

# Dynamic percolation theory for diffusion of interacting particles

Rony Granek and Abraham Nitzan

School of Chemistry, Sackler Faculty of Science, Tel-Aviv University, Tel-Aviv 69978, Israel

(Received 27 June 1989; accepted 8 September 1989)

The recently developed dynamic percolation theory is used to solve the problem of diffusion of interacting particles in lattice-gas models within an effective medium approximation. The approach is based on the observation that the motion of a tracer particle in a system of (similar or different) particles can be viewed as particle motion in a changing random environment. This makes it possible to use effective medium theory (EMT) solutions to the latter problem. The main conceptual problem of this approach is to relate the characteristic microscopic times for the evolution of the disordered background to the macroscopic diffusion. We discuss and compare several possible ansatzs for this relation and conclude that relating these times to the chemical diffusion rate is the most reasonable simple choice. Using this ansatz, we obtain EMT approximations for the tracer diffusion coefficient in the noninteracting lattice-gas (NILG, blocking interactions only) model and an approximate EMT relation between the chemical and the tracer diffusion coefficients in a lattice gas with nearest-neighbor interactions. Agreement with available simulation results is good whenever single bond EMT is expected to be reliable.

## I. INTRODUCTION

There is an ongoing interest in the study of diffusion and conductivity in systems of interacting classical particles.<sup>1-19</sup> Adsorbate diffusion on surfaces,<sup>1,5-9</sup> ionic diffusion and conduction in solid ionic conductors,<sup>2,10,11</sup> impurities and defects migration in solids,<sup>3</sup> and electron/hole mobilities in semiconductors<sup>4</sup> are some examples of solid state transport phenomena where interaction between mobile particles may strongly affect the motion. Measurements in such systems yield directly or indirectly the tracer or the chemical diffusion coefficients and, for charged particles—mobilities, conductivities, and transfer numbers.

Most theoretical studies of such systems are based on noninteracting lattice-gas (NILG) models where only site blocking is taken into account,<sup>12-14, 15(a)-15(b)</sup> or for interactions of longer range, on mean-field approximations.<sup>15(c)</sup> Several attempts to improve upon the mean-field approach for specific models have been described.<sup>5, 9, 16(b), 17</sup> Alternatively, numerical simulations for diffusion in interacting particle systems with nearest-neighbor (NN) and next nearest-neighbor interactions have been performed by several workers.<sup>7, 15, 16, 18</sup>

In this paper we examine the applicability of the recently developed dynamic bond percolation (DBP) theory<sup>20-33</sup> to this problem. The DBP theory was originally designed to calculate the effective diffusion coefficient of a single random walker in a dynamically changing neighborhood. In the model developed by Druger, Ratner, and Nitzan,<sup>20-27</sup> the whole network is "renewed" with a given waiting time distribution, while in the model of Harrison and Zwanzig<sup>28</sup> (HZ, recently extended by us<sup>29</sup>) the fluctuations within single bonds, or bond clusters, are considered. The simplest versions of both theories give identical results for the diffusion rate. The HZ formalism, which is cast in the framework of effective medium theory (EMT), is more easily adapted to our present application and we use it here. The use of dynamic percolation theory to describe diffusion of particles with hard core interactions was recently studied also by Hilfer

and Orbach.<sup>33(b)</sup> Their approach is different from ours and does not involve the connection between the fluctuation time and the chemical diffusion coefficient that is explored in the present work.

The application of the HZ theory to the problem of diffusion of interacting particles is based on the idea that a diffusing tracer particle sees a time-dependent environment due to its interactions with the other moving particles. In the next section, we discuss this analogy in detail for the NILG model (blocking interactions only) and show that this application of the HZ theory yields a simple, but reasonably good approximation to the tracer diffusion rate, especially in the low particle concentration regime where EMT is known to work well. In Sec. III, we use the same formalism to obtain a relation between the tracer and the chemical diffusion coefficients for interacting lattice gases (ILG). The results of this calculation compare well with numerical simulations in systems with nearest-neighbor interactions under circumstances where the resulting ratio between the tracer and the chemical diffusion coefficients is smaller than one. We discuss our results and possible other applications in Sec. IV.

## II. NONINTERACTING LATTICE GAS

The dynamics of a tracer particle  $i$  in the NILG model is described by the master equation

$$\frac{d}{dt} P(il, t) = \Gamma \sum_{l' \in \{l\}} [P(il', \bar{l}, t) - P(il, \bar{l}', t)], \quad (1)$$

where  $\{l\}$  denotes the group of sites nearest neighbors to  $l$ ,  $\Gamma$  is the "bare" hopping rate,  $P(il, t)$  is the probability that particle  $i$  is at site  $l$  at time  $t$ , and  $P(il, \bar{l}', t)$  is the joint probability that at time  $t$  particle  $i$  is at site  $l$  and site  $l'$  is vacant. In the mean-field approximation (MFA)

$$P^{\text{MF}}(il, \bar{l}', t) = (1 - c)P(il, t), \quad (2)$$

where  $c$  is the average site occupation probability. This leads to the mean-field (MF) tracer diffusion coefficient (with  $a$  being the lattice constant)

$$D_i^{\text{MF}} = (1 - c)\Gamma a^2. \quad (3)$$

The exact tracer diffusion coefficient is written as a product of  $D_i^{\text{MF}}$  and a correlation factor  $f(c)$ :

$$D_i = D_i^{\text{MF}} f(c). \quad (4)$$

The dynamics of the local density in the NILG is associated with the master equation<sup>15(a)</sup>

$$\frac{d}{dt} P(l, t) = \Gamma \sum_{l' \in \langle l \rangle} [P(l', \bar{l}, t) - P(l, \bar{l}', t)], \quad (5)$$

where  $P(l, t)$  is the probability to find a particle at site  $l$  at time  $t$  and  $P(l, \bar{l}', t)$  is the joint probability to find a particle at site  $l$  and a vacancy at site  $l'$ . It is easy to show that Eq. (5) is equivalent to the single particle master equation<sup>15(a)</sup>

$$\frac{d}{dt} P(l, t) = \Gamma \sum_{l' \in \langle l \rangle} [P(l', t) - P(l, t)] \quad (6)$$

and therefore one obtains the well-known result for the chemical diffusion coefficient of the NILG

$$D_c = \Gamma a^2 \quad (7)$$

independent of the particle concentration  $c$ .

The HZ treatment<sup>28</sup> of the DBP theory assumes that each bond in the disordered network fluctuates with a characteristic rate  $\tau^{-1}$  between two states: open (available for transfer) and closed (unavailable), independent of all other bonds. If  $p$  and  $q = 1 - p$  are the equilibrium probabilities for a bond to be open and closed, respectively, the probabilities  $f(1, t)$  (bond open) and  $f(0, t)$  (bond closed) evolve according to

$$\frac{\partial}{\partial t} \begin{pmatrix} f(0, t) \\ f(1, t) \end{pmatrix} = \frac{1}{\tau} \begin{pmatrix} -p & q \\ p & -q \end{pmatrix} \begin{pmatrix} f(0, t) \\ f(1, t) \end{pmatrix}. \quad (8)$$

Using effective medium theory (EMT) for this model results in the following self-consistent equation for the effective hopping rate  $\psi$ :

$$\psi(\omega) = \Gamma \frac{p - p_c + p_c \epsilon g(\epsilon)}{1 - p_c + p_c \epsilon g(\epsilon)}, \quad (9)$$

where

$$\epsilon = (i\omega + \tau^{-1})/\psi(\omega), \quad (10)$$

$$p_c = 2/z \quad (11)$$

with  $z$  being the lattice coordination number ( $p_c$  is the EMT percolation threshold) and where  $g(\epsilon)$  is the lattice Green's function at the origin (see Appendix A)

$$g(\epsilon) = G_{ii}(\epsilon) \quad (12a)$$

with  $G_{ij}$  being the solutions of

$$(z + \epsilon)G_{ik} - \sum_{j \in \langle i \rangle} G_{jk} = \delta_{ik} \quad (12b)$$

$$\psi = \Gamma \left[ 1 - \frac{c}{1 - p_c + p_c [(z-1)/(1-c)] g[(z-1)/(1-c)]} \right]. \quad (16)$$

(iii) In contrast to the previous two choices where  $\tau$  was determined by the dynamics of a tracer particle, one may argue that  $\tau$  should be identified with the relaxation time for

(explicit expressions for simple lattices are given in Refs. 34 and 35).

Using this result for tracer diffusion in systems of diffusing interacting particles is made possible by assuming that the bond renewal rate  $\tau^{-1}$  is associated with blocking and unblocking of the tracer particle due to diffusion of the background particles. This assumption involves three approximations: (i) we use a bond renewal model for what is actually a site renewal dynamics; (ii) we neglect correlations between occupying-deoccupying events on neighboring sites; and (iii) we disregard the difference between the dynamics of the NN sites which is dominated by  $z - 1$  neighbors (the tracer site is not counted) and the dynamics of the other sites which is dominated by the availability of  $z$  neighbors. These approximations lead to a single bond dynamics and are therefore consistent with the use of a single bond EMT.

In order to use Eqs. (9)–(12) to find the effective hopping rate  $\psi$  and therefore the associated tracer diffusion coefficient, we need an explicit expression for  $\tau$ . Three possible choices come to mind:

(i) Make a mean-field approximation for the background particles dynamics. Focusing on a particular background particle in a NN site to the tracer, the total MF jump rate out of this site is  $(z - 1)(1 - c)\Gamma$ , where  $c$  is the site occupation probability and where  $z - 1$  (rather than  $z$ ) appears because the tracer site is excluded. Comparing with Eq. (8), noting that  $p = 1 - c$  and  $q = c$ , we get

$$\tau = [(z - 1)\Gamma]^{-1}. \quad (13)$$

We thus use the MFA to get a correction to this approximation. Equation (9) becomes

$$\psi(\omega) = \Gamma \left[ 1 - \frac{c}{1 - p_c + p_c \epsilon g(\epsilon)} \right]; \quad (14)$$

$$\epsilon = \frac{i\omega + (z - 1)\Gamma}{\psi(\omega)}.$$

(ii) Assume an effective medium hopping rate  $\psi$  for the background particles. Under this assumption  $(1 - c)\tau^{-1} = (z - 1)\psi$ , or

$$\tau = \left[ \frac{(z - 1)\psi}{1 - c} \right]^{-1}. \quad (15)$$

Note that with this choice, the DC ( $\omega = 0$ ) value of  $\epsilon$  [Eq. (10)] becomes independent of  $\psi$  so that Eq. (9) provides an explicit solution for  $\psi$ :

*density fluctuations* in sites NN to the tracer particle and is therefore related to the chemical diffusion coefficient. For the NILG case, the relevant master equation is Eq. (6). If we

focus on a particular site  $l$  and use the MFA for all other sites [whereas  $P(l', t) = c$  for all  $l' \neq l$ ], we get

$$\frac{d}{dt} P(l, t) = \Gamma z c - \Gamma z P(l, t). \quad (17)$$

However, for a NN site to our tracer particle, hopping to the tracer site is forbidden and  $z$  in Eq. (17) should be replaced by  $z - 1$ . Finally, identifying  $P(l, t)$  with  $f(0, t)$  of Eq. (8), we find that

$$\tau = [(z - 1)\Gamma]^{-1} \quad (18)$$

which is identical to the result of choice (i).

We now discuss the results obtained from the two choices, Eqs. (13) [or Eq. (18)] and (15). First consider the choice Eq. (13), implying Eq. (14) for  $\psi$ . Equation (14) may be solved numerically, however, an explicit asymptotic expression may be derived for  $\epsilon \rightarrow \infty$ . This limit may be realized in several ways, e.g.,  $\omega \rightarrow \infty$ ,  $z \rightarrow \infty$ , or the small vacancy limit  $c \rightarrow 1$  where  $\psi \rightarrow 0$ . In this limit,  $g(\epsilon) \simeq (z + \epsilon)^{-1} + o(\epsilon^{-3})$  (see Appendix A) and Eq. (14) leads to

$$\psi = \Gamma \frac{1 - c}{1 + (2c/\eta)}, \quad (19)$$

where  $\eta = \epsilon\psi/\Gamma$  is dependent of  $\psi$ , and we have also used Eq. (10). With  $\epsilon$  of Eq. (14) this becomes

$$\psi(\omega) = \frac{1 - c}{1 + [2\Gamma c / (i\omega + (z - 1)\Gamma)]} \Gamma. \quad (20)$$

For  $\omega \rightarrow \infty$  or  $z \rightarrow \infty$ , we get, as expected, the mean-field result  $\psi = \Gamma(1 - c)$ . For  $\omega = 0$  Eq. (20) becomes

$$\psi = \frac{z - 1}{z - 1 + 2c} (1 - c)\Gamma. \quad (21)$$

Noting that the tracer diffusion constant is  $D_t = \psi a^2$  and using Eqs. (3) and (4), the correlation factor  $f(c)$  [Eq. (4)] is obtained in this approximation and in this limit as

$$f(c) = (z - 1)/(z - 1 + 2c) \quad (22)$$

and in the particular case of the small vacancy limit ( $c \rightarrow 1$ )

$$f(c \rightarrow 1) = (z - 1)/(z + 1). \quad (23)$$

These results can be generalized to the case where the tracer B has a bare jump rate  $\Gamma_B$  different from the bare jump rate  $\Gamma_A$  of the background particles A. In this case  $\tau = [(z - 1)\Gamma_A]^{-1}$  and Eq. (14) is replaced by

$$\psi_B = \Gamma_B \left[ 1 - \frac{c_A}{1 - p_c + p_c \epsilon g(\epsilon)} \right]; \quad (24)$$

$$\epsilon = \frac{i\omega + (z - 1)\Gamma_A}{\psi_B}.$$

In this case, the large  $\epsilon$  limit may also correspond to fast moving background particles  $\Gamma_A \gg \Gamma_B$ . Using, for this limit, Eq. (19) leads to

$$\psi_B \simeq \frac{1 - c}{1 + [2c\Gamma_B / (i\omega + (z - 1)\Gamma_A)]} \Gamma_B. \quad (25)$$

In the DC ( $\omega = 0$ ) and low vacancy concentration ( $c \rightarrow 1$ ) limits, this yields (with  $\gamma = \Gamma_B/\Gamma_A$ )

$$\psi_B = \frac{z - 1}{z - 1 + 2\gamma} (1 - c)\Gamma_B, \quad (26)$$

whereas the correlation factor  $f(\gamma) = f(c \rightarrow 1, \gamma)$  becomes

$$f(\gamma) = (z - 1)/(z - 1 + 2\gamma). \quad (27)$$

Note that Eq. (23) is a special case of this result with  $\gamma = 1$ .

A check on the approximate validity of this result is provided by using the following well known approximation for the correlation factor  $f$ <sup>36,37</sup>

$$f = \frac{1 + \langle \cos \theta \rangle}{1 - \langle \cos \theta \rangle}, \quad (28)$$

where  $\theta$  is the angle between two consecutive jumps of the tracer particle. This approximation results from neglecting correlations between nonconsecutive jumps. In the small vacancy concentration limit where this approximation becomes exact, Maning has shown that  $\langle \cos \theta \rangle$  takes the form<sup>12</sup>

$$\langle \cos \theta \rangle = - \frac{\Gamma_B}{\Gamma_B + \Gamma_A \sum_i F_i}, \quad (29)$$

where  $\sum_i$  is a sum over all the NN sites to the A atom, itself a NN to the tracer atom B (so  $\sum_i$  goes over  $z - 1$  sites). The  $F_i$  are reduction factors associated with the fact that a vacancy, interchanging with an A atom, has a larger than statistical probability to return to its original position, and then induce a backward jump of the tracer. If this effect is neglected (in the spirit of the MFA) all the  $F_i$  factors are equal to one and

$$\langle \cos \theta \rangle = - \frac{\Gamma_B}{\Gamma_B + (z - 1)\Gamma_A} = - \frac{\gamma}{\gamma + z - 1}. \quad (30)$$

Using Eq. (30) in Eq. (28) yields again Eq. (27). It is interesting to note that Kickuchi<sup>17(a)</sup> has obtained the same result using the path probability method in the pair approximation.

Finally we note that another consequence of Eq. (29) (based on the observation that  $\sum_i F_i$  does not depend on  $\gamma$ ) is the relation

$$f(\gamma) = \frac{f}{f + (1 - f)\gamma}, \quad (31)$$

where  $f = f(\gamma = 1)$ . This is easily seen to be satisfied by the result (27).

Next consider the choice (15) for  $\tau$ , implying Eq. (16) for  $\psi$  in the DC limit. In the small vacancy concentration limit, Eq. (16) yields

$$\psi = \frac{z - 3}{z - 1} (1 - c)\Gamma \quad (32)$$

implying

$$f = z - 3/z - 1. \quad (33)$$

This obviously fails for the one-dimensional case where  $z = 2$ .

In Figs. 1–3 we show some results of our approximation on an fcc lattice ( $z = 12$ ) compared to numerical simulations of Kehr, Kutner, and Binder.<sup>15</sup> To solve Eqs. (14) and (16), we use a simple form for  $g(\epsilon)$  of the fcc lattice<sup>35</sup>

$$g(\epsilon) = \frac{1}{4} F(3 + \epsilon/4), \quad (34a)$$

where

$$F(u) = (4/\pi^2)(u + 1)^{-1} K(k_+) K(k_-) \quad (34b)$$

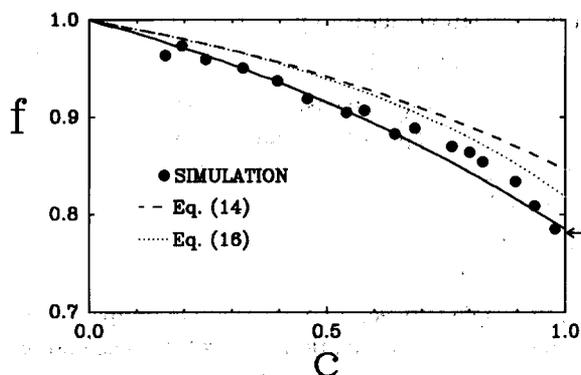


FIG. 1. Correlation factor  $f$  plotted against concentration  $c$  for tracer self-diffusion in a NILG system on fcc lattice ( $z=12$ ). The dashed and the dotted lines are numerical solutions to Eqs. (14) (with  $\omega=0$ ) and (16), respectively. The simulation results are from Ref. 15(b). The full line is the theory of Sankey and Fedders (Ref. 13). The arrow denotes the exact result for  $c \rightarrow 1$  (Ref. 36).

with

$$k_{\pm}^2 = (u+1)^{-2} \left[ \frac{1}{16} \{ (u+1)^{1/2} - (u-3)^{1/2} \}^4 + \{ (u+1)^{1/2} \pm u^{1/2} \}^2 \right], \quad u > 3 \quad (34c)$$

and where  $K(k)$  is the complete elliptic integral of the first kind

$$K(k) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \theta}}. \quad (34d)$$

Figure 1 shows the correlation factor  $f = [\Gamma(1-c)]^{-1} \psi$  for self-diffusion as a function of particle density  $c$ . The full line is the theoretical result of Sankey and Fedders<sup>13</sup> (based on diagrammatic methods). The dashed line is our result based on Eq. (14) and the dotted line is our result based on Eq. (16). The simulation results are taken from Ref. 15(b).

In Figs. 2 and 3 we show the correlation factor  $f$  for a tracer particle  $B$  in a background of  $A$  particles, as a function of  $\gamma = \Gamma_B/\Gamma_A$ . Equation (24) with  $f_B = [\Gamma_B(1-c_A)]^{-1} \psi_B$  and  $\omega=0$  is used to generate the theoretical lines. The simulation results are taken from Ref. 15(e).

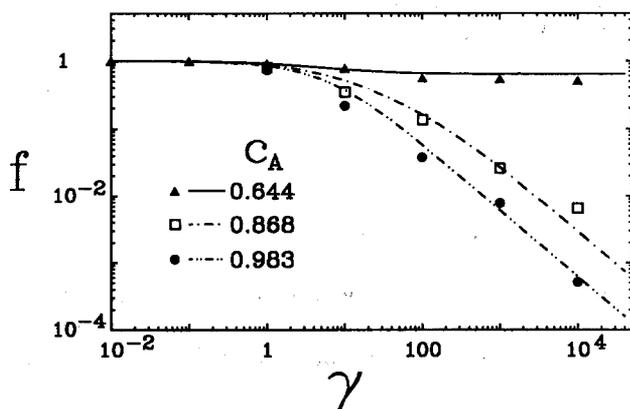


FIG. 2. Correlation factor  $f$  plotted against the ratio  $\gamma$  of the tracer ( $B$ ) to background particles ( $A$ ) jump rates for different concentration  $c_A$  of background particles. The symbols are simulation results from Ref. 15(e). The lines are numerical solutions to Eq. (24) with  $\omega=0$ .

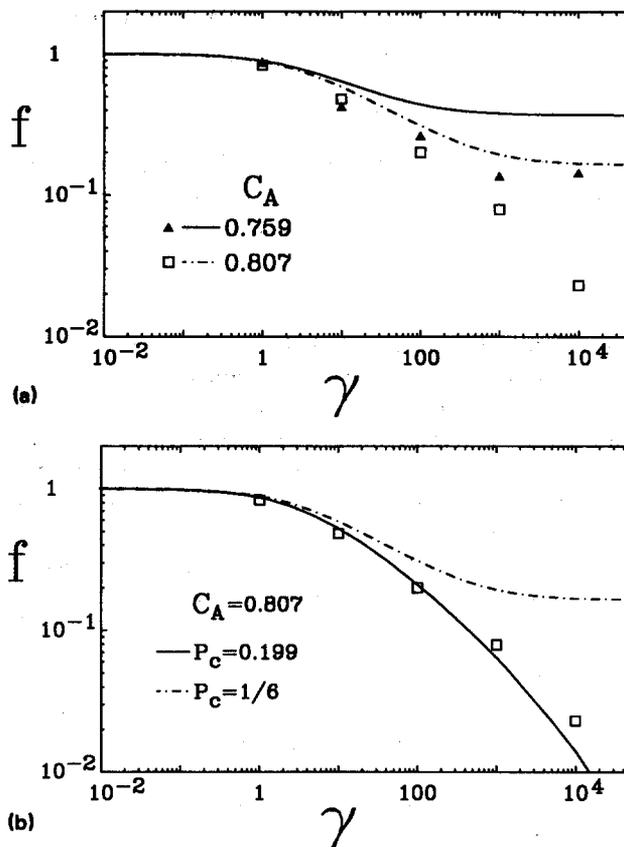


FIG. 3. The same as Fig. 2 for concentrations  $c_A$  near the percolation threshold  $c_A = 5/6 \approx 0.801$ . (a) Comparison of two concentrations near the threshold concentration. (b) Comparison between the solution to Eq. (24) using the EMA percolation threshold  $p_c = 1/6$  (dashed line) and the solution to the same equation using the exact threshold  $p_c = 0.199$  (full line).

It is seen from Figs. 1 and 2 that there is a good agreement between our simple theoretical approximation and the simulation results for the NILG both for the self-diffusion problem (Fig. 1) and for the mixed tracer diffusion problem (Figs. 2 and 3) provided that the background particle density  $c_A$  is not close to the percolation threshold. Figure 3(a) demonstrates our primary source of error close to the percolation threshold: the EMA percolation threshold is  $p_c = 1/6$  (implying the threshold value  $5/6$  for  $c_A$ ) while the exact threshold for an fcc<sup>15(e)</sup> is  $p_c = 0.199$ . Hence, e.g.,  $c_A = 0.807$ , the approximate  $f$  remains finite when  $\gamma \rightarrow \infty$  while the exact  $f$  vanishes in this limit. If we replace in Eq. (24)  $p_c$  by 0.199 rather than  $1/6$ , a substantial improvement of the results is obtained [Fig. 3(b)].

In Table I we compare the results (23) and (33) to the exact result of the correlation factor in the vanishingly small vacancy concentration limit ( $c \rightarrow 1$ ) for different lattices.<sup>32</sup> Both approximations agree with the exact trend and become better for larger coordination number  $z$  as expected from MFA and EMA considerations.

As noted before, the simplest version of our theory neglects both static and dynamical correlations: static correlations are neglected because we use bond percolation results for what is really a site percolation problem; dynamical correlations are neglected between occupying-deoccupying events on neighboring sites. A way to partially incorporate

TABLE I. The correlation factor  $f$  in the small vacancy concentration limit ( $c \rightarrow 1$ ).

$d$	Type	$z$	$f^a$	$f^b$	$f^c$
1		2	0.333		0.000
2	Hexagonal	3	0.500	0.000	0.333
2	Square	4	0.600	0.333	0.467
2	Triangular	6	0.714	0.600	0.560
3	SC	6	0.714	0.600	0.653
3	bcc	8	0.777	0.714	0.727
3	fcc	12	0.846	0.818	0.781

<sup>a</sup> From Eq. (23).

<sup>b</sup> From Eq. (33).

<sup>c</sup> Exact results from Ref. 36.

these correlations is to use the many bond EMT. A many bond EMT solution of the dynamic percolation problem was recently formulated by us<sup>29</sup> and solved explicitly for a two bond exchange model with two perpendicular bonds having a common site, in a two-dimensional square lattice. This model has two rate parameters, renewal and exchange, denoted by  $\tau^{-1}$  and  $\theta^{-1}$ , respectively. Applying this formalism to the NILG (see Appendix B), we find these parameters to be approximately  $\tau^{-1} = (5/2)\Gamma_A$  and  $\theta^{-1} = \Gamma_A/4$ . In Fig. 4 we compare the resulting self-diffusion correlation factor [using Eq. (B9) with  $\omega = 0$  and  $\Gamma_A = \Gamma_B = \Gamma$ ] with the results from Eq. (14) (with  $z = 4$ , i.e.,  $\tau^{-1} = 3\Gamma$  in the HZ model), with the theory of Nakazato and Kitahara<sup>14</sup> and with numerical simulations.<sup>15(f)</sup> Also shown is the exact result for  $c \rightarrow 1$ .<sup>36</sup> It is seen that the use of the two bond exchange model slightly improves the results as compared with the simulation results and the exact  $c \rightarrow 1$  value. The theory of Nakazato and Kitahara<sup>14</sup> is seen to agree rather well with the simulations for this case where  $\gamma = \Gamma_B/\Gamma_A = 1$ . However, we note that this theory, although formulated for arbitrary jump ratio  $\gamma$ , does not lead to a percolation threshold for  $\gamma \rightarrow \infty$ . A better way to account for dynamical correlations on a square lattice is obviously to use a four bond exchange model (still with two rate parameters, renewal rate,

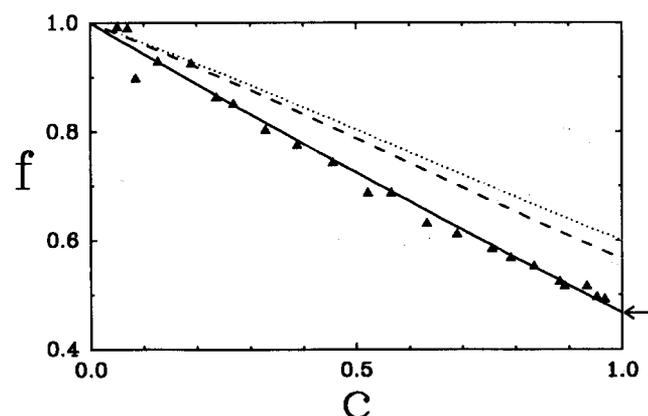


FIG. 4. Correlation factor  $f$  plotted against the concentration  $c$  for tracer self-diffusion in a NILG system on a square lattice ( $z = 4$ ). The dotted line is the solution to Eq. (14). The dashed line is the result of the two bond exchange model, [Eqs. (B8)–(B13)]. The full line is the theory of Nakazato and Kitahara (Ref. 14). The simulation results are from Ref. 15(f). The arrow denotes the exact value for  $c \rightarrow 1$  (Ref. 36).

and exchange rate between perpendicular bonds), or for a general lattice, a “z” bond exchange model. In the rest of this work we shall continue to use the HZ model.

To conclude this section we comment on the suitability of the different choices (i), (ii), or (iii) made above for  $\tau$ . For the NILG model choices (i) and (iii) lead to the same final result, but this is no longer so when other than blocking interactions are considered. It is seen from Fig. 1 and Table I that choice (ii), which postulates that  $\tau$  is determined by the effective medium hopping rate, works somewhat better than the other choice (i/iii). On the other hand, the association of  $\tau$  with  $D_c$  that leads to choice (i/iii) is physically more appealing because  $D_c$  is directly related to the density fluctuations of the background particles. In fact, none of these choices is entirely satisfactory because  $\tau$  reflects a local behavior while both  $D_c$  and  $D_l$  are global quantities. (For the simple NILG model, however,  $D_c$  also controls local dynamics). Thus, for particles moving on a disordered network (static disorder), both the DC ( $\omega = 0$ ) limits of  $D_l$  and  $D_c$  vanish at the percolation threshold, however, the local population fluctuations should remain finite. Moreover, the exact (disorder averaged) local density dynamics is expected to be non-Markovian.

This observation suggests that perhaps a better choice for  $\tau$  (with the Markovian ansatz) may be obtained by relating it to the frequency-dependent chemical diffusion coefficient at finite  $\omega$ , where a reasonable frequency scale is  $\omega \sim \Gamma$ , the bare hopping rate. (For the NILG model used above this will not change our results since  $D_c$  is frequency independent.) In this work, however, we limit ourselves to estimating  $\tau$  from the DC ( $\omega = 0$ ) chemical diffusion coefficient. In the next section we use this same approach for the interacting lattice gas (ILG) model.

### III. INTERACTING LATTICE GAS

We now consider an interacting lattice gas (ILG). We again consider a tracer particle  $B$  moving on a lattice and interacting with a background of particles  $A$ . The tracer diffusion coefficient is conventionally written in the form

$$D_{B/A} = a^2 W_{B/A} V_{B/A} f_{B/A}, \quad (35)$$

where  $W$  is the averaged effective jump rate of the  $B$  particle (i.e., averaged number of jump attempts per unit time to a neighboring site when this site is restricted to be vacant),  $V$  is the averaged vacancy availability factor (i.e., the equilibrium probability to find a vacancy NN to a particle), and  $f$  is the correlation factor correcting the result of random walk for the effects of correlations between subsequent jumps. The subscript  $B/A$  denotes that we focus on a particle  $B$  moving in an  $A$  background. In the NILG case  $V = 1 - c_A$  and  $W = \Gamma_B$ . In the present situation both vacancy availability and effective jump rate depend on the interparticle interactions and can be approximately obtained from configurational averaging of these quantities over an ensemble of configurations about the tracer particle. In simulations  $WV$  may be obtained as the mean number of performed jumps of the tracer particle per unit time.

To apply dynamic percolation theory to the ILG, we assume that in analogy to the NILG case [Eq. (24)] we may now write (for  $\omega = 0$ )

$$(Vf)_{B/A} \approx 1 - \frac{c_A}{1 - p_c + p_c \epsilon g(\epsilon)}, \quad (36a)$$

$$\epsilon = \frac{\tau^{-1}}{W_{B/A} (Vf)_{B/A}}, \quad \tau^{-1} = (z-1) D_{cA} / a^2, \quad (36b)$$

or

$$D_{iB/A} \approx a^2 W_{B/A} \left( 1 - \frac{c_A}{1 - p_c + p_c \epsilon g(\epsilon)} \right), \quad (37a)$$

$$\epsilon = (z-1) \frac{D_{cA}}{D_{iB/A}}. \quad (37b)$$

Equations (37a and 37b) give the  $B/A$  ( $B$  in  $A$  background) tracer diffusion coefficient in terms of the chemical diffusion coefficient of  $A$  and the effective  $B/A$  jump rate  $W_{B/A}$ . An approximation for  $W_{B/A}$  may be easily obtained within the quasichemical approximation<sup>5,9,16(b),38</sup> (QCA) by averaging the (configuration-dependent) jump rate of  $B$  over an equilibrium ensemble of configurations of  $A$  around it and around the vacant site towards which it is hopping (see Appendix C). Thus Eqs. (37a and 37b) provide a relation between  $D_{iB/A}$  and  $D_{cA}$  or when  $B$  and  $A$  are identical, between the tracer and the chemical self-diffusion coefficients. For the latter we may use the MFA result<sup>15(c)</sup>

$$D_c = a^2 \Gamma \left[ 1 - 4c(1-c) \frac{T_c}{T} \right], \quad (38)$$

where

$$k_B T_c = \sum_{j \neq m} J_{mj}; \quad J_{mj} = v_{mj} / 4 \quad (39)$$

with  $v_{mj}$  being the interaction energy between particles at sites  $m$  and  $j$  ( $v_{mj} > 0$  for attractive interactions).<sup>39</sup>

To test the applicability of these results, we have used Eq. (38) for the chemical diffusion coefficient together with the simulation results of Kutner *et al.*<sup>15(c)</sup> for the effective jump rate  $W$  in order to evaluate the tracer self-diffusion coefficient ( $\gamma = \Gamma_B / \Gamma_A = 1$ ) in a fcc lattice with NN attractive interactions. Figure 5 shows the tracer self-diffusion coefficient (in units of  $\Gamma a^2$ ) as a function of concentration

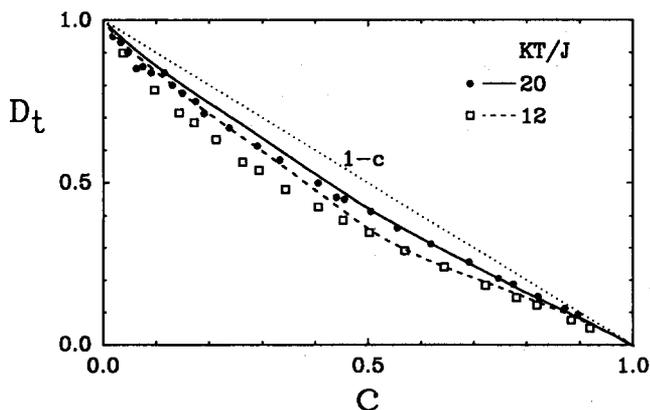


FIG. 5. Tracer self-diffusion coefficient  $D_t$  (in units of  $\Gamma a^2$ ) as a function of the concentration  $c$  for an ILG-fcc system, for two interaction parameters  $kT/J = 20$  and 12. The lines are numerical solutions to Eq. (37) using Eq. (38) for  $D_c$  and the simulation results for  $W$  taken from Ref. 15(c) [shown in Figs. 6(a) and 6(b)]. The symbols are simulation results of Ref. 15(c). The dotted line is the mean-field result  $D_t/\Gamma a^2 = 1 - c$ .

for NN interaction parameters  $k_B T/J_{NN} = 20$  and  $k_B T/J_{NN} = 12$ . Shown are the results obtained from the simulations of Kutner *et al.*<sup>15(c)</sup> and from solving Eqs. (37a) and (37b) using Eq. (38) for  $D_c$  and the numerical simulation results for  $W$ . Also shown is the high temperature limit  $D_t/\Gamma a^2 = 1 - c$ . We note again that  $W$  can also be obtained from configurational averaging: Figs. 6(a) and 6(b) compare the results of a calculation based on the QCA (Appendix C) to the simulation results.

It is seen from Fig. 5 that a close agreement exists between the result of the present theory and the simulations for the higher temperature ( $k_B T/J_{NN} = 20$ ) while for the lower temperature  $k_B T/J_{NN} = 12$  (the MF critical temperature for phase separation) considerable deviations exist for  $c < 0.5$ . The breakdown of the theory in this range is emphasized in Fig. 7, where we show  $D_t$  from the simulation results for  $k_B T/J_{NN} = 12$  together with the result from static percolation simulation (frozen  $A$  particles,  $\gamma \rightarrow \infty$ ) using the effective jump rate  $W$  for the same temperature. The latter (which vanishes at the critical concentration  $c_A = 0.801$ ) should be a lower bound on the actual tracer diffusion rate under our assumptions, however, we see that for  $c < 0.5$  the actual rate is lower.

Several sources of error in the present calculation have been discussed above and are mainly associated with the problematics of choosing  $\tau$  (see the discussion at the end of Sec. II). Figure 7 shows another (familiar) source of error—

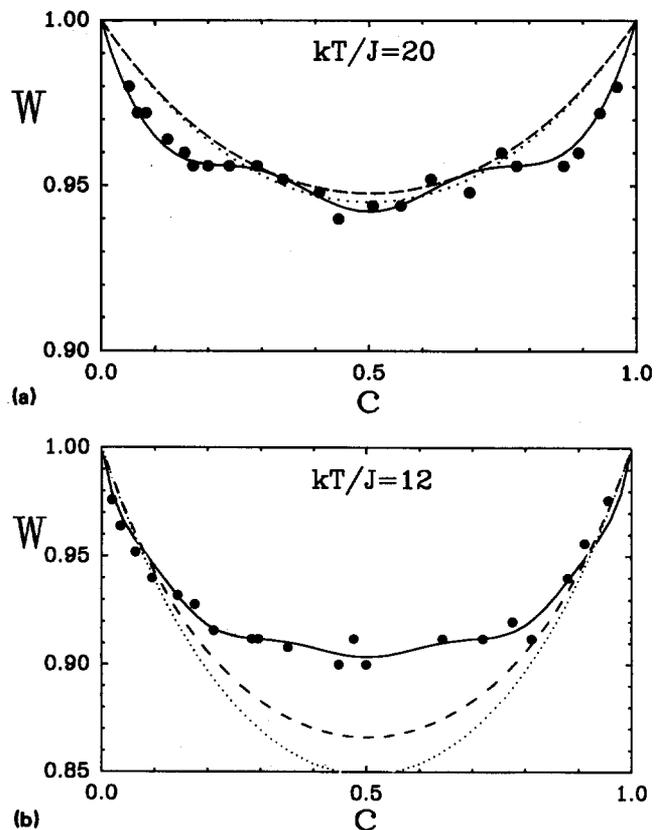


FIG. 6. Effective jump rate  $W$  in an ILG-fcc system. The dashed and the dotted lines are theoretical QCA results, (C8) and (C11), respectively. The symbols are the simulation results of Ref. 15(c) and the full line is a least-square fitting of the simulation results to a polynomial of order 5 in  $c(1-c)$ . (a)  $kT/J = 20$ ; (b)  $kT/J = 12$ .

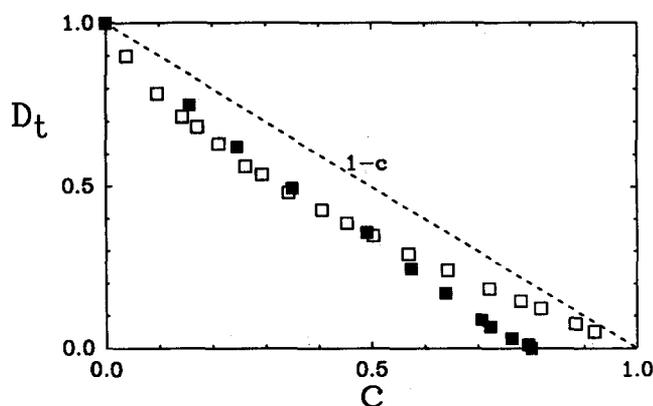


FIG. 7. Dotted line—mean-field result. Open squares—the same data as the open squares of Fig. 5:  $D_t$  (for  $kT/J = 12$ ) obtained by direct simulations in Ref. 15(c). Filled squares— $D_t$  of a single particle in a static site percolation having an effective jump rate  $W$  instead of  $\Gamma$ ; obtained by multiplying  $W$  [simulations from Ref. 15(c)—the same as the circles or the corresponding full line of Fig. 6(b)] by the simulation results [from Ref. 15(e)] for a single particle diffusion in a static disordered lattice. All results are in units of  $\Gamma a^2$ .

the use of single bond dynamics. This approximation neglects *static correlations* in the distribution of the background  $A$  particles (for the NN attractive interactions used here, it neglects the tendency of the  $A$  particles to cluster). These correlations are less important at higher temperatures, hence the much better agreement of simulation and theory at  $k_B T/J_{NN} = 20$ . Also, the effect of such correlations is expected to be larger for  $D_{iB} > D_{cA}$  because, in this case, the tracer particle explores more of these correlations, before they relax via chemical diffusion of the  $A$  background. For self-diffusion this means that the approximation should work better when  $h = D_t/D_c \ll 1$ . Figure 8 shows that there is indeed such correlation between the value of  $h$  and the success of the present theory at moderately low temperatures. The divergence of  $h$  at  $c = 0.5$  results from the vanishing of the (mean field)  $D_c$  at this concentration at the critical temperature ( $kT/J = 12$ ).

To end this section we note that we have applied here a particularly simple version of dynamic bond percolation theory, using a single bond dynamics and taking for each bond a transition rate  $W$  (the effective jump rate) or 0 according to whether the accepting site is populated or not and associating the transition rate between these two “states” with the

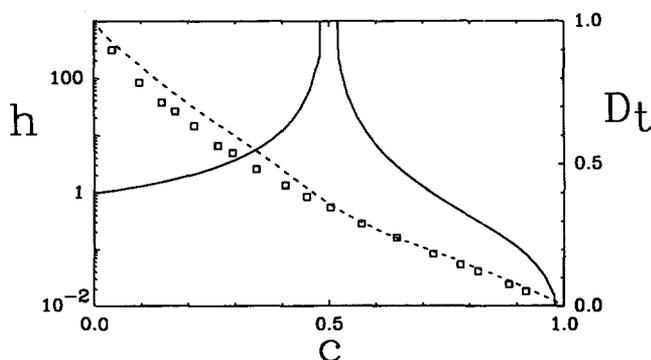


FIG. 8. Theoretical ratio  $h = D_t/D_c$  against the concentration for  $kT/J = 12$  together with the results for  $D_t$ , shown in Fig. 5.

chemical diffusion rate. A better (more complicated, but still straightforward) approach would be to associate many states (each with a different jump rate) with the bond defined by the origin and destination sites. A zero jump rate is related to occupied destination site as before; other jump rates are associated with the local microscopic environment of the two sites in question. The equilibrium probabilities for these bond states may be obtained from the quasichemical approximation. The transition rates between these states are associated with the local microscopic environmental changes and therefore may be related to the chemical diffusion coefficient (using the detailed balance conditions). Given these, the many bond states dynamic percolation theory<sup>29</sup> may be used to yield the final tracer diffusion rate. Such an approach will be explored in future work.

#### IV. CONCLUSIONS

In this paper we have developed an effective medium theory for the diffusion of interacting particles in lattice-gas models with hard core (the so-called noninteracting lattice gas) and with nearest neighbor interactions. The method is based on an approximate adaptation of the recently developed effective medium theory for dynamic bond percolation and has been shown to constitute a considerable improvement over mean-field approximations. As expected the method fails quantitatively when aggregation or phase separation begin to dominate the diffusion dynamics and also for a two component system with a large difference in jump rates, near the percolation threshold for the concentration of the slow component. A considerable improvement of our results for the latter case is achieved if we replace (artificially) in our theoretical expression [e.g., Eq. (24)], the EMT value for  $p_c$  ( $= 2/z$ , where  $z$  is the coordination number) by the actual value for  $p_c$ .

The method advanced in this paper is based on the observation that tracer diffusion in a system of interacting particles may be viewed as a motion of a tagged particle in a system characterized by a time-dependent disorder. Our main assumption involves the use of an ansatz for the characteristic fluctuation time of the disorder. Obviously, this time is associated with the diffusion of the background particles and, for practical reasons, it should be expressed either in terms of the given elementary jump rate, or in terms of the macroscopic diffusion rate. In the present paper we have taken the second route and concluded that a fluctuation time based on the chemical diffusion rate is the best choice within the present framework. For a lattice gas with hard core interactions (“noninteracting lattice gas”), this gives a complete approximate solution [by solving the self-consistent equation (14)] for the tracer diffusion coefficient, since the chemical diffusion for this problem is trivial. For longer range (e.g., nearest neighbor) interactions, this procedure yields a relation between the chemical and the tracer diffusion coefficients.

The procedure described here is approximate and can be improved both by using more accurate effective medium theories (e.g., many bond theories<sup>29</sup>) and better choices for the relation between the timescale of the dynamic disorder and

between the diffusion process. Such improvements will be considered in future work.

**ACKNOWLEDGMENTS**

This research was supported by the US–Israel Binational Science Foundation. We thank Professors M. A. Ratner, M. Silverberg, and B. Whaley for useful discussions.

**APPENDIX A: LARGE  $\epsilon$  LIMIT OF  $g(\epsilon)$**

The lattice Green’s function at the origin  $g(\epsilon)$  is related to the autocorrelation function of random walk  $P_0(t)$ , the probability to return to the origin at time  $t$ , by Laplace transform, namely

$$g(\epsilon) = \int_0^\infty dt \exp(-\epsilon t) P_0(t). \tag{A1}$$

At very short times  $P_0(t)$  is clearly given by

$$\frac{\partial}{\partial t} \begin{pmatrix} f(0,0) \\ f(1,0) \\ f(0,1) \\ f(1,1) \end{pmatrix} = \begin{pmatrix} -2p/\tau & q/\tau & q/\tau & 0 \\ p/\tau & -(1/\tau + 1/\theta) & 1/\theta & q/\tau \\ p/\tau & 1/\theta & -(1/\tau + 1/\theta) & q/\tau \\ 0 & p/\tau & p/\tau & -2q/\tau \end{pmatrix} \begin{pmatrix} f(0,0) \\ f(1,0) \\ f(0,1) \\ f(1,1) \end{pmatrix}, \tag{B1}$$

where  $f(\sigma_\alpha, \sigma_\beta) \equiv f(\sigma_\alpha, \sigma_\beta, t)$  is the joint probability that at time  $t$  bond  $\alpha$  will have the (hopping rate) value  $\sigma_\alpha$  and bond  $\beta$  will have the value  $\sigma_\beta$ , and where  $p + q = 1$ . For  $\theta^{-1} = 0$ , the evolution equation (B1) is just the independent single bond on–off switching process considered by HZ.<sup>28</sup> For  $\tau^{-1} = 0$ , this equation describes a direct exchange mechanism. From Eq. (B1) we get

$$\begin{aligned} \frac{d}{dt} [f(0,0) + f(0,1)] &= q/\tau - \tau^{-1}f(0,0) - (\tau^{-1} + \theta^{-1})f(0,1) \\ &\quad + \theta^{-1}f(1,0), \end{aligned} \tag{B2a}$$

$$\begin{aligned} \frac{d}{dt} [f(0,0) + f(1,0)] &= q/\tau - \tau^{-1}f(0,0) - (\tau^{-1} + \theta^{-1})f(1,0) \\ &\quad + \theta^{-1}f(0,1). \end{aligned} \tag{B2b}$$

In order to find the NILG parameters  $\tau^{-1}$  and  $\theta^{-1}$  for a tracer  $B$  moving in an  $A$  background, we start from the master equation for the site occupation probabilities  $P(a,t)$ ,  $P(b,t)$ , and  $P(c,t)$  for the sites  $a$ ,  $b$ , and  $c$  in Fig. 9, respectively, where the tracer is taken to sit at site  $o$  [denoting  $\alpha = (oa)$ ,  $\beta = (ob)$ ]. From Eq. (6) we have

$$\frac{d}{dt} P(a,t) = \Gamma_A \sum_{l \in \{a\}}' [P(l,t) - P(a,t)], \tag{B3a}$$

$$\frac{d}{dt} P(c,t) = \Gamma_A \sum_{l \in \{c\}} [P(l,t) - P(c,t)], \tag{B3b}$$

$$\frac{d}{dt} P(b,t) = \Gamma_A \sum_{l \in \{b\}}' [P(l,t) - P(b,t)]. \tag{B3c}$$

The tracer site  $o$  is not included in the sums in Eqs. (B3a) and (B3c). We now use the MFA for all sites other than  $a, b$ ,

$$P_0(t) \approx 1 - zt + o(t^2), \tag{A2}$$

where  $z$  is the coordination number of the lattice and where  $t$  is dimensionless (measured in units of the walker hopping time  $\Gamma^{-1}$ ). Thus, for large  $\epsilon$  ( $\epsilon \gg z$ ),  $g(\epsilon)$  is approximately

$$g(\epsilon) \approx \epsilon^{-1} - z\epsilon^{-2} + o(\epsilon^{-3}) \approx (z + \epsilon)^{-1} + o(\epsilon^{-3}) \tag{A3}$$

valid for any lattice in all dimensions.

**APPENDIX B: DYNAMICAL CORRELATIONS**

Here we use a two bond exchange model,<sup>29</sup> recently solved by us, to incorporate some of the dynamical correlations associated with the site occupation. The model assumes that the lattice is formed from distinct identical pairs of bonds and that the dynamics occurs independently within each pair and is described by<sup>29</sup>

and  $c$ , namely  $P(l,t) = c_A$  for all  $l \neq a, b, c$ . This leads to

$$\frac{d}{dt} P(a,t) = \Gamma_A [2c_A + P(c,t) - 3P(a,t)], \tag{B4a}$$

$$\frac{d}{dt} P(c,t) = \Gamma_A [2c_A + P(a,t) + P(b,t) - 4P(c,t)], \tag{B4b}$$

$$\frac{d}{dt} P(b,t) = \Gamma_A [2c_A + P(c,t) - 3P(b,t)]. \tag{B4c}$$

Eliminating  $P(c,t)$  from Eqs. (B4a), and (B4c), in or-

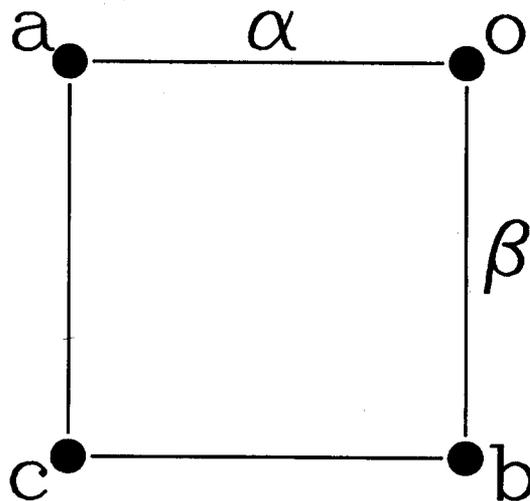


FIG. 9: Sites and bond labels for a specific connected pair (bonds  $\alpha$  and  $\beta$ ) in the two bond exchange model (Appendix B).

der to arrive to an independent two bond description, will generally lead to a non-Markovian dynamics. A Markovian approximation can be obtained by making a steady-state assumption for Eq. (B4b),  $d/dt P(c,t) \simeq 0$ , to obtain

$$P(c,t) \simeq \frac{1}{2} c_A + \frac{1}{4} (P(a,t) + P(b,t)), \quad (\text{B5})$$

which, inserting in Eqs. (B4a) and (B4c), leads to

$$\frac{d}{dt} P(a,t) = \Gamma_A \left[ \frac{1}{2} c_A + \frac{1}{4} P(b,t) - \frac{1}{4} P(a,t) \right], \quad (\text{B6a})$$

$$\frac{d}{dt} P(b,t) = \Gamma_A \left[ \frac{1}{2} c_A + \frac{1}{4} P(a,t) - \frac{1}{4} P(b,t) \right]. \quad (\text{B6b})$$

Finally, identifying  $c_A = q$  and

$$P(a) = f(0,0) + f(0,1), \quad (\text{B7a})$$

$$P(b) = f(0,0) + f(1,0) \quad (\text{B7b})$$

and comparing with Eq. (B2) we find

$$\tau^{-1} = \frac{1}{2} \Gamma_A; \quad \theta^{-1} = \frac{1}{4} \Gamma_A. \quad (\text{B8})$$

We use this result in the solution for the two bond exchange model (in a square lattice), which is<sup>29</sup>

$$\psi_B \simeq \Gamma_B \left[ 1 - \frac{2c_A}{B(\epsilon_1) - B(\epsilon_2) + 1 + \epsilon_1 g(\epsilon_1)} \right], \quad (\text{B9})$$

where

$$B(\epsilon) = g(\epsilon) + G_{ab}(\epsilon), \quad (\text{B10})$$

$$\epsilon_1 = \frac{i\omega + \tau^{-1}}{\psi}; \quad \epsilon_2 = \frac{i\omega + \tau^{-1} + 2\theta^{-1}}{\psi} \quad (\text{B11})$$

and where<sup>30</sup>

$$\begin{aligned} g(\epsilon) &= \frac{1}{2} \int_0^\infty dt \exp\left(-2t - \frac{1}{2} \epsilon t\right) I_0^2(t) \\ &= \frac{1}{2\pi} (1 + \epsilon/4)^{-1} K([1 + \epsilon/4]^{-1}), \end{aligned} \quad (\text{B12})$$

$$G_{ab}(\epsilon) = -\frac{1}{2} \int_0^\infty dt \exp\left(-2t - \frac{1}{2} \epsilon t\right) I_1^2(t), \quad (\text{B13})$$

where  $I_m(t)$  is the modified Bessel function of order  $m$  and  $K(k)$  is the complete elliptic integral of the first kind [Eq. (34c)].

### APPENDIX C: EFFECTIVE JUMP RATE $W$ IN THE QCA

Here we calculate  $W$ , the averaged jump rate of the tracer particle to a NN vacant site, in the framework of the quasi-chemical approximation<sup>5,9,16(b),38</sup> (QCA), for the self-diffusion problem with NN interactions. Let  $W_{i-k}$  be the actual jump rate if there are  $i$  particles NN to the tracer and  $k$  particles NN to the vacancy (itself a NN to the tracer)  $i, k = 0, \dots, z-1$ . Let  $P_1^{(k)}$  and  $P_0^{(k)}$  be the equilibrium probabilities to find  $k$  particles NN to a particle or to a vacancy, respectively. Assuming the configurations around the particle and the NN vacancy to be independent (in consistency with the QCA), the averaged jump rate  $W$  is given approximately by

$$W = \langle W_{i-k} \rangle \simeq \sum_{i,k=0}^{z-1} P_1^{(i)} P_0^{(k)} W_{i-k}. \quad (\text{C1})$$

The NN correlation functions  $P_{11}$  and  $P_{10}$  are defined as the probabilities to find a particle NN to a particle or to a vacancy, respectively. In terms of these functions, we may write

$$P_1^{(k)} = \binom{z-1}{k} (P_{11})^k (1 - P_{11})^{z-1-k}, \quad (\text{C2a})$$

$$P_0^{(k)} = \binom{z-1}{k} (P_{10})^k (1 - P_{10})^{z-1-k}. \quad (\text{C2b})$$

In the QCA the NN correlation functions are given by<sup>38</sup>

$$P_{11} = \eta\epsilon / (1 + \eta\epsilon), \quad (\text{C3a})$$

$$P_{10} = \epsilon / (1 + \epsilon), \quad (\text{C3b})$$

where

$$\eta = \exp(v/k_B T), \quad (\text{C4a})$$

$$\epsilon = (\beta - 1 + 2c) / (2\eta(1 - c)), \quad (\text{C4b})$$

$$\beta = [1 - 4c(1 - c)(1 - \eta)]^{1/2}, \quad (\text{C4c})$$

where  $v$  is the NN interaction energy ( $v > 0$  for attractive interaction).

In choosing  $W_{i-k}$  we need to satisfy the detailed balance condition

$$\frac{W_{i-k}}{W_{k-i}} = \exp\left[\frac{v(k-i)}{k_B T}\right], \quad (\text{C5})$$

and one needs another condition for a unique determination. Kutner *et al.*<sup>15(c)</sup> have chosen the symmetric condition

$$W_{i-k} + W_{k-i} = 2\Gamma, \quad (\text{C6})$$

where  $\Gamma$  is the bare jump rate. This and Eq. (C5) lead to

$$W_{i-k} = \frac{2\Gamma}{1 + \eta^{i-k}}, \quad (\text{C7})$$

where  $\eta$  is defined in Eq. (C4a). Using Eqs. (C2), (C3), and (C7) in Eq. (C1) finally leads to

$$\begin{aligned} W &= \frac{2\Gamma}{(1 + \eta\epsilon)^{z-1} (1 + \epsilon)^{z-1}} \\ &\times \sum_{i,k=0}^{z-1} \binom{z-1}{i} \binom{z-1}{k} \frac{(\eta\epsilon)^i \epsilon^k}{1 + \eta^{i-k}}, \end{aligned} \quad (\text{C8})$$

which can be shown to have the symmetry property  $W(c) = W(1 - c)$ . This symmetry is clearly a result of the choice (C6). For  $c \rightarrow 0$  (or  $c \rightarrow 1$ ) at any temperature, or for  $T \rightarrow \infty$  at any concentration, we have  $W \rightarrow \Gamma$  as expected.

A more compact expression may be obtained by using a mean-field-like approximation

$$\langle (1 + \eta^{i-k})^{-1} \rangle \simeq (1 + \eta^{(i-k)})^{-1}, \quad (\text{C9})$$

which results from expanding the expression in  $\langle \dots \rangle$  on the right-hand side of Eq. (C9) in a power series of  $(i - k)$  [ $(i - k)$  is the difference in number of NN particles to the tracer particle and to a neighboring vacancy] and approximating all moments as being equal to the corresponding powers of the average. This should be a good approximation when the probability distributions (C2a) and (C2b) are strongly peaked, i.e., for large coordination number  $z$ . We then have in the QCA

$$\langle i - k \rangle \simeq (z - 1)(P_{11} - P_{10}) \quad (\text{C10})$$

and together with Eqs. (C3) and (C4), we find

$$W = \Gamma \left[ 1 - \tanh \left[ \frac{(z - 1)v(\beta - 1)}{2k_B T(\beta + 1)} \right] \right], \quad (\text{C11})$$

which is also symmetric with respect to  $c = 1/2$ , since  $\beta(c) = \beta(1 - c)$ . In Figs. 6(a) and 6(b), we compare both results (C8) and (C11) to the simulation results of Kutner *et al.*<sup>15(c)</sup> for  $k_B T/J = 20$  and  $k_B T/J = 12$  with<sup>39</sup>  $J = v/4$ .

<sup>1</sup>For a review, see G. Ehrlich and K. Stolt, *Annu. Rev. Phys. Chem.* **31**, 603 (1980).

<sup>2</sup>For reviews, see M. A. Ratner and A. Nitzan, *Solid State Ionics* **28-30**, 3 (1988); G. Mahan, in *Superionic Conductors*, edited by G. Mahan and W. Roth (Plenum, New York, 1976); W. Dieterich, P. Fulde, and I. Pechel, *Adv. Phys.* **29**, 527 (1980); W. Dieterich, *Solid State Ionics* **5**, 21 (1981); T. Geisel, in *The Physics of Superionic Conductors*, edited by M. B. Salamon (Springer, Berlin, 1979).

<sup>3</sup>G. E. Murch, *Atomic Diffusion Theory in Highly Defective Solids* (Trans Tech SA, Zurich, 1980); J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, edited by W. Shockley (Wiley, New York, 1952).

<sup>4</sup>H. Böttger and V. V. Bryksin, *Hopping Conduction in Solids* (Akademie, Berlin, 1985); J. N. Pratt and R. G. R. Sellors, *Electrotransport in Metals and Alloys* (Trans Tech SA, Zurich, 1973).

<sup>5</sup>V. P. Zhdanov, *Surf. Sci.* **194**, 1 (1988); **111**, 63 (1981); **63**, 123 (1982); **106**, 133 (1983); **137**, 515 (1984).

<sup>6</sup>R. D. Foggio and R. Gomer, *Phys. Rev. B* **25**, 3490 (1982); J. R. Chen and R. Gomer, *Surf. Sci.* **79**, 413 (1979); **81**, 589 (1979); M. Tringides and R. Gomer, *ibid.* **155**, 254 (1985).

<sup>7</sup>C. H. Mark, H. C. Andersen, and S. M. George, *J. Chem. Phys.* **88**, 4052 (1988), and references therein.

<sup>8</sup>M. Silverberg and A. Ben Shaul, *Surf. Sci.* **214**, 17 (1989), and references therein.

<sup>9</sup>S. Sundaresan and K. R. Kaza, *Surf. Sci.* **160**, 103 (1985).

<sup>10</sup>K. Funke and I. Riess, *Z. Phys. Chem. Nene Folge* **140**, 217 (1984); K. Funke, *Solid State Ionics* **18/19**, 183 (1986); K. Funke, *Z. Phys. Chem. Nene Folge* **154**, 251 (1987).

<sup>11</sup>U. Thomas and W. Dietrich, *Z. Phys. B* **62**, 287 (1986); H. E. Roman and W. Dietrich, *J. Phys. C* **19**, L801 (1986); F. Bill, H. E. Roman, and W. Dietrich, *Solid State Ionics* **28-30**, 58 (1988).

<sup>12</sup>J. R. Manning, *Phys. Rev.* **116**, 819 (1959); *Phys. Rev. A* **136**, 1758 (1964); *Diffusion Kinetics for Atoms in Crystals* (Van Nostrand, Princeton, 1968); *Phys. Rev. B* **4**, 1111 (1971).

<sup>13</sup>O. F. Sankey and P. A. Fedders, *Phys. Rev. B* **15**, 3586 (1977).

<sup>14</sup>K. Nakazato and K. Kitahara, *Prog. Theor. Phys.* **64**, 2261 (1980).

<sup>15</sup>(a) R. Kutner, *Phys. Lett. A* **81**, 239 (1981); (b) K. W. Kehr, R. Kutner and K. Binder, *Phys. Rev. B* **23**, 4931 (1981); (c) R. Kutner, K. Binder, and K. W. Kehr, *ibid.* **26**, 2967 (1982); (d) **28**, 1846 (1983); (e) R.

Kutner and K. W. Kehr, *Philos. Mag. A* **48**, 199 (1983); (f) K. W. Kehr and K. Binder, in *Applications of the Monte Carlo Method in Statistical Physics*, edited by K. Binder (Springer, New York, 1987), p. 181.

<sup>16</sup>(a) D. A. Reed and G. Ehrlich, *Surf. Sci.* **102**, 588 (1981); (b) **105**, 603 (1981).

<sup>17</sup>(a) R. Kikuchi, *Prog. Theor. Phys. Suppl.* **35**, 1 (1966); (b) H. Sato and R. Kikuchi, *Phys. Rev. B* **28**, 648 (1983) and references therein; A. Suzuki, H. Sato, and R. Kikuchi, *ibid.* **29**, 3550 (1984); T. Ishii, H. Sato, and R. Kikuchi, *ibid.* **34**, 8335 (1986).

<sup>18</sup>G. E. Murch and R. J. Thorn, *Philos. Mag.* **35**, 493 (1977); *J. Phys. Chem. Solids* **38**, 789 (1977).

<sup>19</sup>S. Havlin and D. Ben Avraham, *Adv. Phys.* **36**, 695 (1987); A. Bunde, S. Havlin, R. Nossal, and H. E. Stanley, *Phys. Rev. B* **32**, 3367 (1985).

<sup>20</sup>S. D. Druger, A. Nitzan, and M. A. Ratner, *J. Chem. Phys.* **79**, 3133 (1983).

<sup>21</sup>S. D. Druger, M. A. Ratner, and A. Nitzan, *Solid State Ionics* **9/10**, 1115 (1983).

<sup>22</sup>S. D. Druger, M. A. Ratner, and A. Nitzan, *Phys. Rev. B* **31**, 3939 (1985).

<sup>23</sup>S. D. Druger, in *Transport and Relaxation Processes in Random Materials*, edited by J. Klafter, R. J. Rubin, and M. F. Shlesinger (World Science, Singapore, 1986).

<sup>24</sup>A. Nitzan, S. D. Druger, and M. A. Ratner, *Philos. Mag. B* **56**, 853 (1987).

<sup>25</sup>R. Granek, A. Nitzan, S. D. Druger, and M. A. Ratner, *Solid State Ionics* **28-30**, 120 (1988).

<sup>26</sup>S. D. Druger and M. A. Ratner, *Chem. Phys. Lett.* **151**, 434 (1988).

<sup>27</sup>S. D. Druger and M. A. Ratner, *Phys. Rev. B* **38**, 12,589 (1988).

<sup>28</sup>A. K. Harrison and R. Zwanzig, *Phys. Rev. A* **32**, 1072 (1985); denoted by HZ in the paper.

<sup>29</sup>R. Granek and A. Nitzan, *J. Chem. Phys.* **90**, 3784 (1989).

<sup>30</sup>G. S. Grest, I. Webman, S. A. Safran, and A. L. R. Bug, *Phys. Rev. A* **33**, 2842 (1986).

<sup>31</sup>A. R. Kerstein and B. F. Edwards, *Phys. Rev. B* **33**, 3353 (1986).

<sup>32</sup>A. L. R. Bug and Y. Gefen, *Phys. Rev. A* **35**, 1301 (1985).

<sup>33</sup>(a) R. Hilfer and R. Orbach, *Chem. Phys.* **128**, 275 (1988); (b) R. Hilfer and R. Orbach, in *Dynamical Processes in Condensed Molecular Systems*, edited by J. Klafter, J. Jortner, and A. Blumen (World Scientific, Singapore, 1989), p. 175.

<sup>34</sup>M. Sahimi, B. D. Hughes, L. E. Scriven, and H. T. Davis, *J. Chem. Phys.* **78**, 6849 (1983).

<sup>35</sup>M. L. Glaser and I. J. Zucker, *Proc. Natl. Acad. Sci. USA* **74**, 1800 (1977), Eq. (3). Note that there is a missing power 2 for the curly brackets in Eq. (3a), corrected in Eq. (39) in this paper.

<sup>36</sup>G. L. Montet, *Phys. Rev. B* **7**, 650 (1973).

<sup>37</sup>See, e.g., H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971), pp. 35-37; for a more general formula, see R. Howard, *Phys. Rev.* **144**, 650 (1966).

<sup>38</sup>(a) R. Peierls, *Proc. Cambridge Philos. Soc.* **32**, 471 (1936); (b) R. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University, Cambridge, 1949), Chap. X.

<sup>39</sup> $J_m$  is the usual spin-spin interaction energy in the Ising model equivalent of the lattice-gas model.