Tracer diffusion in lattices with double occupancy of sites

L. F. Perondi and R. J. Elliott
Department of Physics, Theoretical Physics, University of Oxford, 1 Keble Road, Oxford OX1 3NP, United Kingdom

R. A. Barrio
Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, 01000 México D.F., México

K. Kaski*
Tampere University of Technology, P.O. Box 692, FIN-33101 Tampere, Finland
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Comprehensive computer simulations of a tracer particle hopping in a lattice where the sites could be either empty or occupied by one or two background particles are performed using a standard Monte Carlo technique. The results for the diffusion coefficient are compared with those of a mean-field theory derived from a random-walk approach. The blocking effects due to dynamical background particles are obtained exactly. The correlation effects due to many-particle interactions are analyzed qualitatively. This kind of double-occupancy model can be applied to the study of ionic conduction in glasses.

I. INTRODUCTION

For many years various tracer diffusion models in a disordered lattice have been intensively studied[1] and been applied to a wide range of physical situations. The case of bond disorder has been considered by Webman,[2] while Perondi and Elliott have recently discussed a special model of topological disorder.[3] Site disorder in the mathematically similar case of magnets was treated some time ago.[4] More realistic theoretical models of disorder are untractable by analytic methods, due to many-body effects which, in general, are not correctly accounted for in any mean-field approximation. However, most of the experimental probes are not sensitive enough to encourage a more quantitatively predictive model. In these models one usually considers a single-particle hopping from a site to one of its unoccupied neighbors at a given rate. The presence of other particles will diminish the individual probability of a given jump. As a consequence, the diffusion coefficient will also be diminished. On the one hand, this arises because of the *dynamical blocking* of available sites for the tracer by the mobile background particles, and on the other hand, there appear *correlation effects* due to the fact that successive tracer jumps are not statistically independent. (The reason for this dependence is that the site left behind after a jump is empty with probability 1, while the other neighboring sites could be occupied by background particles.)

This complex many-body problem only admits suitable approximate solutions in the limits of low concentration (single particle) or high concentration (single vacancy) of particles. These limits are attainable by a linear decoupling procedure of the equations of motion for the relevant generating functions[5] or by random-walk approach.[6] In the intermediate-concentration region, one would have to devise a reasonable interpolation scheme.[5] With random-walk techniques one finds mean-field values of the diffusion coefficient that agree extremely well with other much more complicated interpolation schemes or numerical simulations.[7]

These techniques could also be applied to the case in which a given lattice site could be occupied by more than one particle. Such an extension is relevant when studying transport of ions in glasses, such as $(1-x)B_2O_3+xLi_2O$, in which experimental data suggest that there could be more than one ion bound to a negatively charged site in the lattice.[8] This is to be expected because there are usually as many ions as there are available sites provided by the host material.[9] A model of diffusion allowing double occupancy of sites has been applied[10] to the case of ion conduction in borate glasses.[11] The success of this application suggests that double occupancy is more important than the topological disorder of the glass. The model uses mean-field expressions for the effective hopping rates, derived from a master equation and random-walk technique.

Although in the mean-field approach the correlation effects are not properly accounted for, its results are reasonably good. Therefore it is desirable to make a comparative analysis of these predictions using Monte Carlo results, which is the main purpose of this paper. The model used for ionic conduction in glasses[10] includes possible variations in the barrier heights due to a Coulomb repulsion of two particles occupying the same site. It also includes variations in the attempt jump frequencies for doubly occupied sites. Furthermore, one also makes an assumption that there could be various types of negatively charged centers, i.e., some random static defects need to be included. Such a complicated situation is difficult to reproduce in a computer simulation. Fortunately, the basic hypotheses to be tested by the simulation can be investigated with a simpler model, in which one assumes that doubly occupied sites only induce a change in the hopping rate. This basic model is analyzed here analytically and numerically.

This paper is organized as follows. First, the model is

explained, the mean-field expressions are derived, and a qualitative interpolation scheme is devised for calculating the correlation effects between the two extremes of particle concentration. Then the characteristics of the numerical simulations are presented followed by a comparison with the theoretical results and a discussion. Finally, some conclusions are drawn.

II. MODEL AND MEAN-FIELD TREATMENT

In a perfect hypercubic lattice, a process in which a single classical particle performs a random series of hoppings between nearest-neighbor sites is characterized by a diffusion coefficient

$$D_0=\frac{l^2Z}{2d}J\ , \tag{1}$$

where l is the hopping length, d is the number of spatial dimensions, Z is the number of nearest neighbors, and J is the hopping rate. If one considers that the time spent in a jump is much shorter than the mean residence time in a site, the process takes place in thermal equilibrium. Therefore the hopping is thermally activated and $J=\nu\exp(-\Delta E/kT)$, where ν is the attempt jump frequency. In the many-body case we consider a relative concentration of particles $c=N_p/N_s$, where N_p is the total number of mobile particles and N_s is the number of lattice sites. As mentioned earlier, dynamical blocking and correlation effects change the jump probabilities and result in a lower value for the tracer diffusion coefficient. In order to distinguish between these two effects, it is convenient to write the diffusion coefficient for the many-body system as

$$D=f_bf_cD_0\ , \tag{2}$$

where f_b is a blocking factor and f_c is a correlation factor. f_b is defined by the ratio between the number of successful jumps and the total number of attempted jumps. This can be calculated exactly by counting all the possible local configurations. Note that by definition all many-body correlations are included in f_c. Then a mean-field approach for the diffusion problem will give f_b exactly, since in that case one neglects correlations. However, the calculation of f_c requires an approach beyond the mean field, as will be discussed later.

A. Blocking factor

Let us start with the uncorrelated case ($f_c=1$) and assume that at every site of the lattice there is a probability n_0, n_1, or n_2 for it to be occupied by zero, one, or two particles, respectively. The tracer particle could only be located in a vacant site, with probability P_1, or in a singly occupied site, with probability P_2. Then we assume that the hopping rates are J and J' for making a jump away from a singly or doubly occupied site, respectively. In this case the averaged hopping rate of the tracer is

$$J^0=P_1J+P_2J' \tag{3}$$

and the blocking factor is

$$\begin{aligned} f_b&=(1-n_2)J^0/J \quad \text{for } J\geq J'\ ,\\ f_b&=(1-n_2)J^0/J' \quad \text{for } J<J'\ , \end{aligned} \tag{4}$$

since diffusion is dominated by the largest of the hopping rates. Likewise, D_0 in Eq. (2) now includes the largest of the hopping rates.

For a concentration c of background particles, proper normalization gives

$$n_1=2-c-2n_0 \quad \text{and} \quad n_2=c-1+n_0\ , \tag{5}$$

where c could vary between 0 and 2. The equilibrium value of the site occupation probabilities can be found by considering the master equation for any n_i, from which one derives the rate equation

$$\begin{aligned} \frac{d\langle n_1(i)\rangle}{dt}=\sum_j\,&[J\langle n_1(j)n_0(i)\rangle+2J'\langle n_2(j)n_0(i)\rangle+2J'\langle n_2(i)n_0(j)\rangle+2J'\langle n_2(i)n_1(j)\rangle\\ &-J\langle n_1(i)n_0(j)\rangle-J\langle n_1(i)n_1(j)\rangle-J\langle n_1(i)n_1(j)\rangle-2J'\langle n_1(i)n_2(j)\rangle]\ , \end{aligned} \tag{6}$$

where $\langle\cdots\rangle$ means an average over the distribution of configurations at a given time. This equation can be visualized with the help of Fig. 1, where all the possible situations for a particle hopping between two sites (i and j) are shown. The four diagrams in Fig. 1 correspond exactly to the positive terms on the right-hand side of Eq. (6). The negative ones can be obtained from this figure by reversing the time. Notice that the situations in which the jumping particle is initially in a doubly occupied site have to be multiplied by 2, since the particle that performs the jump is indistinguishable. Similarly, equations may be obtained for $d\langle n_2(i)\rangle/dt$ and $d\langle n_0(i)\rangle/dt$. After a long time, the system will approach the steady state ($dn_1/dt\approx0$), and in this regime the distribution is canonical and thus it is clear that $\langle n_1(i)\rangle=n_1$ is the same for all sites. Since the total energy of a given configuration only depends on the single-site occupation

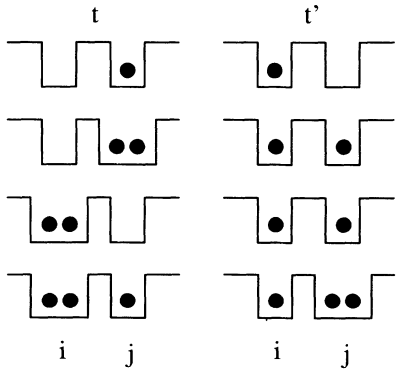

FIG. 1. Diagram that shows all the possible situations for a single jump between sites i and j. If time t is before time t', these diagrams correspond to the terms with + sign in Eq. (6), and the negative terms there are obtained by reversing the time.

probabilities, the partition function can be factorized and the multiple-site averages can be decoupled into products of single-site averages. Therefore the steady-state condition reads

$$2n_2n_0J'=n_1^2J\ , \tag{7}$$

which could be combined with Eq. (5) to give

$$n_0=\frac{2a+(1-c)(2a-1)-\sqrt{2a-(2a-1)(1-c)^2}}{2(2a-1)}\ , \tag{8}$$

where $a=J/J'$.

A rate equation for the tracer can be obtained also with the aid of Fig. 1, except that one has to treat the tracer as a distinguishable particle. In this case one obtains

$$\frac{dP_1}{dt}=\sum_j [J\langle P_1(j)n_0(i)\rangle+J'\langle P_2(j)n_0(i)\rangle+J'\langle P_2(i)n_0(j)\rangle+J'\langle P_2(i)n_1(j)\rangle$$
$$-J\langle P_1(i)n_0(j)\rangle-2J\langle P_1(i)n_1(j)\rangle-2J'\langle P_1(i)n_2(j)\rangle]\ . \tag{9}$$

The equilibrium condition now reads

$$2P_1(an_1+n_2)=P_2(2n_0+n_1)\ , \tag{10}$$

which can be solved with the normalization condition ($P_1+P_2=1$) to give

$$P_1=\frac{2n_0+n_1}{2(an_1+n_2)+2n_0+n_1}\ . \tag{11}$$

This completes the exact calculation of the blocking factor in Eq. (4). As seen in Eqs. (6) and (9), the rate equation for a single-site average involves two-site averages, and the equation of motion for the two-site averages involves three-site averages, and so on, forming a hierarchical set of equations. Therefore the solution of the complete correlated dynamics calls for an approximation. The mean-field result is obtained when one decouples the set of equations to the first order, thus ignoring correlations. For this reason the blocking factor can be calculated exactly as shown above.

B. Correlation factor

Next, we will briefly discuss the role of correlations at the single-particle and single-vacancy limits. After that we attempt to devise an interpolation scheme for intermediate particle concentrations. In the single-site occupancy case (lattice gas model),[5,6] it was found that decoupling the hierarchical set of equations to second order gives the leading contribution to the correlation factor. Thus good approximations in the extreme limits of particle concentration were obtained. This was also necessary for devising a reasonable interpolation scheme at intermediate particle concentrations. In the double-occupancy case, the single-particle limit ($c\approx 0$) can be described exactly using the same ideas as in the lattice gas model. There are three types of sites with zero (0), one (1), and two (2) background particles. Sites (1), although mobile, do not cause correlations to the tracer motion, but affect the average hopping rate of the tracer [$J^0=J(P_1+P_2/a)$]. Therefore sites (2) are the only and direct cause of correlations. The detailed dynamics of these two-particle complexes could be very complicated, but their average concentration is fixed and known. Therefore, if one assumes that these complexes move like rigid objects with hopping rate J', the system becomes effectively a lattice gas model. As a consequence, one would use the single-particle limit expression as derived for the lattice gas model either by decoupling the equation of motion to second order[5] or by a random-walk approach.[6]

In the single-vacancy limit ($c\approx 2$), we consider a situation in which all sites but one are doubly occupied. Now the lattice gas picture is not appropriate, because the vacancy could move through the tracer site either by exchanging places with the tracer or with the companion particle. Thus the hopping rate of the vacancy is $2J'$. Using random-walk theory, one now obtains

$$f_c=\frac{1+\frac{1}{2}\cos\theta_0}{1-\frac{1}{2}\cos\theta_0}\ , \tag{12}$$

where $\cos\theta_0$ measures the imbalance between forward and backward jumps in a random walk.[12] In this paper we shall compare this result with simulations in two dimensions where $\cos\theta_0=2/\pi-1=-0.36338$. Note that apart from $\frac{1}{2}$ in front of the cosines this result is the same as obtained for the lattice gas using either the decoupling scheme[5] or the random-walk approach.[6] This is understood because the vacancy exchanges places with the tracer at the rate J', while the vacancy can return from such a site with the rate $2J'$.

As a first attempt to devise an interpolation scheme of f_c for all intermediate concentrations, one is tempted to use a Tahir-Kheli- and Elliott-like expression[5]

$$f_c=\left[1-\frac{2J^0n_2\cos\theta(c)}{\{J'+J^0(1-n_2)\}\{1+\cos\theta(c)\}}\right]^{-1}\ . \tag{13}$$

Note that in this expression we emphasize the concentration dependence of $\cos\theta$, because the value of this imbalance measure in the single-vacancy limit is half of that in the single-particle limit. The simplest assumption for the functional form of $\cos\theta(c)$ is the weighted average

$$\cos\theta(c)=\frac{2-c}{2}\cos\theta_0+\frac{c}{2}\left[\frac{P_1\cos\theta_0+(P_2/2a)\cos\theta_0}{J^0/J}\right]\ . \tag{14}$$

It is noted that there is obviously room for improving this scheme. For example, one could introduce self-consistency by defining a mean-field diffusion coefficient containing f_c. However, in the double-occupancy problem correlations are expected to be less important than in the simple lattice gas model. Thus we do not pursue this matter further.

III. NUMERICAL SIMULATIONS

In the numerical simulations a standard random-walk Monte Carlo method was used.[7] The simulations have been performed in a square lattice of size $l_s \times l_s$ with periodic boundary conditions for various fixed values of c and a, chosen to span the parameter space thoroughly. The first step is to set up the initial configuration of the system. In some preliminary calculations the vacant sites, the singly occupied sites, and the doubly occupied sites were distributed at random, obeying the constraint in Eq. (5). After a fair number of Monte Carlo steps (defined below), the resulting probabilities of occupation were always very close to the equilibrium values given by Eqs. (5) and (8). Therefore the final results of the simulations do not depend on the initial configuration. In order to speed up the calculations, the equilibrium numbers for each value of c and a were chosen to give the initial configuration for the simulations. Then one labels all the particles and performs a series of Monte Carlo steps in the following way.

One selects a particle at random and also one of its nearest-neighbor sites and tests if the site is doubly occupied, in which case the particle cannot move and the configuration of the system is kept unchanged. If the neighbor is not doubly occupied, then on identifies the site occupied by the particle. Here one needs to be careful, because the time scale that defines a Monte Carlo step per particle (MCS) is different for $a > 1$ from that for $a \leq 1$. When $a > 1$ and if the particle is in a singly occupied site, it moves to the neighbor site. If the site is doubly occupied, then one generates a random number (m) within the interval (0,1) and compares it with $1/a$. If $m < 1/a$, then the particle moves; otherwise, it does not move. In contrast, when $a \leq 1$ the inverse is true, that is, if the site is doubly occupied, the particle moves to the neighbor site, and if it is singly occupied, then one compares a with a random number m: if $m < a$, the particle remains in the site; otherwise, it moves.

This procedure is repeated N_p times, defining the time unit of 1 MCS. In the simulations, $l_s = 100$ was chosen, i.e., $N_s = 10^4$, which according to our earlier experiences is large enough to render very small finite-size effects.[7] Moreover, it was found that 2000 MCS for most pairs (a,c) gave a sufficiently long time to very accurately determine diffusion coefficients and various factors in them. As for the random number generation, the R250 shift-register generator was used.[13] This routine is known to produce very good pseudorandom numbers.

In order to explore a wide range of values in the parameter space (a,c) and to prevent unnecessary calculations, two sets of simulations were made, one for a few extreme values of c, spanning a wide range of values for a, and another with a restricted range of a's and covering all the range of variation in c. In the first set we chose $c = 0.1$, 1.0, and 1.9, for $a = \frac{1}{1000}, \frac{1}{200}, \frac{1}{100}, \frac{1}{20}, \frac{1}{10}, \frac{1}{9}, \frac{1}{7}, \frac{1}{5}, \frac{1}{3}$, 1, 3, 5, 7, 9, 50, 100, 500, and 1000. In the second set we took the restricted set of 12 values of a between $\frac{1}{9}$ and 9 and varied $c = 0.3$, 0.5, 0.7, 0.9, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, and 1.95.

From the simulations one can obtain the equilibrium probabilities of site occupation n_i. After each MCS one counts the number of vacant, singly, and doubly occupied sites and scales by N_s. Then one averages over the last 50 MCS to ensure good approximations for the equilibrium values. The blocking factor f_b is calculated according to its definition, that is, by counting the number of successful jumps and dividing by the total number of attempts, which is N_p times the number of MCS. The averaged hopping rate $\langle J \rangle = (1-n_2)J^0$ is obtained by multiplying the correlation factor by the largest of the J's according to the definition in Eq. (3).

The diffusion coefficient for the many-particle system, and thus the correlation factor f_c, can be calculated after each MCS from the mean-square displacement

$$\langle R^2 \rangle = \frac{1}{N_p} \sum_i [(x_i - x_{0i})^2 + (y_i - y_{0i})^2] , \tag{15}$$

where (x_{0i}, y_{0i}) are the initial configuration coordinates of particle i. Because of the periodic boundary conditions, one has to add up a hopping length l each time a particle crosses a boundary. Performing a least-squares linear fitting within the range of MCS from 500 to 2000, one gets the slope which yields directly $2dD/Z$, where D is defined in Eq. (2). To obtain f_c, one divides D by $\langle J \rangle$.

IV. DISCUSSION

The results of the simulations can be compared with the theoretical predictions of Sec. II. In Fig. 2 the dependence of the probabilities of occupation, n_i, on c is shown. It is found that the theoretical predictions of Eqs. (5) and (8) and the points from the computer simulations agree perfectly well, within the precision of the simulations, for all values of (a,c). (A fair estimate for the error bars in all the figures is less or about the size of symbols in them.) This means that the mean-field approach and the master equation that gives the equilibrium condition in Eq. (7) produce the exact result. Furthermore, the theory also gives exact results for the equilibrium values of the tracer probabilities, since the predictions from Eqs. (10) and (11) agree perfectly well with the Monte Carlo simulations throughout the parameter space. An example of this is shown in Fig. 3, where the concentration dependence of the average hopping rate $\langle J \rangle$ is compared with the simulation points for selected values of a. By looking at these results, one can be convinced that finite-size effects, usually found in Monte Carlo simulations, are not jeopardizing the accuracy of the numerical calculation.

The blocking factor is obtained exactly with the theoretical model even for extreme values of a. In Fig. 4(a) one can notice a complete agreement between the

Monte Carlo simulations and the theoretical predictions in a wide range of values of a.

The effects of correlations in the diffusion coefficient are shown in Fig. 4(b), where one can observe deviations of the numerical calculations for D from the $f_c=1$ case (shown by the lines in the figure). These are particularly important when a is very different from 1, and the deviations are more pronounced for larger values of c, as expected. One can also note some fluctuations in the numerical results (see, for instance, the point at $c=0.7$ for $a=\frac{1}{9}$), due to the fact that for some extreme values of the parameters, there occur very few jumps even for a large number of MCS.

In Fig. 5 the results for f_c obtained with the Tahir-Kheli- and Elliott-like interpolation scheme of Eq. (13) are shown as a function of c for selected values of a and they are compared with the results of the Monte Carlo simulations. It is seen that the theory agrees well with

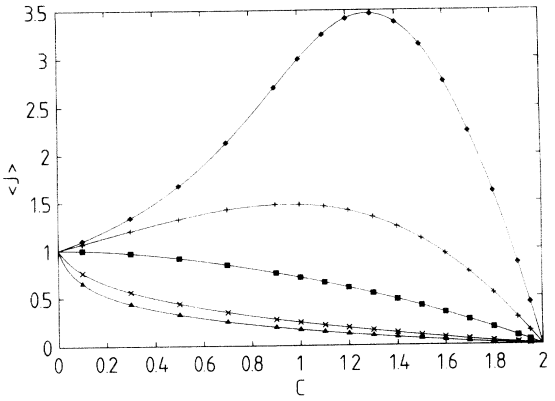

FIG. 3. Dependence of the average hopping rate on the concentration of background particles. The simulation points are shown for $a=\frac{1}{9}$ (♦), $a=\frac{1}{3}$ (+), $a=1$ (■), $a=5$ (×), and $a=9$ (▲). The predicted values from the theoretical model are shown with lines.

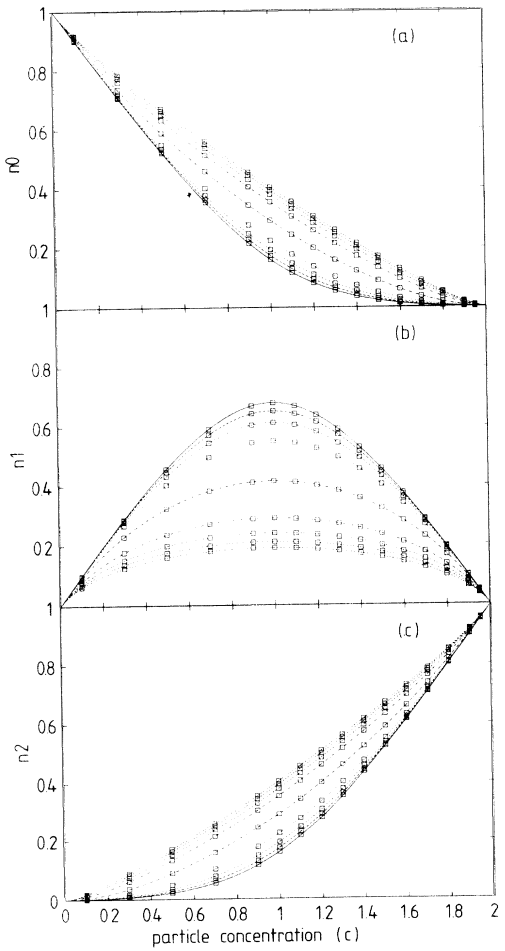

FIG. 2. Dependence of the site probabilities of occupation on the concentration of background particles (a) for vacancies, (b) for singly occupied sites, and (c) for doubly occupied sites. The squares are the results from the computer simulations, and the lines are the theoretical predictions from Eqs. (5) and (8). The values of $a=J/J'$ are $\frac{1}{9}$ (solid lines), $\frac{1}{7}$, $\frac{1}{5}$, $\frac{1}{3}$, 1, 3, 5, 7, and 9.

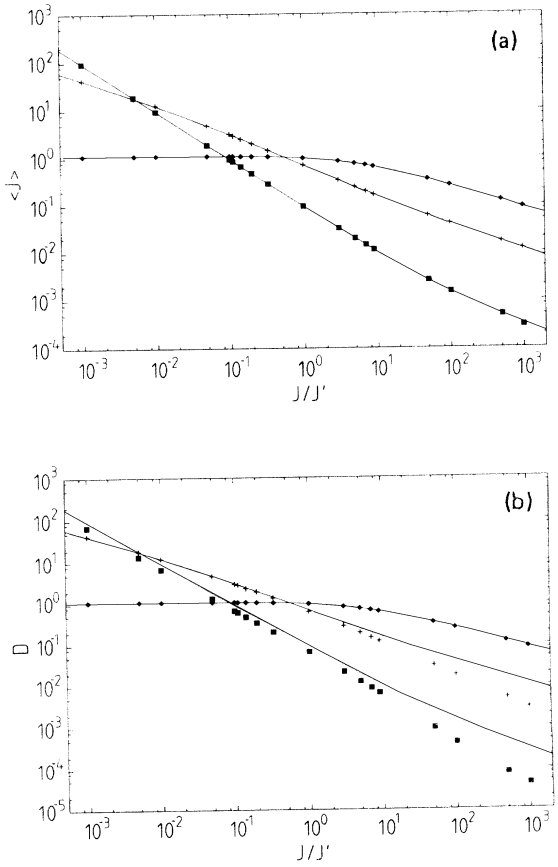

FIG. 4. Theoretical dependence of the averaged hopping rate $\langle J\rangle$ on the ratio of hopping rates a shown for three selected values of the concentrations of background particles: $c=0.1$, $c=1.0$, and $c=1.9$. In (a) the corresponding points (diamonds, crosses, and squares) from the simulations are shown and agree with the results from Eq. (3). In (b) the results for $D=f_c\langle J\rangle$ are shown.

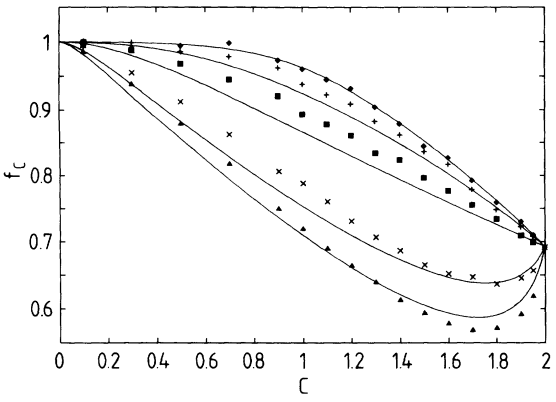

FIG. 5. Correlation factor as a function of the concentration of background particles calculated with Eq. (13) (lines) and from the numerical results. The symbols for the simulation points are the same as in Fig. 3.

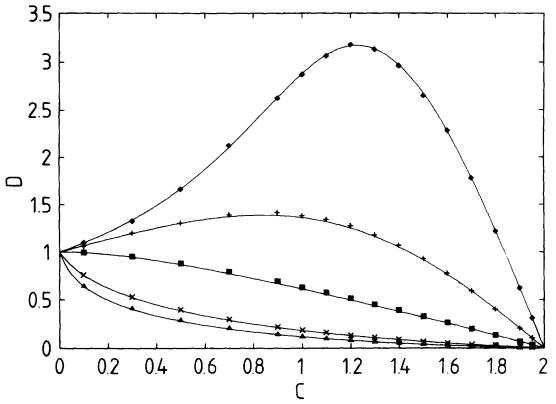

FIG. 6. Comparison of the theoretical $D=f_c\langle J\rangle$ [where f_c is calculated with Eq. (13)] and the numerical results for D as a function of the concentration of background particles. The selected values of a and the symbols are the same as in Fig. 3.

the numerical results only for low values of a, as expected. This is because in the limit $J'\rightarrow\infty$ only the particles in doubly occupied sites diffuse and there are very few of them, and thus the correlation factor is nearly unity for concentrations lower than 1. As a increases, so does the number of doubly occupied sites and the interplay of singly occupied sites affects the correlations in an important way. In the limit of large a, the doubly occupied sites are nearly stationary, an in this case a better description of the dynamics could be made by considering normal diffusion of particles in a lattice with a random distribution of static blocking defects. All the theoretical curves in Fig. 5 approach the same value when $c=2$ irrespective of the value of a. This is given by Eq. (13) as $f_c(c=2)=0.6925$, and it is suggested that the numerical results agree with it. This is to be expected, because in this limit diffusion could be described simply by considering a single-vacancy hopping in a full lattice, and the correlation effects can be calculated from purely geometrical considerations.[14] Note that the same limit in the lattice gas model, i.e., no double occupancy, is $f_c=0.4669$, obtained from Eq. (13) using $\cos\theta_0$ instead of $\frac{1}{2}\cos\theta_0$. In Fig. 5 the curves for large $a=J/J'$ extrapolate linearly to this value. Then one realizes that the minimum displayed by this curve is a consequence of the competition between the two terms in Eq. (14).

Furthermore, Fig. 5 demonstrates that the single-interpolation scheme does not agree quantitatively with the numerical results. However, the qualitative behavior is reproduced. The physics behind this behavior is that there are two possible local environments for a tracer-vacancy exchange, with different dynamics: tracer alone in a site and tracer sharing with another particle. Each environment gives a different value of $\cos\theta$. Thus the interpretation of the observed behavior of f_c is as follows. For low values of c the great majority of tracer-vacancy exchanges take place with a tracer alone site, as in the lattice gas. As c increases, the shared sites increasingly dominate the dynamics, and eventually one approaches the single-vacancy limit of the double-occupancy model. As for the turning point in f_c, it is natural that for larger a values doubly occupied sites are less mobile, and thus their effect becomes more apparent for larger c values.

In most practical cases, one does not measure tracer diffusion but chemical diffusion of particles, which differ in principle by correlation effects. Even in the case when one measures tracer diffusion—for example, in transport of radioactive particles—the deviations detected in the present work are not likely to be resolved in a real experiment. To illustrate this point the calculated diffusion coefficient using Eq. (13) is compared with the numerical results in Fig. 6 as a function of particle concentration. It is seen that both results agree remarkably well for moderate values of a.

V. CONCLUSIONS

There are some important conclusions drawn from this work. First, one should be reminded about the fact that in the diffusion coefficient the geometrical blocking effect can be separated from the many-body correlations. This is based on the observation that in the rate equation (6) multiple-site averages can be separated into single-site averages without any loss of generality, as in any system where the total energy only contains sums of single-particle energies. This in turn makes the mean-field theory exact for the site occupation probabilities n_i and tracer particle occupation probabilities P_j and then for the blocking factor f_b.

Second, it should be pointed out that the Monte Carlo simulations corroborate the theoretical results without correlations very accurately, with a minimum of finite-size effects. Thus our simulation scheme can be considered trustworthy for most of the parameter space and can then with confidence be used to study many-body correlation effects for which there is no exact theory.

However, in order to account for these correlations, a suitable interpolation scheme was developed using a lattice gas approximation, from which a Tahir-Kheli- and Elliott-like equation was derived. Although this scheme

does not give good quantitative agreement with the numerical results, it gives the salient features of the correlation factor qualitatively correctly. The small and large limits are found exactly, and a very good approximation for the corresponding slopes (df_c/dc) is obtained. To make the picture about the correlation behavior complete, some limit values of a were also discussed. First, when $a \to 0$—i.e., the jumping rate from doubly occupied sites dominates strongly—f_c would be 1, until c reaches 2, when it should suddenly go to the value 0.6925. Second, when $a \to \infty$—i.e., doubly occupied sites would stay static—f_c would seem to go monotonically toward the value 0.4669, given by the lattice gas approximation, but at $c = 2$ it should attain the value 0.6925 again. It is pointed out that although there is a discrepancy between theoretical and numerical results in the correlation behavior, it would be expected to fall below the experimental resolution of any practical measurement of the diffusion coefficient. Finally, in order to connect the present calculations with ionic conduction in borate glasses,[10] it should be pointed out that the tracer diffusion coefficient differs from that defined by ionic conductivity, their ratio being called the Haven ratio.[15] This ratio is significant if correlation effects are important. However, in glasses with low alkali ion content the Haven ratio is nearly 1. Therefore correlation effects are not important and the mean-field approach of this paper should be valid.

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*Present address: Department of Physics, Southern Illinois University, Carbondale, IL 62901. Also at Research Institute for Theoretical Physics, University of Helsinki, P.O. Box 9, FIN-00014 Helsinki, Finland.

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