by Harrison and Zwanzig[8] (HZ), to deal with transport processes in dynamically disordered systems, where the disorder (e.g., bond availability) changes in time. It was later generalized by Granek and Nitzan,[10] and was used to develop an effective medium theory for the tracer diffusion in a system of interacting identical particles in a perfect lattice.[6] The idea behind this approach is that a tracer particle in such a system moves in a dynamically disordered environment made of the instantaneous local configuration of other particles. A similar idea has been recently explored by Hilfer and Orbach.[11] In the present problem the situation is similar, however, in addition to this dynamic disorder we now have a static disorder associated with the time independent random distribution of broken bonds.

In using DBP theory for the tracer diffusion in interacting particle systems, we encounter two difficulties. First, the blocking of occupied sites by the background particles corresponds to a random site system, and approximating it by a random bond system amounts to disregarding correlations that may be important. Second, the results of a DBP model are obtained in terms of a "renewal" time τ, which is the characteristic time for the bond (or site) to change its character between the blocked and unblocked state. This time has to be related to the motion of the diffusing particles in order to make the calculation self-consistent. In fact, a complete description of the process should be non-Markovian. Granek and Nitzan[6] have suggested that the best choice of τ within a Markovian description of the problem is the characteristic time of the chemical diffusion in the system (i.e., $\tau = D_c^{-1} a^2$, where D_c is the chemical diffusion coefficient and a is the lattice length parameter) which for the case of only blocking interaction is simply the effective single-particle hopping time. The good agreement shown below between the calculation based on these concepts and our numerical

simulations indicate that sufficiently above the percolation threshold our approximations and our choice of τ are justified.

In Sec. II we derive our effective medium approximation for tracer diffusion on a bond disordered lattice in a system of many diffusing mutually interacting particles. We use here the Granek–Nitzan extension[10] of the Harrison Zwanzig EMA[8] which is particularly suitable for our calculation. In Sec. III the calculated values of the tracer diffusion coefficients at various coverages and for various values of the bond availability are reported for a square lattice and for a simple cubic lattice, and compared with Monte Carlo simulations. Additional discussions and conclusions appear in Sec. IV.

II. THE EFFECTIVE MEDIUM APPROXIMATION

A many bond state generalization of the HZ formalism has been developed by Granek and Nitzan.[10] Our present discussion is based on this generalization.

Consider a system of many identical particles with concentration (per site) ϑ, diffusing on an incomplete lattice characterized by a coordination number Z and by the fraction $1 - p$ $(0 < p < 1)$ of broken bonds. We focus on one of these particles, the "tracer particle". All other particles are referred to as background particles. The probability $P_i(t)$ of finding the tracer particle at site i at time t is modeled as a dynamic bond percolation problem described by the stochastic master equation

$$\frac{d\mathbf{P}}{dt} = -\widehat{\mathbf{W}} \cdot \mathbf{P} = -\sum_\alpha \sigma_\alpha(t) \widehat{\mathbf{V}}_\alpha \cdot \mathbf{P}. \tag{2}$$

Here $\alpha = (ij)$ designates the bond between nearest-neighbor sites i and j,

$$\widehat{\mathbf{V}}_\alpha = (|i\rangle - |j\rangle)(\langle i| - \langle j|) \tag{3}$$

and

$$\mathbf{P}(t) = \sum_i P_i(t)|i\rangle. \tag{4}$$

In Eqs. (2) and (3) and in what follows the carat sign denotes the operator in site space. Here $|i\rangle$ denotes a column vector with ith entry equal to 1 and all others zero. Each "state" $\mathbf{P}$ of the system therefore specifies the probability distribution of the tracer over all sites of the lattice.

The time-dependent hopping rate across bond α, $\sigma_\alpha(t)$, is determined by the state n of this bond $[\sigma_\alpha(t) = \sigma(n_\alpha(t))$, see below]. There are three possible bond states: (a) absent or broken (due to the static disorder), (b) blocked at the target site (by a background particle), and (c) available for hopping (unblocked and unbroken). One may further distinguish between a broken bond whose target site is blocked and a broken one whose target site is vacant, but this is superfluous and does not lead to any additional results. As mentioned in the previous section we introduce here an approximation in treating the background particle dynamics: only their effect on blocking the bonds accessible to the tracer particle is taken into account. This in effect amounts to replacing the dynamic site disorder associated with the background particles with dynamic bond disorder

as implied by Eq. (2). This dynamic disorder exists in addition to the static bond disorder.

Consider now the time evolution of the states of bond $\alpha = (ij)$. We denote the probability that bond α is in state n $(n = a,b,c$ where a, b, and c denote the three possible bond states listed above) by $\phi_\alpha(n,t)$. The corresponding transition probabilities are $\sigma(n)$ so that $\sigma(a) = \sigma(b) = 0$ and $\sigma(c) = 1$. The tracer particle is taken to be on site i and the evolution of $\phi_\alpha(n,t)$ is associated with motion of background particles into and out of site j. These background particles are assumed to hop with an (as yet undetermined) effective rate v, and the total rate of hopping out of an occupied site j into any of its $Z - 1$ neighbors (excluding i) is taken to be $v(Z - 1)(1 - \vartheta)$. By taking this rate to be proportional to the averaged site availability $1 - \vartheta$ we have made a mean field approximation to the motion of the background particles. Additional effects of particle–particle interaction beyond the mean field approximation may in principle appear in v. The value of v should also reflect the influence of the static disorder on the motion of the background particles.

Similarly the total rate of hopping into an unoccupied site j is $v(Z - 1)\vartheta$. Finally, when the bond α is in state a (broken) it remains in this state which corresponds to the static disorder. Thus

$$\frac{\partial}{\partial t} \begin{bmatrix} \phi_\alpha(a,t) \\ \phi_\alpha(b,t) \\ \phi_\alpha(c,t) \end{bmatrix}$$

$$= \begin{bmatrix} 0 & 0 & 0 \\ 0 & -(Z-1)v(1-\vartheta) & (Z-1)v\vartheta \\ 0 & (Z-1)v(1-\vartheta) & -(Z-1)v\vartheta \end{bmatrix}$$

$$\times \begin{bmatrix} \phi_\alpha(a,t) \\ \phi_\alpha(b,t) \\ \phi_\alpha(c,t) \end{bmatrix} \tag{5}$$

or

$$\frac{\partial}{\partial t} \boldsymbol{\phi}_\alpha(t) = \boldsymbol{\Omega}_\alpha \boldsymbol{\phi}_\alpha(t), \tag{6}$$

where $\boldsymbol{\Omega}_\alpha$, the matrix in Eq. (5), is an operator in the space of bond states and $\boldsymbol{\phi}_\alpha$ is a vector in the same space. The eigenvalues of $\boldsymbol{\Omega}_\alpha$ are nonpositive and will be denoted $-\lambda_j$, $j = 0,1,\ldots$. There is at least one zero eigenvalue, $\lambda_0 = 0$ with the right eigenvector given by $\phi_\alpha^{(\text{eq})} = \rho_\alpha$, the equilibrium solution of Eq. (6):

$$\rho_\alpha(a) = 1 - p,$$
$$\rho_\alpha(b) = p\vartheta, \tag{7}$$
$$\rho_\alpha(c) = p(1 - \vartheta),$$

and the corresponding left eigenvector $(1,1,1)$. Note that $\boldsymbol{\rho}_\alpha$ satisfies $\boldsymbol{\Omega}_\alpha \boldsymbol{\rho}_\alpha = 0$ for any choice of p, and the identification of p as the fraction of unbroken bonds is additional information, not contained in $\boldsymbol{\Omega}$.[12] In our particular case there is another zero eigenvalue $(\lambda_1 = 0)$ corresponding to the left eigenvector $(-p, 1 - p, 1 - p)$. Finally, the third eigenvalue $-\lambda_2$, where $\lambda_2 = (Z - 1)v$, corresponds to the eigen-

vector $(0, \vartheta - 1, \vartheta)$. Both latter eigenvectors should be (and are) orthogonal to ρ_α.[12]

Next define the joint probability distribution $f(\mathbf{P}, \mathbf{n}, t)$ as the probability to find at time t the tracer particle distributed according to $\mathbf{P}$ and the background particles and bonds distributed so that $\mathbf{n} = n_1, n_2 \dots = \{n_\alpha\}$ $(n_\alpha, (\alpha = 1, 2 \dots))$, is a, b, or c). f is governed by the Liouville master equation

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

where

$$\Omega = \sum_\alpha \Omega_\alpha. \tag{9}$$

Equations (6) and (9) imply that we ignore correlated fluctuations of the bond states. Such correlations inevitably exist since a hopping background particle, unblocking some bond will end up blocking others. Ignoring such correlations is consistent with replacing the dynamic site disorder by a dynamic bond disorder above, and with the use of a single bond EMA in what follows. Such correlations can in principle be included within EMA treatments,[10] however we limit ourselves here to the simplest approximation.

Starting from the distribution $f(\mathbf{P}, \mathbf{n}, t)$, one defines a partial average

$$\mathbf{P}(\mathbf{n}, t) = \int d\mathbf{P} \ \mathbf{P} f(\mathbf{P}, \mathbf{n}, t), \tag{10}$$

yielding

$$\frac{\partial}{\partial t} \mathbf{P}(\mathbf{n}, t) = -\widehat{\mathbf{W}} \cdot \mathbf{P}(\mathbf{n}, t) + \Omega \mathbf{P}(\mathbf{n}, t). \tag{11}$$

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

$$f(\mathbf{P}, \mathbf{n}, 0) = \delta(\mathbf{P} - \mathbf{P}_0) \rho(\mathbf{n}), \tag{12}$$

where

$$\rho(\mathbf{n}) = \prod_\alpha \rho_\alpha(n_\alpha), \tag{13}$$

where the elements of $\rho_\alpha(n)$ $(n = a, b, c)$ are given in Eq. (7).

These equations are of the form characteristic of the many bond state generalization[10] of the Harrison–Zwanzig effective medium theory[8] of the dynamic bond percolation problem. The solution of this problem (within the single bond EMA) is obtained as the condition for the existence of a nontrivial solution to a set of homogeneous linear equations. This condition is the vanishing of the determinant of a square matrix whose order is the number of possible bond states (3 in our case), given by

$$\begin{pmatrix} \sigma(a) - \psi & \sigma(b) - \psi & \sigma(c) - \psi \\ C_a^{(1)}(1 + (\sigma(a) - \psi)h_1) & C_b^{(1)}(1 + (\sigma(b) - \psi)h_1) & C_c^{(1)}(1 + (\sigma(c) - \psi)h_1) \\ C_a^{(2)}(1 + (\sigma(a) - \psi)h^2) & C_b^{(2)}(1 + (\sigma(b) - \psi)h_2) & C_c^{(2)}(1 + (\sigma(c) - \psi)h_2) \end{pmatrix}, \tag{14}$$

where $\psi (= \psi(z))$ is the desired effective hopping rate which is a function of the Laplace variable z, $C_n^{(l)}$ $(l = 1, 2; n = a, b, c)$ are elements of the left eigenvectors of the matrix Ω_α [Eqs. (5), (6)] except the vector $\mathbf{C}^{(0)} = (1, 1, 1)$, and where h_l $(l = 1, 2)$ are scalar quantities defined by the identity

$$\widehat{\mathbf{V}}_\alpha \cdot \left[(z + \lambda_l) + \psi(z) \sum_\alpha \widehat{\mathbf{V}}_\alpha \right]^{-1} \cdot \widehat{\mathbf{V}}_\alpha = h_l \widehat{\mathbf{V}}_\alpha. \tag{15}$$

Using $\sigma(a) = \sigma(b) = 0$; $\sigma(c) = 1$ and the results for the left eigenvectors of Ω_α given above, the EMA equation for ψ becomes

$$\begin{vmatrix} -\psi & -\psi & (1 - \psi) \\ -p(1 - \psi h_1) & (1 - p)(1 - \psi h_1) & (1 - p)(1 + h_1 - \psi h_1) \\ 0 & (\vartheta - 1)(1 - \psi h_2) & \vartheta(1 + h_2 - \psi h_2) \end{vmatrix} = 0. \tag{16}$$

The quantities h_l have been explicitly calculated in Ref. 10. They are given by

$$h_l = \frac{p_c}{\psi} \left[1 - \frac{z + \lambda_l}{\psi} g\left(\frac{z + \lambda_l}{\psi} \right) \right], \tag{17}$$

where $-\lambda_l$ are the eigenvalues of Ω_α, Eqs. (5), (6) $(\lambda_0 = 0, \lambda_1 = 0,$ and $\lambda_2 = (Z - 1)v$; $P_c = (2/Z)$ is the EMA percolation threshold, and where $g = -G_{ii}$ with G_{ii} being the diagonal element of the lattice Green's function.[13–15] For a simple cubic lattice in d dimensions $g(\varepsilon)$ is given explicitly by

$$g(\varepsilon) = \frac{1}{2} \int_0^\infty \exp\left[-\frac{1}{2} t(2d + \varepsilon) \right] (I_0(t))^d \, dt. \tag{18}$$

Here I_0 is the zeroth-order modified Bessel function. For the case of the simple square lattice $(d = 2)$ this simplifies to

$$g(\varepsilon) = \frac{1}{2\pi} \left(1 + \frac{\varepsilon}{4} \right)^{-1} K\left[\left(1 + \frac{\varepsilon}{4} \right)^{-1} \right], \tag{19}$$

where K is the complete elliptic integral of the first kind. For the case of the simple cubic lattice $(d = 3)$:[14(a)]

$$g(\varepsilon) = \frac{4}{\pi^2 (3 + \tfrac{1}{2}\epsilon)}$$

$$\times \left\{ \frac{(\xi + 1)(\xi + 4)}{\xi^2 + 8\xi + 8 + 4(2 + \xi)(\xi + 1)^{1/2}} \right\}^{1/2}$$

$$\times K(k_+)K(k_-), \tag{20}$$

where

$$k_{\pm}^2$$

$$= \frac{\xi [(\xi + 1)^{1/2} \pm (\xi + 4)^{1/2}] - 2[1 - (\xi + 1)^{1/2}]}{\xi [(\xi + 1)^{1/2} \pm (\xi + 4)^{1/2}] + 2[1 + (\xi + 1)^{1/2}]} \tag{21}$$

and

$$\xi = \frac{(3 + \tfrac{1}{2}\epsilon)^2 + 3 - \{[(3 + \tfrac{1}{2}\epsilon)^2 - 9)((3 + \tfrac{1}{2}\epsilon)^2 - 1]\}^{1/2}}{(3 + \tfrac{1}{2}\epsilon)^2 - 3 + \{[(3 + \tfrac{1}{2}\epsilon)^2 - 9][(3 + \tfrac{1}{2}\epsilon)^2 - 1]\}^{1/2}}. \tag{22}$$

Equation (16) and (17) lead to the following final form of the EMA equation for the dc effective tracer hopping rate ψ:

$$\psi = \frac{p(1 - \vartheta) - p_c}{1 - p_c} + \frac{\vartheta p_c [(Z - 1)\nu/\psi] g[(Z - 1)\nu/\psi]}{(1 - p_c)\{1 - p_c + p_c [(Z - 1)\nu/\psi] g[(Z - 1)\nu/\psi]\}}. \tag{23}$$

In order to find an explicit solution for ψ one has to specify the characteristic rate ν of the background particles. Several possible models for ν were suggested, compared and discussed in Ref. 10. These are (a) $\nu = \psi(1 - \vartheta)$, namely, the hopping rate of the background particles is taken to be equal to the desired EMA tracer hopping rate. This yields

$$\psi = \frac{p(1 - \vartheta) - p_c}{1 - p_c} + \frac{\vartheta p_c X g(X)}{(1 - p_c)[1 - p_c + p_c X g(X)]}, \tag{24a}$$

$$X = \frac{Z - 1}{1 - \vartheta} \tag{24b}$$

(b) ν is equal to the hopping rate associated with the chemical diffusion coefficient. In the present case (blocking interactions only) the chemical diffusion is independent of coverage so that ν is taken to be

$$\nu = \begin{cases} (p - p_c)/(1 - p_c) & p > p_c \\ 0 & p \leqslant p_c \end{cases} \tag{25}$$

which is the EMA result for the effective hopping rate of a single particle on the random network. (c) $\nu = p$, namely, a simple mean field result, which becomes exact in the $\omega \to \infty$ limit.

The first choice is appealing because it constitutes an explicit result for ψ. In Ref. 10 it was argued that this choice is questionable, because ν^{-1} represents a time scale for a local rearrangement process while ψ^{-1} is a time scale for the effective motion, which is based on a long range average. Here we encounter another unphysical feature associated with this choice, as it is easy to see from Eq. (24) that it leads to a percolation threshold which depends on the coverage ϑ.

The rationale for the second choice is that blocking and unblocking of sites adjacent to the tracer particle corresponds to density fluctuations, which are controlled by the chemical diffusion rate. The weakness of this choice is that Eq. (25) is an averaged quantity which contains information on the long range effects of the bond disorder, while hopping of background particles to and from adjacent sites is a short-range process (that exists even below the percolation threshold).

The third choice $\nu = p$, focuses on the shortest time ($\omega \to \infty$) and range (motion along a single bond) of the disorder. We expect that a better choice for ν should correspond to the chemical diffusion at intermediate frequency (implying the need for a non-Markovian formalism) of the order of the single-particle jump rate. We defer such more elaborate approximations to future work and limit ourselves here to the simple possibilities described above. In what follows we compare results based on these choices with computer simulations.

III. RESULTS AND DISCUSSION

The simulation results reported in this section are based on standard Monte Carlo (MC) simulations performed on a two-dimensional simple square and three-dimensional simple cubic lattices. The square lattice was of size 300×300 and the cubic lattice—of size $50 \times 50 \times 50$, both with periodic boundary conditions. Bonds between any two adjacent sites were present with probability p. Particles were added randomly up to a specified occupancy ϑ and each site could be occupied by no more than one particle. For each specified pair of values of p and ϑ the results shown below represent averages over three different realizations of the random lattice and over the trajectories of all the particles. A standard MC algorithm was employed for the particle motion, randomly sampling the diffusing particles and randomly choosing a NN site next to each one. Hopping occurs with 50% probability into the chosen NN site if it is unoccupied. Otherwise hopping is blocked. The trajectories (one multiparticle trajectory for each of the three realizations of the random lattice) were 50 000 MC steps long, and the diffusion constant was extracted from the last 10 000 steps, far into the region where $\langle r^2 \rangle$ grows linearly with time.

The mean-squared displacement becomes a linear function of time after an initial nonlinear regime. The duration of
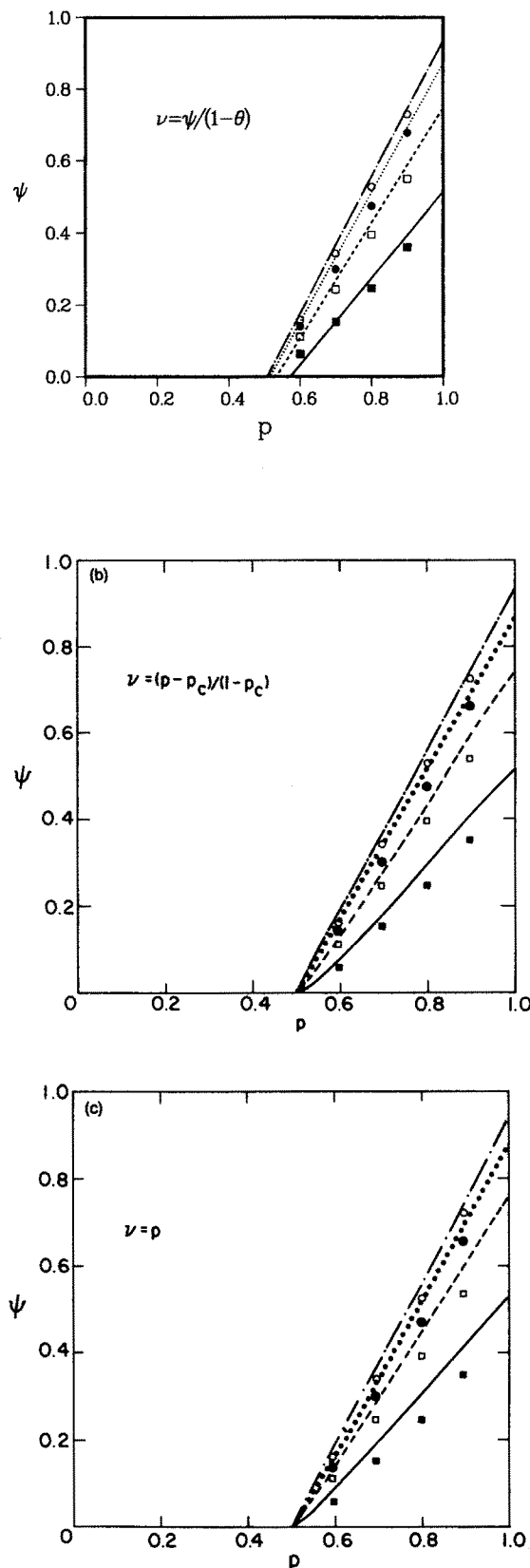
FIG. 1. Effective hopping rate ψ calculated according to Eq. (24), for the two-dimensional simple square lattice. (a), (b), (c) correspond to the different models for v: (a) $v = \psi(1 - \vartheta)$; (b) $v = (p - p_c)/(1 - p_c)$; (c) $v = p$. The coverages ϑ are 0.4 (full line), 0.2 (dashed line), 0.1 (dotted line) and 0.05 (dashed dotted line). The MC simulation results shown are the same in all figures. Full squares, empty squares, full circles, and empty circles are MC results for $\vartheta = 0.4, 0.2, 0.1$, and 0.05 respectively. For each of these coverages there are four points calculated for $p = 0.6, 0.7, 0.8$, and 0.9.

TABLE I. A comparison of EMA and MC results for the tracer diffusion coefficient for the two-dimensional simple square lattice and for $p = 0.6$. Model A is $v = \psi$; model B is $v = (p - p_c)/(1 - p_c)$; model C is $v = p$. Values for four coverages are reported.

ϑ	Model A	Model B	Model C	Monte Carlo
0.05	0.175	0.176	0.184	0.157 ± 0.001
0.10	0.151	0.154	0.168	0.139 ± 0.003
0.20	0.106	0.117	0.140	0.110 ± 0.003
0.40	0.032	0.066	0.092	0.062 ± 0.001

this transient depends on the specific values of p and ϑ in the system. The diffusion coefficient is obtained from the mean square displacement for a time interval Δt (typically 10 000 Monte Carlo steps), following the onset and stabilization of the linear regime, by dividing by $2d \, \Delta t$ ($d = 2$ or 3) and averaging over the several realizations of the system for the given values of p and ϑ. Thus for each individual particle in turn, all other particles present on the lattice were regarded as background particles in the sense of our EMA formulation.

Our results for the two-dimensional square lattice are summarized in Fig. 1 and in Tables I and II. Figure 1 depicts the EMA hopping rate ψ in the range $p_c \leqslant p \leqslant 1$ for several values of ϑ. Figure 1(a) uses $v = \psi(1 - \vartheta)$, namely, the result (24) for ψ. Figure 1(b) uses Eq. (25) for v and Fig. 1(c) uses $v = p$ in Eq. (23). In Fig. 1 we have also included the MC results for the tracer diffusion coefficient. All models behave similarly as $p \rightarrow 1$. The differences between them become apparent near p_c. In particular, the percolation threshold depends on the density of particles in Fig. 1(a), an unphysical behavior. Another interesting aspect is associated with the other choices for v. The choice (25) leads to $\psi \sim (p - p_c)^2$ near p_c, while the choice $v = p$ leads to $\psi \sim p - p_c$. Our MC simulations are not sufficiently accurate near p_c to distinguish between these results.

In Tables I and II, we compare the EMA results for the three models (or choices) discussed above to results of the MC simulations. We do so for two representative values of p. In Table I the values of the tracer diffusion coefficients are displayed for several coverages and for $p = 0.6$. In Table II the simulation results and EMA values are presented for the same coverages and for $p = 0.9$. Far above p_c (Table II), the model $v = \psi$ has the best quantitative agreement with the simulation results. All the models closely coincide with each other for the lowest coverages reported. Closer to the percolation threshold (Table I) and at high coverages, we see

TABLE II. Same as Table I but for $p = 0.9$.

ϑ	Model A	Model B	Model C	Monte Carlo
0.05	0.745	0.745	0.746	0.729 ± 0.012
0.10	0.691	0.692	0.694	0.677 ± 0.006
0.20	0.586	0.589	0.593	0.548 ± 0.006
0.40	0.392	0.403	0.409	0.359 ± 0.004

TABLE III. EMA and MC results for ψ for the three-dimensional simple cubic lattice. $p = 0.4$

ϑ	Model A	Model B	Model C	Monte Carlo
0.05	0.086	0.085	0.091	0.107 ± 0.003
0.10	0.071	0.073	0.083	0.097 ± 0.001
0.20	0.042	0.052	0.068	0.079 ± 0.001
0.40	0.000	0.026	0.044	0.026 ± 0.001

again the dependence of the diffusion threshold on the particle density in the $\nu = \psi$ model. Sufficiently above the threshold this model works quite well. In all the examined cases, results based on the choice (25) are in a reasonable agreement with the MC simulations, although they consistently overestimate the value of the tracer diffusion coefficient by about 10%.

Results for the three-dimensional simple cubic lattice are given in Fig. 2 and in Tables III–V. Figure 2 presents the resulting tracer diffusion coefficients for our three choices for ν, together with the results of the MC simulations. Qualitatively, these graphs appear similar to those of the two-dimensional studies and their critical properties are like the corresponding cases of Fig. 1. The actual percolation threshold for this system is 0.2495,[5] while the EMA threshold is $\frac{1}{4}$. Sufficiently above threshold, results based on the choice $\nu = \psi(1 - \vartheta)$ are in good agreement with the simulation results. This choice is superior in this region to the other two choices, as may be inferred from Tables III, IV, and V. Closer to p_c, this choice leads to incorrect behavior of ψ which vanishes at values of p_c which unphysically depend on ϑ.

IV. DISCUSSION AND CONCLUSIONS

A particularly simple dynamic bond percolation model has been used to develop an effective medium theory of tracer diffusion rates for systems of interacting particles on disordered lattices. The dynamic aspect arise not from the motion of the host matrix (as is true in, say, polymers above their glass transition temperature) but from motion of the particles themselves. When appropriate models are used, relating the diffusion rate of the background particles (thus the time scale for the lattice evolution as observed by the tracer particle) to the chemical diffusion rate, good agreement with the results of MC simulations is achieved far enough from the percolation threshold. Furthermore, mean field approaches are increasingly accurate as dimension is increased. In the present study, an EMA has been formulat-

FIG. 2. Same as Fig. 1, for a $3d$ simple cubic lattice. The four MC results are for $p = 0.4$, 0.6, 0.8, and 0.9. The coverages and the line notations are as in Fig. 1. Effective hopping rate ψ calculated according to Eq. (25) for the three.

TABLE IV. Same as Table III but for $P = 0.6$.

ϑ	Model A	Model B	Model C	Monte Carlo
0.05	0.371	0.370	0.372	0.371 ± 0.004
0.10	0.341	0.341	0.345	0.338 ± 0.002
0.20	0.282	0.286	0.293	0.286 ± 0.001
0.40	0.162	0.188	0.190	0.153 ± 0.001

TABLE V. Same as Table III but for $P = 0.9$.

ϑ	Model A	Model B	Model C	Monte Carlo
0.05	0.798	0.797	0.798	0.795 ± 0.013
0.10	0.746	0.746	0.746	0.741 ± 0.006
0.20	0.642	0.644	0.645	0.636 ± 0.004
0.40	0.432	0.453	0.455	0.404 ± 0.001

ingly accurate as dimension is increased. In the present study, an EMA has been formulated for tracer diffusion, incorporating a mean field treatment of the distribution of the background particles. As expected, the results are better in three dimensions as compared to those in two dimensions.

Correlations among different bonds were ignored in the present work. Such correlation necessarily exists: First, particle occupation of a site implies that all bonds leading to that site are blocked. Such static correlations were neglected by treating the system as a dynamic single bond problem and not as a dynamic site percolation problem. Furthermore, dynamic correlations exist: As a particle moves from one site to another, it simultaneously blocks some bonds and unblocks others. Such correlations can be taken into account within the present formalism,[10] which will improve to some extent the results obtained here. The main limitations remain however those imposed by using the effective medium approximation.

The present work has focussed on occupation exclusion interaction (no more then one particle at a site). Such models are useful for some alloys and for vacancy diffusion in highly defective solids. The main challenge in such applications is the incorporation of more realistic interparticle interactions into the formulation. This can be achieved by incorporating extended mean field methods (e.g., the quasichemical approximation) into the dynamic percolation formalism. We are currently proceeding in this direction.

ACKNOWLEDGMENTS

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[15] $G_{ij}(\epsilon)$ are solutions of

$$(Z + \epsilon)G_{ij} - \sum_{k \in \{i\}} G_{kj} = -\delta_{ij},$$

where $\{i\}$ is the set of nearest neighbors to i and where Z is the number of these neighbors.