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I. Tracer diffusion in bond-disordered square lattices

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Abstract. A model of the diffusion of a tagged particle moving by hopping on a lattice, where a finite concentration c of background particles gives rise to blocking due to forbidden multiple occupancy of sites, is extended to the situation where disorder exists on the lattice. In this paper the specific case of variable bond hopping rates is considered in the strongly disordered limit where a finite concentration p of the bonds are completely blocked. The resulting self-diffusion coefficient takes the form $(1-c)(1-p/p_c)D_0 f$ where p_c is the percolation limit and f is the dynamical correlation factor. It is expected that f is affected by the disorder and this is estimated by random-walk theory through a calculation of $\langle\cos\theta\rangle$ where θ is the angle between successive jumps of a particle and a vacancy. Also a quite comprehensive simulation study of tracer diffusion in a two-dimensional square lattice for $0 < c < 1$ and $0 < p < p_c$ is performed. The results are in good agreement with the analytical results which are known for small concentrations. Our approximate theory gives a good description over the entire range provided that the corrected form of $\langle\cos\theta\rangle$ is used.

1. Introduction

Systems of classical particles undergoing thermally activated hopping motion between vacant sites on a perfect or somehow disordered lattice have been widely used as models of atomic diffusion in solids. The bulk of this work has been concerned with ordered lattices and with the study of the characteristics of the motion of a single tagged tracer particle. In the limit of interstitial diffusion such a particle is taken to move in a largely empty lattice of interstitial sites. At the opposite extreme where the particle is confined to a lattice which is completely full except for a few vacancies, its motion is restrained by the small number of vacant sites through which motion can occur. This takes place under the usual assumption that double occupancy of any site is forbidden, although this condition has been relaxed in some models [1]. Other extensions of the theory where interactions between adjoining atoms and vacancies favour clustering have also been considered [2].

In many physical systems an appreciable fraction of the sites available for hopping motion will also be occupied by other moving atoms. Examples include the diffusion of hydrogen in metal hydrides [3] and ionic motion in superionic conductors. This has led to an extensive study of the motion of a tagged particle in a many-body system. Several methods have been used with considerable success in ordered lattices. This work has been extensively reviewed by Allnatt and Lidiard [4] and by Haus and Kehr [5]. It should be noted that collective diffusion on lattices with symmetric transition rates reduces to the single-particle problem [6, 7].

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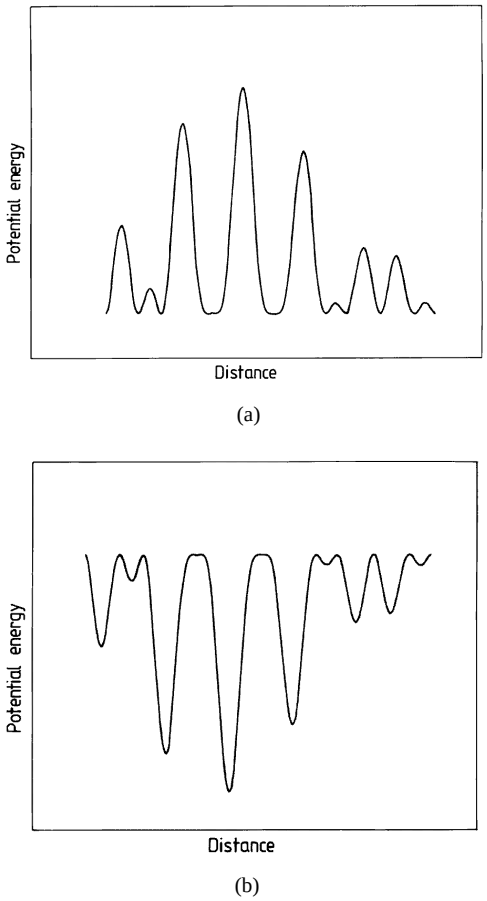

Figure 1. Schematic representations of the potential energy seen by the diffusing particle in a random system, (a) with equal well depth and random barrier heights, and (b) with random trap depths.

With increasing interest in the ionic conductivity of new materials such as glasses, as well as theoretical progress in the properties of disordered systems, it is natural to extend such studies to disordered lattices. Work on special non-periodic structures such as fractals and percolating clusters had been widely reviewed by Havlin and Ben-Avraham [8] and by Bouchaud and Georges [9]. In a disordered system such as a glass the static structure of the basic atomic framework is not a regular periodic lattice and hence the preferred positions for the mobile ions are irregularly distributed. Further, the potential wells associated with these sites will vary with the environment, so in equilibrium the relative occupation of such sites will also vary. In addition, because of the irregular arrangement of the immobile ions, the potential barriers for ionic motion between sites will also vary. It is difficult to evaluate a model which includes all of these effects and which isolates the various contributions to the conductivity. Therefore, we have confined our attention to idealized models where the underlying structure remains a regular periodic lattice. In this paper and its sequel [10] we study two simple models in which disorder is introduced to a periodic lattice by varying at random the barrier heights and hence the rates of hopping between the available sites, and by varying the depths of the potential at each site, so giving rise to traps. A

schematic representation of the potential energy function for these two cases is shown in figure 1. Figure 1(a) with wells of fixed depth but of varying heights relates to the bond disorder model used in this paper. Figure 1(b) is a model for site disorder treated in the accompanying paper [10].

In a lattice gas of particles where double occupancy of the sites is forbidden, there is an interplay between the random nature of the allowed hops and the self-avoidance of the hopping particles. This fact gives rise to two important effects on the motion of the single tagged particle, that substantially differentiate it from the random walk of the single particle on an otherwise empty lattice. First there is a blocking effect which decreases the number of successful hops of the tagged particle. Second the walk performed by the tagged particle is correlated with successive jumps in opposite directions being more probable than successive jumps in the same direction. This effect can be envisaged as a consequence of the fact that immediately after a successful hop by the tracer particle there is with certainty a vacancy behind it, hence enhancing the tendency for a return hop. Both effects contribute to a decrease in the diffusion coefficient of the tracer.

If static disorder is introduced into the lattice, which affects the probability of site occupation and of the hopping rates between sites, there are both direct and indirect consequences on the motion of the tagged particle. The direct interaction with the defects modifies the hopping rate and can introduce additional blocking effects as well as new correlation into the particle motion. In addition the defects influence the motion of the remaining particles causing changes in their interaction with the tagged particle. The behaviour of the tracer diffusion coefficient will reflect this interplay between static and dynamic correlations. These effects are largest if the disorder takes the form of prohibited sites or missing bonds. From a macroscopic point of view the static nature of these defects gives rise to a percolation problem, where the allowed sites are grouped in clusters and the occurrence of diffusion is conditioned on the existence of an infinite percolating cluster. At the percolation limit diffusion becomes anomalous, but these effects are beyond the scope of this paper.

The present system has previously been considered by Brak and Elliott [11] who attempted to calculate the blocking and correlation effects in the presence of bond disorder on a three-dimensional cubic lattice using a two-particle rate equation. This was an extension of the method introduced by Tahir-Kheli and Elliott (TKE) based on a truncation of the hierarchy of master equations [12]. This proved to be a useful way of interpolating between the exact results for high and low concentrations, and to be versatile enough to handle a number of more complex situations [13]. In the present paper we extend the treatment of particle diffusion using the concepts of random-walk theory as employed in the derivation of the diffusion coefficient of a tagged particle in the interstitial limit and in the single-vacancy limit of non-defective lattices. As in those cases, the results in disordered lattices are obtained by considering an effective-medium description of the system, and by considering the correlation effects to be described by an interpolation scheme similar to that found by TKE.

In this and the accompanying paper we shall consider in detail the simple example of the square net in two dimensions. In this paper, which treats bond disorder only, explicit numerical results will be obtained for the strongly disordered case where some bonds have zero hopping rate. This system has been simulated by using the Monte Carlo method.

This paper is arranged as follows. Section 2 summarizes the results of the TKE theory in an effective medium. Section 3 outlines the random-walk approach and derives an improved expression for the case of the two-dimensional bond-diluted square lattice. Section 4 describes the simulation in this system, the results of which are reported in section 5.

2. Effective-medium theory

The theory developed by TKE and others in its self-consistent form [14] gives an approximation for the diffusion coefficient of a tracer particle which can hop with a transition rate J_0 to nearest-neighbour sites on a d-dimensional cubic lattice with bond length a, in the presence of a concentration c of background particles which have transition rate J as

$$D = (1 - c)D_0 f \tag{1}$$

where

$$D_0 = J_0 a^2 \tag{2}$$

and

$$f^{-1} = 1 - \frac{2cJ_0\langle\cos\theta\rangle}{(J + J_0 f v)(1 + \langle\cos\theta\rangle)}. \tag{3}$$

The term $v = (1 - c)$, the concentration of vacancies into which hops can take place, represents the blocking factor and gives the mean-field approximation to the problem. f is the correlation factor which is a measure of the fraction of successful jumps which are effective in increasing the mean square displacement of the tagged particle since some successful jumps are 'wasted' due to an imbalance between the probabilities for a sequential hop in the forward and backward direction. This is related to $\langle\cos\theta\rangle$ which is defined as the average cosine of the angle between successive jumps on a lattice containing a single vacancy. For the case of self-diffusion when $J_0 = J$, f given by equation (3) depends only on $\langle\cos\theta\rangle$:

$$f^{-1} = 1 - \frac{2c\langle\cos\theta\rangle}{(1 + fv)(1 + \langle\cos\theta\rangle)}\,. \tag{4}$$

For a square lattice which we shall study numerically it can be shown (see Montet [15]) that

$$\langle\cos\theta\rangle = \frac{2}{\pi} - 1. \tag{5}$$

When defects are introduced in the form of a concentration p of missing bonds through which hopping is forbidden, there is a further blocking effect. The mean-field approximation yields

$$D = (1 - c)(1 - p)D_0 f. \tag{6}$$

However, it is well known that such a system breaks up into finite clusters when $p > p_c$, the percolation concentration, so $D = 0$ in this region. For $p < p_c$ it is generally accepted that diffusion is normal [16] but it becomes anomalous [17] at $p = p_c$. A detailed description of the percolation problem yields a scaling form of $D(p) \sim (p_c - p)^s$ where s is the critical exponent, but this is beyond the scope of the present paper.

An improvement to mean-field theory which gives a better approximation to the percolation effects is obtained by effective-medium theory which includes multiple scattering of the diffusing particles by the defects. In this problem [18, 19] the effective hopping rate takes the simple form

$$J_p = (1 - p/p_c)J \tag{7}$$

where

$$p_c = 1 - 2/Z \tag{8}$$

for a cubic lattice where Z is the number of neighbours. For a square net this gave $p_c = 1/2$ which is the correct result [20]. However, we note that the scaling form for $D(p)$ with $s = 1$ is incorrect in this limit. Nevertheless, it provides a very convenient working approximation:

$$D(p) = (1 - c)(1 - p/p_c)D_0 f. \tag{9}$$

The correlation factor f has been seen to be independent of J_p and hence is unaffected in this approximation. However, this factor depends on the microscopic environment of the interacting particle and vacancy. Since a successful jump must take place through a non-defective bond, not all neighbouring bonds are statistically equivalent after a successful jump. This characterizes a departure from the homogeneous situation implicit in the effective-medium approximation and introduces further correlation into the walk performed by a tagged particle on a defective lattice. We assume with Brak and Elliott [11] that these effects can be considered as a modification of $\langle \cos\theta \rangle$ for which we attempt to find a suitable approximation from random-walk concepts.

The basic argument is as follows. The TKE approximation is an extrapolation between the asymptotically correct form of f in the limits of small concentration c of background particles and of small concentration v of vacancies. We assume that the relationship between f and $\langle \cos\theta \rangle$ is preserved in the disordered lattice. By applying random-walk theory to the single-vacancy limit in the disordered lattice we obtain an expression for $\langle \cos\theta \rangle$ which accounts for the dynamical correlations, and which depends on the concentration of defects.

3. The random-walk approach

In what follows we will briefly review the derivation of the dynamical correlation factor in the single-vacancy limit in a non-defective lattice using random-walk concepts. We restrict the discussion to square lattices. In the next subsection we will consider the modifications induced by the presence of defects.

3.1. The non-defective lattice

The derivation of the dynamical correlation factor via random-walk theory has been extensively studied in the past [21, 22]. In order to introduce the main definitions we outline the main steps of this derivation.

The average mean square displacement of a tagged particle after a large number N' of successful jumps can be expressed as

$$\overline{R^2} = \sum_{i=1}^{N'} \sum_{j=1}^{N'} \overline{\boldsymbol{r}_i \cdot \boldsymbol{r}_j} \simeq N' \left(1 + 2 \sum_{l} \cos\theta_l \right) \tag{10}$$

where $\cos\theta_l$ is the average cosine of the angle between displacements l steps apart. In the single-vacancy limit, displacements arbitrarily far apart are correlated and it is possible to show that

$$\cos\theta_l = (\cos\theta)^l \tag{11}$$

where $\cos\theta \equiv \cos\theta_1$ designates the average cosine of the angle between two consecutive jumps of the tagged particle. Substituting equation (11) into equation (10), the following expression for the diffusion coefficient is obtained:

$$D = f_b f_0 \tag{12}$$

where

$$f_0 = \frac{1+\cos\theta}{1-\cos\theta} \tag{13}$$

and f_b, the blocking factor, is the fraction of successful jumps out of a given number N of attempts, i.e., $f_b = N'/N$. For the sake of simplicity we are working with units in which $D_0 = 1$. In order to evaluate $\cos\theta$, one has to consider the random walk performed by a single vacancy in the lattice just after an exchange with the tagged particle. Let r and i designate the positions of the tagged particle and the vacancy, respectively, after such an exchange. Let m designate the other neighbour of site r, opposite to the vacancy. In this situation $\cos\theta$ is given by

$$\cos\theta = P_{mi}^{(r)} - P_{ii}^{(r)} \tag{14}$$

where $P_{mi}^{(r)}$ and $P_{ii}^{(r)}$ are the probabilities of the vacancy returning to site r, for the first time, through site m or site i, respectively. These probabilities can be expressed in terms of generating functions which satisfy the difference equation

$$U_{lj}(\lambda) = \delta_{lj} + \lambda \sum_{l_1} p_{ll_1} U_{l_1 j}(\lambda) \tag{15}$$

and are defined by

$$U_{lj}(\lambda) = \sum_{N=0}^{\infty} \lambda^N P_{lj}(N). \tag{16}$$

In equation (15) p_{ll_1} is the probability for a transition between sites l and l_1, i.e., $p_{ll_1} = 1/4$ if l and l_1 are nearest neighbours, and zero otherwise. $P_{lj}(N)$ in equation (16) is the probability that a random walker initially occupying site j is at site l after N steps. In terms of these functions it is possible to show that (see appendix A)

$$P_{li}^{(r)} = \frac{1}{4}\left(U_{li}(1) - \frac{U_{lr}(1)U_{ri}(1)}{U_{rr}(1)}\right) \qquad (l = m, i). \tag{17}$$

Since by symmetry $U_{mr} = U_{ir}$, it follows that

$$\langle\cos\theta\rangle = \frac{1}{4}(U_{mi}(1) - U_{ii}(1)). \tag{18}$$

Equations (17) and (18) should be interpreted as being defined by a limiting process, since the generating functions in two dimensions are divergent for $\lambda = 1$ although these divergencies cancel in (17) and (18). Equations (12), (13) and (18) with the fact that $f_b = (1-c)$ completely specify the dynamic correlation factor for the limit of vanishingly small vacancy concentration.

The dynamical correlation factor for vanishingly small concentration of particles is given by

$$f_0 = 1 + \left(\frac{c}{1-c}\right)\left(\frac{\langle\cos\theta\rangle}{1+\langle\cos\theta\rangle}\right) \tag{19}$$

where $\langle\cos\theta\rangle$ is given by equation (18). A derivation of this expression from the solution of a second-order rate equation can be found in reference [12].

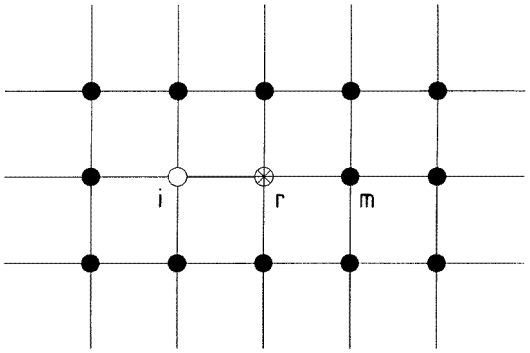

Figure 2. A schematic diagram of the situation just after a tracer–vacancy exchange in the single-vacancy case. The bond connecting the site occupied by the vacancy (i) to the site occupied by the tagged particle (r) is non-defective with probability one. The bond connecting r to site m has probability p of being defective.

3.2. The disordered lattice

According to the discussion of section 2, in the effective-medium picture, the dynamical correlation factor, equation (3), is, for vanishingly small concentration of vacancies, given by equation (13). In this approximation the interaction of a vacancy with the tracer particle is not affected by the presence of defects. In the actual system, however, we note that just after a successful jump of the tagged particle, the bond connecting the vacancy to the tagged particle is with probability one a non-defective bond. In an average sense, this fact leads to an enhancement in the probability for a return jump, since the bond connecting the tagged particle to the site opposite to the vacancy has a probability p of being defective. Figure 2 illustrates the situation. We expect this fact to enhance the correlation in the walk performed by the tagged particle, leading to a decrease in the correlation factor.

In the notation of the preceding subsection, the presence of disorder will change the probabilities $P_{mi}^{(r)}$ and $P_{ii}^{(r)}$, leading to a consequent change in the value of $\cos\theta$. The new value of $\cos\theta$ has to be evaluated by considering all possible bond environments, weighted by their respective probabilities, just after a successful jump of a tagged particle. This average will be approximated by considering an average medium for the vacancy, in which the vacancy hops to a nearest neighbour with probability $(1-p)/4$. As discussed above, the probability for a transition from site i to site r will be $1/4$. Since the value of $\cos\theta$ is highly sensitive to the existence or not of the bond connecting site r to site m, $\cos\theta$ will be evaluated separately for the two situations. The final result will, then, be given by the sum of the two values with weights $1-p$ and p, respectively. Note that the effective-medium approximation reflects characteristics of the large-scale arrangement of bonds in a defective lattice. The effective lattice appropriate to the evaluation of local or microscopic quantities, such as $\cos\theta$ or f_b, is the 'mean-field lattice' in which a transition between nearest neighbours is given by $(1-p)/4$ instead of $(1-2p)/4$.

In order to evaluate $\cos\theta$ for the two situations discussed above, we define the 'restricted' generating functions

$$U_{li}^{(r)} = \delta_{li} + \sum_{l_1 \neq r} p_{ll_1} p_{l_1 i} + \sum_{l_1 \neq r} \sum_{l_2 \neq r} p_{ll_1} p_{l_1 l_2} p_{l_2 i} + \cdots . \tag{20}$$

These functions can be interpreted as the average number of visits to site l by a random walker that starts at site i and avoids site r. In terms of these functions, $\cos\theta$ is expressed

as (see appendix A)

$$\cos\theta = p_{rm}U_{mi}^{(r)} - p_{ri}U_{ii}^{(r)}. \tag{21}$$

From equation (15), by iterating and at each iteration isolating the terms that involve sites i, r and m, it is possible to show that the functions $U_{mi}^{(r)}$ and $U_{ii}^{(r)}$ satisfy the following system of equations:

$$U_{ii}^{(r)} = 1 + a_{ii}U_{ii}^{(r)} + a_{im}U_{mi}^{(r)} \tag{22}$$

$$U_{mi}^{(r)} = a_{mi}U_{ii}^{(r)} + a_{mm}U_{mi}^{(r)} \tag{23}$$

where

$$a_{lj} = p_{lj} + \sum_{l_1 \neq i,r,m} p_{ll_1}p_{l_1 j} + \sum_{l_1 \neq i,r,m}\sum_{l_2 \neq i,r,m} p_{ll_1}p_{l_1 l_2}p_{l_2 j} + \cdots. \tag{24}$$

Note that the functions $U_{lj}^{(r)}$ and a_{lj} are symmetrical with respect to interchange of the subscript indices. The above equations are general. Noting that the functions a_{lj} $(l, j = i, m)$, involve only paths that do not 'visit' sites i, r and m, one can express the solution for general values of the transition probabilities p_{ri} and p_{rm} in terms of the solution for a perfect lattice, i.e., a lattice in which all transition probabilities have the same value. In the present case the perfect lattice is the one in which all transition probabilities are equal to $(1 - p)/4$. For this lattice, it is possible to show that (see appendix A)

$$\left[U_{ii}^{(r)}\right] = \frac{2}{1-p} \tag{25}$$

$$\left[U_{mi}^{(r)}\right] = \frac{2(2\cos\theta_0 + 1)}{1-p} \tag{26}$$

where from now on we enclose the quantities referring to the perfect lattice in square brackets and denote the corresponding value of $\cos\theta$ by $\cos\theta_0$. From equations (22) and (23) one obtains

$$[a_{ii}] = [a_{mm}] = 1 + \left(\frac{1-p}{8}\right)\left(\frac{1}{\cos\theta_0(1+\cos\theta_0)}\right) \tag{27}$$

$$[a_{im}] = [a_{mi}] = \frac{-1}{8}\left(\frac{1+2\cos\theta_0}{1+\cos\theta_0}\right)\frac{1-p}{\cos\theta_0}. \tag{28}$$

From equation (24), one can express the functions a_{lj} for the lattice with general p_{ri} and p_{rm} in terms of the corresponding functions for the perfect lattice

$$a_{ii} = [a_{ii}] + \lambda_i \tag{29}$$

$$a_{mi} = [a_{mi}] \tag{30}$$

$$a_{mm} = [a_{mm}] + \lambda_m \tag{31}$$

where

$$\lambda_l = p_{ll} - \left[p_{ll}\right] \qquad (l = i, m). \tag{32}$$

Substituting equations (29), (30) and (31) in equations (22) and (23) and taking into account equation (21) one finally obtains

$$\cos\theta = -\frac{p_{ri}(1 - [a_{ii}] - \lambda_m) - p_{rm}[a_{im}]}{(1 - [a_{ii}] - \lambda_i)(1 - [a_{ii}] - \lambda_m) - [a_{im}]^2}. \tag{33}$$

For the case in which $p_{ri} = 1/4$ and $p_{rm} = 0$, equation (33) yields

$$(\cos\theta)_I = -\frac{1 + 2\cos\theta_0(1+\cos\theta_0)}{1 + 2p\cos\theta_0(1+\cos\theta_0)} \tag{34}$$

while for $p_{ri} = 1/4$ and $p_{rm} = 1/4$ the following result is obtained:

$$(\cos\theta)_{II} = \frac{\cos\theta_0}{1 - p(1 + \cos\theta_0)}. \tag{35}$$

The final expression for $\cos\theta$ is, therefore, given by

$$\langle\cos\theta\rangle = -p\frac{1 + 2\cos\theta_0(1 + \cos\theta_0)}{1 + 2p\cos\theta_0(1 + \cos\theta_0)} + (1 - p)\frac{\cos\theta_0}{1 - p(1 + \cos\theta_0)}. \tag{36}$$

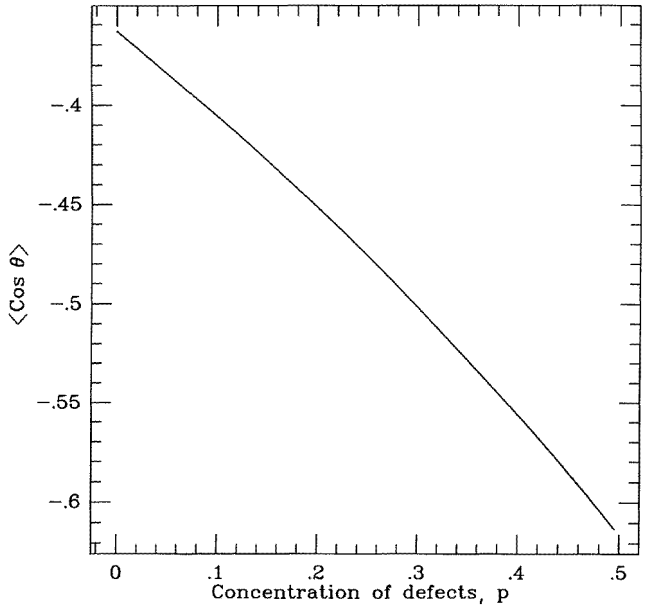

Figure 3. The average cosine of the angle between successive displacements of the tagged particle as given by equation (36), as a function of the defective bond concentration p.

We expect this expression to be valid only for low to intermediate concentrations of defects. For higher concentrations, i.e., p near the percolation threshold, the average procedure followed in the derivation of equation (36) clearly breaks down, since it does not account properly for the existence of dead ends and finite clusters. In figure 3, the corrected value of $\langle\cos\theta\rangle$ is plotted as a function of p. As expected, the tendency for a backward jump increases with increasing p leading, therefore, to a decrease in the dynamical correlation factor with increasing concentration of defects.

4. Simulation

A system of hopping particles in a lattice is generally described by the continuous-time master equation

$$\frac{\mathrm{d}P(\alpha, t)}{\mathrm{d}t} = \sum_{\beta} W_{\alpha\beta} P(\beta, t) - \sum_{\beta} W_{\beta\alpha} P(\alpha, t) \tag{37}$$

where $W_{\alpha\beta}$ is the probability per unit time for a transition from configuration β to configuration α and $P(\alpha, t)$ is the probability of configuration α at time t, for a given initial

condition. For such a lattice system in configuration ν we can define p_i^ν as the tagged particle and n_i^ν as the background particle occupation number (with value 0 or 1) such that the average occupation (or the probability of occupation) of site i is $\langle p_i \rangle = \sum_\nu p_i^\nu P(\nu, t)$ or $\langle n_i \rangle = \sum_\nu n_i^\nu P(\nu, t)$, respectively.

Since in our model the transitions between configurations α and β correspond to the hopping of particles between sites i and j with rate J_{ij}, the set $[W_{\alpha\beta}]$ can be mapped to the set $[J_{ij}]$. This reduces the master equation to the rate equations used by TKE. Furthermore, it can be shown that equation (37) has a solution expressed in terms of a discrete-time Poisson process with the one-step transition matrix A and some total transition rate λ. Now if J denotes the probability per unit time for a transition of a single particle between two sites, the total transition rate λ can be conveniently fixed to the maximum transition rate out of the possible configurations, i.e. $\lambda = N_p Z J$, where N_p is the number of particles in the system. Then the elements of A assume the form

$$A_{\alpha\beta} = \frac{1}{N_p Z} n_{\alpha\beta} \tag{38}$$

$$A_{\alpha\alpha} = 1 - \frac{1}{N_p Z} \sum_\beta n_{\alpha\beta} \tag{39}$$

where $n_{\alpha\beta}$ is equal to unity if the transition between configurations α and β is possible, and zero otherwise. These matrix elements specify completely the simulation procedure.

For a tracer particle initially positioned at the origin the mean square displacement after N discrete steps calculated over all M initial configurations, forming a set F, is

$$\langle R^2(N) \rangle = \frac{1}{M} \sum_{\beta \in F} \sum_\alpha R_\alpha^2 (A^N)_{\alpha\beta}. \tag{40}$$

In the case of a diffusive tracer, and for a sufficiently large number of system steps, the relation between $\langle R^2(N) \rangle$ and N is essentially linear, such that

$$\langle R^2(t) \rangle = \langle R^2(\tilde{N}) \rangle \tag{41}$$

where $\tilde{N} = N_p Z J t$ is the average number of system steps in time t. Note that if the relation between $\langle R^2(N) \rangle$ and N involves non-linear terms, equation (41) is no longer valid.

In the case of a disordered system the above equations have to be modified to reflect the absence of spatial homogeneity and to incorporate an additional average over the disorder. In particular, for the bond-disordered system discussed before, equation (40) assumes the form

$$\langle R^2(N) \rangle = \frac{1}{N_c} \frac{1}{M} \sum_b \sum_\beta \sum_\alpha (R_\alpha - R_\beta)^2 (A^N)_{\alpha\beta}^b \tag{42}$$

where N_c is the total number of bond configurations and the sum over b denotes the sum over all different bond configurations. The superscript b accounts for the fact that for each bond configuration there is a different transition matrix A.

4.1. Procedure

In this paper all simulations were carried out on square lattices with $N_s \times N_s$ sites and periodic boundary conditions. In most cases we chose $N_s = 100$, but used also $N_s = 150$ to check finite-size effects. Out of the $2N_s^2$ bonds, a fraction p were randomly selected and considered as 'open' bonds. They were labelled in such a way that they could be distinguished from the remaining 'normal' bonds. Next, a total number of N_p ($N_p = cN_s^2$)

particles were randomly distributed to the lattice sites. In the simulations p ranged from 0.00 to 0.40 and c from 0.00 to 0.90. A label was assigned to each site indicating whether it was empty or not. A different label was assigned to each particle. The simulation loop starts by randomly selecting both a particle and one of its nearest neighbours. If there is a normal bond between the selected particle and the nearest-neighbour site and if the latter is not, already, occupied by another particle, the selected particle is moved. Otherwise the configuration of the system is kept unchanged. It is easily checked that this procedure correctly reproduces the probabilities for a transition between two configurations and for staying at the same configuration, as given by equations (38) and (39), respectively.

In the simulations time is measured by Monte Carlo steps per particle (MCS/p), while the unit of time is set equal to $1/JZ$. The basic simulation loop is repeated $\tilde{N}$ $(=N_pJZt)$ times and the total time span was chosen to be 2000 MCS/p. After each MCS/p the average tracer particle mean square displacement is evaluated and the complete time history is recorded. In order to get improved statistics the whole process is repeated N_d times and the final result is obtained by taking an average over these time histories.

The movement of a particle in a finite system with periodic boundary conditions can be translated to the movement in an infinite system formed by spatially repeating the original finite system. Thus it is possible to follow a particle up to arbitrarily large displacements. Since all particles have the same hopping rate, we can improve the statistics of calculating the mean square displacement of the tracer by including the histories of background particles and averaging over them. Since each particle has a distinct initial position in the lattice, this average is an approximation to the one defined in equation (42).

In order to obtain an estimate of the uncertainty in the values of $\langle R^2\rangle$, the average value of $\langle R^4\rangle$ is also calculated for determining the variance

$$\sigma^2 = \langle R^4\rangle - \langle R^2\rangle^2. \tag{43}$$

This quantity is relevant to a weighted linear fitting discussed in the next section.

4.2. Data analysis

As stated before, the computation of $\langle R^2\rangle$ involves an average over the histories of all particles in the lattice for different configurations of missing bonds. A question that naturally arises is that of how large should the ensemble of bond-disordered systems be in order to obtain good statistics. It should be noted that each additional average over the bond disorder adds N_p histories of tracer particle to the averaging process leading to $\langle R^2\rangle$. In the preliminary runs, it was noticed that, for large number of particles in the lattice, after a few averages over the bond disorder, the variance of the values of R^2 remained practically constant. This fact was taken as an indication that for the range of values in p investigated and for the lattice size considered, the fluctuations in the distribution of clusters were small. It also indicates that the average performed gives a self-averaging property [9] and, accordingly, it was assumed that relatively few averages over the bond disorder would be sufficient to approximate the distribution of R^2. This number (N_d) was then chosen in such a way that the total number of tracer particle histories involved in the evaluation of $\langle R^2\rangle$ remained practically constant for all values of c. Using the variance σ^2/N_dN_p defined in equation (43) the number of histories was fixed for each pair of p and c in the range 47 000–55 000. With this choice, the estimated value of the standard deviation of $\langle R^2\rangle$ remained within 0.5%–1.5%.

The diffusion coefficient was obtained from the $\langle R^2\rangle$ data through a fitting procedure, as follows. Below the percolation threshold there exists, in the average sense, a percolating

cluster, regardless of the value of p (see Stauffer [23]). Let P_∞ denote the probability that a randomly selected site belongs to the percolating cluster and n_s the number of clusters with s sites, normalized with the total number of sites in the lattice. Then the average value of $\langle R^2 \rangle$ after N MCS/p is expected to assume the form (neglecting the possible existence of a logarithmic term as discussed by van Beijeren and Kutner [24])

$$\langle \tilde{R^2} \rangle = P_\infty D_\infty N + \sum_s s n_s R_s^2 \tag{44}$$

where D_∞ is the tracer diffusion coefficient in the percolating cluster and R_s^2 denotes the average mean square displacement of a tracer particle confined to a finite cluster of size s. For sufficiently large N, the second term on the right-hand side becomes independent of N, rendering the relation between $\langle \tilde{R^2} \rangle$ and N linear. Then the definition of the tracer diffusion coefficient is $D = P_\infty D_\infty$ and thus the fitting function is a straight line with the slope giving D. The intercept is related to the long-time contribution of finite clusters to $\langle \tilde{R^2} \rangle$.

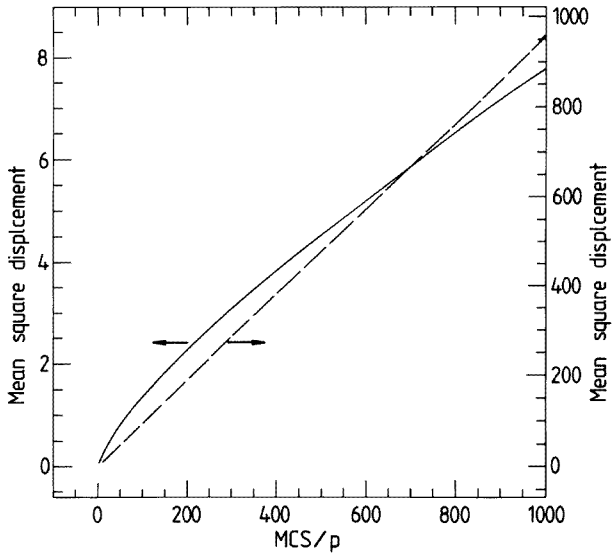

Figure 4. Mean square displacement (in units of bond length) versus time for (a) $p = 0.40$, $c = 0.90$ (solid line) and (b) $p = 0.01$, $c = 0.01$ (dashed line).

In order to perform the linear fitting we have to first estimate the number of time steps necessary for the finite-cluster contribution to become independent of N. This was found to be dependent on p being about 500 MCS/p for $p = 0.40$ (see figure 4). Since the distribution of $\langle R^2 \rangle$ has a variance that changes with N, a weighted linear least-squares fitting was used to obtain D. Following Bevington [25] the estimated variances of each data point were used as weighting factors. If we assume that the values of $\langle R^2 \rangle$ for different values of N are statistically independent, which is not the case, an estimation of the standard deviation of D can be evaluated. However, the estimator thus obtained proved to be much smaller than the actual variability observed in some ensembles generated through additional runs. We then resorted to a more direct method. The estimated variance of $\langle R^2 \rangle$ increases with increasing value of p and it is plausible to expect similar behaviour in the standard deviation of D. Ensembles with statistically independent samples were generated for the

extreme values of p and an estimation of the standard deviation of D was then evaluated. With fifteen samples in each ensemble, the results suggest a standard deviation of the order of 0.5% for small values of p ($p = 0.00$) and 1% for large values of p ($p = 0.40$). For the intermediate values of p the standard deviation is expected to lie within these limits.

As mentioned previously we checked finite-size effects for $N_s = 150$ and two pairs of parameters: ($p = 0.09, c = 0.01$) and ($p = 0.40, c = 0.50$). The fluctuations observed in the results were of the same order as the expected standard deviation. Previous simulations of tracer diffusion in perfect lattices [26], also in two dimensions, did not show any noticeable influence of the finite-size effects on the results, and none is expected as long as the tracer root mean square displacement along either the x- or y-direction is small compared to the system dimensions. In the case under consideration, the presence of disorder has the effect of decreasing the mean square displacement, hence attenuating the influence of any finite-size effects that would, eventually, be present in a perfect lattice.

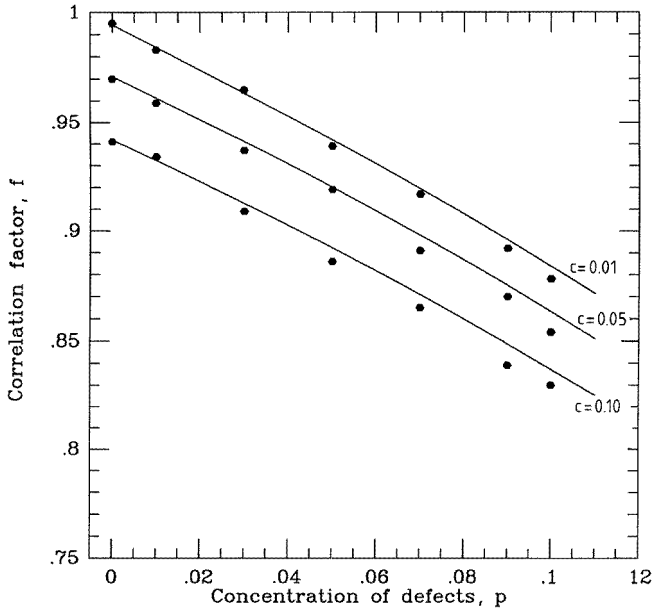

Figure 5. Simulation results (points) for the correlation factor for small p and c. The full lines give the results of the theory (equation (45)) using $\langle \cos\theta \rangle$ given by equation (5) which is the analytically correct result as $c \to 0$, $p \to 0$. The results obtained using the improved formula (equation (36)), though not shown here, give complete agreement with the points.

5. Results and conclusions

The simulations were carried out in two regimes: a coarse grid of points for $0 < c < 1$ and $0 < p < 0.5$ at intervals of approximately 0.1, and a more detailed study for small values of $c = 0.01, 0.05$ and 0.10 and $0.01 < p < 0.09$. Special consideration was given to the case of $p = 0$ in which direct comparison can be made with the simulations of Tahir-Kheli and El-Meshad [26]. Their results were obtained from averages involving around 10^6 tracer particle histories and they quote an error of around 0.6%. Extrapolating from our results using about 50 000 tracer particle histories we would expect this error to be smaller

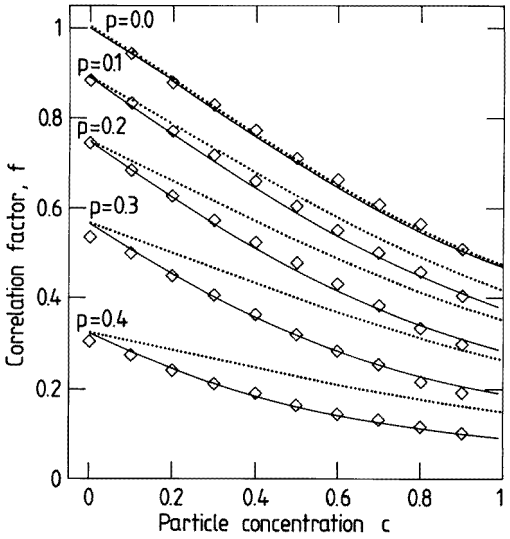

Figure 6. Simulation results of the correlation factor for a wide range of p and c. The results of the theory (equation (45)) obtained using the uncorrected value (equation (5)) of $\langle\cos\theta\rangle$ are shown by the dotted lines. The results obtained using the improved formula (equation (36)) are shown by full lines. The two theories are identical for $p = 0$.

Table 1. Comparison between the correlation factors obtained from (a) simulations by Tahir-Kheli and El-Meshad (reference [26]), from (b) our simulations and from approximate theory (equations (45)–(46)) for $p = 0$.

c	Simulation (a)	Simulation (b)	Approximation (equations (45)–(46))
0.2002	0.882	0.876	0.881
0.3003	0.824	0.826	0.821
0.4002	0.767	0.772	0.761
0.5001	0.710	0.708	0.705
0.6000	0.657	0.662	0.647
0.6991	0.604	0.605	0.596
0.8002	0.552	0.561	0.548
0.9002	0.507	0.505	0.506

i.e. within the range 0.1%–0.2%. Results from the two simulations given in table 1 and show good agreement within the quoted error bars. They are also compared there with the approximate theory for f given by equation (3) which has the solution

$$f = \frac{-rc + \sqrt{(rc)^2 + 4v}}{2v} \tag{45}$$

where

$$r = \frac{1 - \langle\cos\theta\rangle}{1 + \langle\cos\theta\rangle}. \tag{46}$$

The main results of our simulation studies are shown in figures 5 and 6. The correlation factor plotted in the figures is $D(p)/(1-v)D_0$ as defined by equation (9), namely $(1-2p)f$. The agreement with the simple TKE theory obtained using the geometrical value of $\langle\cos\theta\rangle$

given by equation (5) is reasonably good for small c (see figure 5) where it is asymptotically correct and in any case $f \to 1$, but the deviations increase as c and p increase. The agreement using the improved value of $\langle \cos\theta \rangle_p$ given by equation (36) is much better (see figure 6) over the whole range of values of c and p.

Our results of the computer simulation of tracer diffusion on a square lattice with static bond disorder show the expected dependence on bond concentration with the diffusion constant falling to zero at the percolation concentration $p_c = 1/2$. In addition the characteristic dependence on vacancy concentration is as found in a many-particle system. The dynamical correlation effects are found to be significantly affected by the static disorder, and this interplay is effectively described by an approximate treatment using random-walk theory. The method can be readily generalized to three-dimensional lattices. In an accompanying paper similar arguments are applied to study a system where the disorder consists of variations in the site energies and their occupation.

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Appendix A

We consider a two-dimensional lattice in the single-vacancy limit, just after a tracer particle–vacancy exchange. Let i and r designate the sites occupied by the vacancy and the tracer particle, respectively, and let m designate the other site neighbour to r, opposite to the vacancy (see figure 2). The probability that the vacancy returns to r, for the first time, through site i (m), is given by the sum of all weighted paths that connect site i to site i (m), avoiding site r, multiplied by the probability of the final jump $i \to r$ ($m \to r$). Formally one can write

$$P_{li}^{(r)} = p_{rl} U_{li}^{(r)} \qquad (l = i, m) \tag{A1}$$

where

$$U_{li}^{(r)} = \delta_{li} + p_{li} + \sum_{l_1 \neq r} p_{ll_1} p_{l_1 i} + \sum_{l_1 \neq r} \sum_{l_2 \neq r} p_{ll_1} p_{l_1 l_2} p_{l_2 i} + \cdots . \tag{A2}$$

The average cosine of the angle between two successive jumps of the tagged particle is, therefore, given by

$$\cos\theta = p_{rm} U_{mi}^{(r)} - p_{ri} U_{ii}^{(r)} . \tag{A3}$$

In the case of a perfect lattice, in which all transition probabilities are the same, with $p_{ll'} = q$ for l and l' being nearest neighbours and $p_{ll} = 1 - 4q$, the restricted generating functions $U_{li}^{(r)}$ assume a particularly simple form. Departing from equation (15) we have

$$U_{li} = \delta_{li} + \sum_{l_1 \neq r} p_{ll_1} U_{l_1 i} + p_{lr} U_{ri} . \tag{A4}$$

If one iterates equation (A4) and at each iteration isolates the term involving site r, the following expression is obtained:

$$U_{li} = U_{li}^{(r)} + U_{lr}^{(r)} U_{rj} \qquad (l \neq r). \tag{A5}$$

On the other hand, by iterating the equation for U_{lr} in a similar way, it is possible to show that

$$U_{lr}^{(r)} = U_{lr}^{(r)} U_{rr}. \tag{A6}$$

From equations (A5) and (A6) one, then, obtains

$$U_{li}^{(r)} = U_{li} - \frac{U_{lr} U_{ri}}{U_{rr}}. \tag{A7}$$

From equation (15) it can be shown that the generating functions U_{li} for a given q are related to the ones for $q = 1/4$, $\overline{U_{li}}$, by

$$4q U_{li} = \overline{U_{li}}. \tag{A8}$$

From symmetry one obtains

$$\overline{U_{lr}} = \overline{U_{ii}} - 1 \qquad (l \text{ is a nearest neighbour of } r) \tag{A9}$$

$$\overline{U_{ii}} = \overline{U_{rr}}. \tag{A10}$$

For two dimensions it is a known result that $\lim_{\lambda \to 1^-} \overline{U_{ii}} \to \infty$. From these results, it is shown that

$$U(r)_{ii} = \frac{2}{4q} \tag{A11}$$

$$U(r)_{mi} = \frac{2(2\cos\theta_0 + 1)}{4q}. \tag{A12}$$

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