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A model of diffusion in a spatially disordered lattice

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Abstract. An approximate method for the study of one-particle diffusion in a three-dimensional (3D) disordered lattice is proposed. The method is based on the locator expansion of a generalized discrete version of the diffusion equation. Approximations are performed through a convenient interpretation of the resulting equations in terms of known quantities that characterize a discrete-time random walk. The method is applied to a model of a disordered lattice in which allowed sites are randomly distributed in a continuum at a given concentration n and hopping is allowed between sites separated by a distance not greater than a specified fixed value a_0. The results are in good agreement with the expected physical situation, showing the existence of two regions in the parameter space (n, a_0), one of which is characterized by the existence of normal diffusion and the other by the vanishing of the diffusion constant, with the random walker confined in a cluster of finite size. The two regions are separated by a critical curve, along which the diffusion is shown to be anomalous. The three different regimes are characterized by a single parameter, the average number of nearest neighbours. A connection with percolation theory is made, the formalism yielding values for the exponents γ and ν. The results $\gamma = 2$ and $\nu = 1$ are obtained in the 3D case. For dimensions greater than four it is shown that the predicted critical exponents agree with the mean field values $\gamma = 1$ and $\nu = \frac{1}{2}$.

1. Introduction

There has been a growing interest in the problem of classical diffusion in disordered systems. This problem is relevant to a number of physical situations. Current applications include the study of electronic hopping transport in amorphous semiconductors (Scher and Lax 1973) and the modelling of tracer diffusion in glassy electrolytes (Brak and Elliott 1989).

In the present work we shall be concerned with the problem of a single particle diffusing in an otherwise empty lattice. Several versions of this problem, with different types of disorder, have been investigated. Typical examples are the diffusion in lattices with forbidden sites (Kaski *et al* 1982) and various models of diffusion in lattices with random barriers (Haus and Kehr 1987). The main current theoretical approach to these systems is based on the application of a version of the coherent potential approximation (CPA), which is also known in this context as the effective medium approximation (EMA) (Webman 1981). As is well known the CPA is based on the propagator expansion of a Dyson-type equation and its practical implementation requires an ordered underlying lattice. Another possible expansion of the aforementioned equation is given by the so-called locator expansion (Ziman 1979). In this form the resulting equation is particularly suitable for the implementation of approximate schemes to deal with spatially disordered lattices. Departing from this expansion Matsubara and Toyozawa (MT) (1961) proposed an approximate method for the investigation of the spectrum of a tight-binding Hamiltonian corresponding to a spatially disordered lattice. Our purpose here is to present a modified version of the MT scheme

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appropriate to the treatment of a one-particle diffusion problem in a spatially disordered lattice.

In the remaining part of this section we discuss the relevant aspects of the model we shall consider. In section 2 the basic definitions pertinent to the proposed method are presented. An application to an ordered linear chain illustrates its general aspects. In section 3 a correspondence between continuous-time and discrete-time random walks is established. This correspondence provides a conceptual framework for the interpretation of relevant quantities that naturally appear in the method. Section 4 is dedicated to the application of the method to the model in consideration. In section 5 we discuss the implications of the results obtained in the previous section and derive the long-time behaviour of the particle mean-square displacement. A connection with percolation theory in a disordered lattice is made. Section 6 contains the concluding remarks.

The model we shall consider is characterized by a particle performing a random walk in a lattice with allowed sites randomly distributed at a given concentration n. The 'dynamics' of the system is described by the rate equation

$$\frac{\mathrm{d}P_{mi}}{\mathrm{d}t} = \sum_l J_{ml} P_{li} - \sum_l J_{lm} P_{mi} \tag{1.1}$$

where P_{mi} is interpreted as the conditional probability of finding the random walker at site m at time t if it started at site i at time $t = 0$. The hopping rates J_{ij} are assumed to be symmetrical and dependent only on the distance between sites i and j. Due to the short-range nature of the hopping process, we will assume the following form for the hopping rates:

$$J_{ij} = \begin{cases} J_0 & \text{if } |\boldsymbol{R}_i - \boldsymbol{R}_j| \leqslant a_0 \\ 0 & \text{otherwise.} \end{cases} \tag{1.2}$$

Equation (1.2) is in fact the definition of nearest neighbour in the present system. We note that this equation also defines a percolation problem since depending on the concentration n of sites and the range a_0 of the hopping rates there will exist or not an infinite percolating cluster of 'connected' sites. It is well known that the diffusion problem is intimately related to the percolation one since a particle departing from a given site will only have access to the sites connected to that site. The relation between the diffusion and the percolation problems is further explored in Section 5.

For further reference we note that in the limit of high concentrations, here characterized by the inequality $4/3\pi a_0^3 \gg 1/n$, a fair approximation to the diffusion constant is obtained by taking the configurational average of equation (1.1) and decoupling the average on the right-hand side. This approximation leads to the result

$$D_0 = \tfrac{1}{10} J_0 a_0^2 Z \tag{1.3}$$

where

$$Z = n \tfrac{4}{3}\pi a_0^3 \tag{1.4}$$

is the average number of nearest neighbours.

2. The method

The Laplace transform of equation (1.1) is given by

$$sG_{mi} - P_{mi}(0) = \sum_l J_{ml}(G_{li} - G_{mi}) \tag{2.1}$$

where

$$G_{mi} = \int_0^\infty P_{mi}(t)\exp(-st)\,dt. \tag{2.2}$$

The initial condition

$$P_{mi}(0) = \delta_{mi} \tag{2.3}$$

implies the following normalization condition over the Green functions G_{mi}

$$\sum_m G_{mi}(s) = \frac{1}{s}. \tag{2.4}$$

By iterating equation (2.1) it is possible to obtain the following expressions for the diagonal and off-diagonal Green-function elements:

$$(s + \varepsilon_i - \Sigma_{ii})G_{ii} = 1 \tag{2.5}$$

$$G_{mi} = \Gamma_{mi}^{(i)} G_{ii} \qquad (m \neq i) \tag{2.6}$$

where

$$\Sigma_{ii} = \sum_{l\neq i} J_{il} g_l J_{li} + \sum_{l\neq i}\sum_{l_1\neq i} J_{il} g_l J_{ll_1} g_{l_1} J_{l_1 i} + \dots \tag{2.7}$$

$$\Gamma_{mi}^{(i)} = g_m J_{mi} + \sum_{l_1\neq i} g_m J_{ml_1} g_{l_1} J_{l_1 i} + \sum_{l_1\neq i}\sum_{l_2\neq i} g_m J_{ml_1} g_{l_1} J_{l_1 l_2} g_{l_2} J_{l_2 i} + \dots \tag{2.8}$$

$$g_l = 1/(s + \varepsilon_l) \qquad \varepsilon_l = \sum_r J_{rl}.$$

The series appearing in equations (2.5), (2.6), (2.7) and (2.8) can be conveniently interpreted as a sum of an infinite number of weighted paths. Each path is labelled by a sequence of sites and is weighted in a systematic way by the hopping elements J_{ij} and the locators g_l. We note for the time being that Σ_{ii} can be interpreted as the sum of the weighted paths that link site i to itself with only one return to site i, while G_{ii} is the sum of all the weighted paths that connect site i to itself. $\Gamma_{mi}^{(i)}$, on the other hand, can be interpreted as the sum of the weighted paths that connect site i to site m without any return to site i and G_{mi} is the sum of all the weighted paths that connect site i to site m. With further manipulation it is possible to rewrite equations (2.7) and (2.8) in the following form:

$$\Sigma_{ii} = \sum_l J_{il} G_{ll}^{(i)} J_{li} + \sum_l \sum_{l_1}{}' J_{il} G_{ll}^{(i,l_1)} J_{ll_1} G_{l_1 l_1}^{(i)} J_{l_1 i} + \dots \tag{2.9}$$

$$\Gamma_{mi}^{(i)} = J_{mi} G_{mm}^{(i)} + \sum_l G_{mm}^{(i,l)} J_{ml} G_{ll}^{(i)} J_{li} + \sum_l \sum_{l_1}{}' G_{mm}^{(i,l,l_1)} J_{ml} G_{ll}^{(i,l_1)} J_{ll_1} G_{l_1 l_1}^{(i)} J_{l_1 i} + \dots \tag{2.10}$$

where the primes indicate that there is no repetition of summation indices in the multiple sums. The factors $G_{l_\nu l_\nu}^{(i,l_1,l_2,\ldots)}$ can be interpreted as the sum of the paths that connect site l_ν to itself avoiding sites $i, l_1, l_2, \ldots$. Their formal definition is given by equations similar to equations (2.5) and (2.7), with the restrictions over $(i, l_1, l_2, \ldots)$ incorporated into equation (2.7).

Equations (2.5)–(2.10) are similar to those obtained by MT with the exception that in their work the 'restricted' diagonal Green functions $G_{l_\nu l_\nu}^{(i,l_1,l_2,\ldots)}$ were identified with the 'unrestricted' diagonal Green function G_{ii}.

To illustrate the basic aspects of the method, we consider the case of an ordered infinite chain. In the case of a one-dimensional lattice, due to the simple topology, equations (2.9) and (2.10) simplify and it is possible to work out a closed solution using equation (2.4). In particular equation (2.9) reduces to

$$\Sigma_{ii} = \sum_{l}{}' J_{il} G_{ll}^{(i)} J_{li}. \tag{2.11}$$

On the other hand, equation (2.10) will have only one term corresponding to the direct path from site i to site m. A restricted Green function G is associated with each site except site i. Since the paths contained in each factor G exclude the sites already 'visited', G will be constituted by the sum of the weighted paths to the right or left, according to the position of site m with respect to site i, that begin and end at the particular site with which it is associated. In an infinite chain, all paths of such a collection associated with any particular site are equivalent and therefore all the factors G are equal. Let

$$G = G_{l_\nu l_\nu}^{(i,l_1,\ldots)}.$$

Since the hopping rates are also constant, $J_{ij} = J$, equation (2.10) reduces to

$$\Gamma_{mi}^{(i)} = (GJ)^m \tag{2.12}$$

for each site m situated to the right or left of site i. For convenience we are considering site i as the origin for the labelling of the sites, i.e., site m is the mth site to the right or left of site i. Equations (2.4), (2.5), (2.11) and (2.12) define the following closed system of equations:

$$2G_{ii}GJ/(1 - JG) + G_{ii} = 1/s \tag{2.13a}$$

$$G_{ii} = 1/(s + \varepsilon_0 - \Sigma_{ii}) \tag{2.13b}$$

$$\Sigma_{ii} = 2J^2 G \tag{2.13c}$$

with $\varepsilon_0 = 2J$. Solving the system for G and G_{ii} and making use of equations (2.12) and (2.6) the following expression for the Green functions G_{mi} is found:

$$G_{mi} = \left\{\left[s + \varepsilon_0 - \sqrt{(s+\varepsilon_0)^2 - \varepsilon_0^2}\right]/\varepsilon_0\right\}^m \left(\sqrt{(s+\varepsilon_0)^2 - \varepsilon_0^2}\right)^{-1}. \tag{2.14}$$

The inverse Laplace transform of equation (2.14) is given by

$$P_{mi} = \frac{1}{2\pi}\int_0^{2\pi} \exp\{im\theta - 2Jt[1 - \cos(\theta)]\}\,\mathrm{d}\theta = I_m(2Jt)\exp(-2Jt) \tag{2.15}$$

where I_m denotes the modified Bessel function of order m. Equation (2.15), as is well known, is the solution of the difference equation (2.1) for the initial condition (2.3) in the case of an ordered infinite chain.

3. Discrete- and continuous-time random walk

In this section we investigate the relation between a continuous-time random walk (CTRW) and a discrete-time random walk (DTRW) performed on the same lattice. In a CTRW the probability that site j is visited in the time interval $t, t+dt$ is given by the probability that the random walker is occupying site j at time t multiplied by the probability that it suffers a transition out of this site in the subsequent time interval dt, i.e., $P_{ji}(t)ZJdt$, where Z is the number of nearest neighbours and i denotes the site of departure at time $t = 0$. The average number of visits to site j is hence given by the integral of $P_{ji}(t)ZJ$ from $t = 0$ to infinity. Let $Q_{ji}(n)$ be the probability that a particle undergoing a random walk on the same lattice arrives at site j from site i in n steps. The average number of visits to a given site, in this discrete version, in complete analogy to the continuous-time case, is given by the sum of the probabilities $Q_{ji}(n)$ from $n = 0$ to infinity. In what follows we show formally that the average numbers of visits obtained in the two cases are equivalent and that this equivalence is a consequence of a general relation existing between the Laplace transform of the probabilities $P_{ji}(t)$ and the generating functions for the probabilities $Q_{ji}(n)$.

The discrete-time probabilities satisfy the following recursive relation:

$$Q_{ji}(n) = \sum_l p_{jl} Q_{li}(n-1) \tag{3.1}$$

where p_{jl} is the probability for a transition from site l to site j. These latter quantities satisfy the normalization equation

$$\sum_j p_{jl} = 1. \tag{3.2}$$

The generating function for the probabilities $Q_{ji}(n)$ is defined by

$$U_{ji}(z) = \sum_{n=0}^{\infty} z^n Q_{ji}(n). \tag{3.3}$$

It is easily shown that these functions satisfy the equation

$$U_{ji}(z) = \delta_{ji} + z \sum_l p_{jl} U_{li}(z) \tag{3.4}$$

where we have made use of the initial condition $Q_{ji}(0) = \delta_{jl}$. Comparing equations (3.4) and (2.1) we note that they have a similar structure. A brief analysis reveals that two cases have to be considered. If the total rate with which the particle leaves a given site is site-independent, i.e.,

$$\sum_r J_{rl} = \varepsilon_l = \varepsilon_0 \tag{3.5}$$

then equations (3.4) and (2.1) are isomorphic, and their solutions are related by the following identifications:

$$(s + \varepsilon_0) G_{ji} = U_{ji} \tag{3.6a}$$

$$\varepsilon_0 / (s + \varepsilon_0) = z \tag{3.6b}$$

$$J_{jl}/\varepsilon_0 = p_{jl}. \tag{3.6c}$$

If ε_l is site dependent, then the solutions are related only in the limit $z \to 1^-, s \to 0^+$, the identifications being

$$\lim_{s\to 0^+} \varepsilon_j G_{ji}(s) = \lim_{z\to 1^-} U_{ji}(z) \tag{3.7a}$$

$$J_{jl}/\varepsilon_l = p_{jl}. \tag{3.7b}$$

The quantity on the left-hand side of equation (3.7*a*) is the integral of $\varepsilon_j P_{ji}(t)$ from zero to infinity and can be interpreted, as discussed before, as the average number of visits to site j for a random walker departing from site i. The quantity $U_{ji}(1)$, on the other hand, is the equivalent quantity for a DTRW walk.

We now turn our attention to the probability $f_{ji}(n)$ of a particle departing from site i arriving at site j for the first time after n steps. The generating function for these probabilities is defined by

$$F_{ji}(z) = \sum_{n=1}^{\infty} z^n f_{ji}(n). \tag{3.8}$$

The relation between the generating functions U and F is a well known result of DTRW theory and is expressed by

$$U_{ji} = \delta_{ji} + F_{ji}U_{jj}. \tag{3.9}$$

In particular we have that

$$U_{ii} = 1/(1 - F_{ii}). \tag{3.10}$$

Comparing equation (3.10) with equation (2.5) and taking into account equation (3.7*a*) the following additional identification is obtained:

$$\lim_{s\to 0^+} \frac{\Sigma_{ii}(s)}{\varepsilon_i} = \lim_{z\to 1^-} F_{ii}(z). \tag{3.11}$$

Within the framework of DTRW theory, $F_{ii}(1)$ is interpreted as the probability of return to the origin. Evidently this same interpretation applies to the corresponding quantity in the CTRW theory. These analogies between U and G and between F and Σ play an important role in the interpretation of the results presented in the following sections.

4. Disordered system

In this section we extend the application of the formalism presented in section 2 to a 3D spatially disordered lattice. The effects of disorder will be taken into account by considering the conditional ensemble average of the relevant quantities. The averages will be performed assuming that N_s allowed sites are randomly distributed in a volume Ω. The limit $N_s \to \infty$, $\Omega \to \infty$ with N_s/Ω finite is implicitly considered throughout the calculations. It will also be assumed that the allowed sites are distributed in a statistically independent way. All correlations that arise when a finite volume is associated to each site are thus disregarded. Another important aspect of the averaging procedure concerns the average over the distribution of clusters. Depending on the values of the concentration n

of allowed sites and of the range a_0 of the hopping rates the system will present or not an infinite percolating cluster. Let P_∞ be the probability that a randomly chosen site belongs to the infinite percolating cluster and n_k be the number of clusters with k sites normalized by the total number of allowed sites. Since the origin of the random walk can be either inside a finite cluster of any size or inside the infinite percolating cluster, it is clear that quantities such as $\Gamma_{mi}^{(i)}$, which depend explicitly on the number of sites linked to the origin, should be averaged simultaneously over the disorder in the position of the allowed sites and over the distribution of clusters, i.e.,

$$\langle \Gamma_{mi}^{(i)} \rangle = \sum_k k n_k \langle \Gamma_{mi}^{(i)}(k) \rangle + P_\infty \langle \Gamma_{mi}^{(i)}(\infty) \rangle$$

where $\Gamma_{mi}^{(i)}(k)$ denotes the value of the respective series for a cluster with k sites. Since the distribution of clusters is not known, we will adopt a kind of EMA assuming that the average in the above equation can be replaced by

$$\langle \Gamma_{mi}^{(i)} \rangle = \begin{cases} \langle \Gamma_{mi}^{(i)}(N) \rangle & \text{below the percolation threshold} \\ \langle \Gamma_{mi}^{(i)}(\infty) \rangle & \text{above the percolation threshold} \end{cases}$$

where N is an effective cluster size to be determined self-consistently from the formalism. The percolation threshold will be characterized by the divergence of N. Subsequently N will be interpreted as the average number of sites in the finite clusters below the percolation threshold

$$N = \sum_k k^2 n_k.$$

Taking into account the above considerations the ensemble averages of equations (2.5), (2.6), (2.9) and (2.10) will be approximated by

$$\langle G_{ii} \rangle = 1/\big(s + \langle \varepsilon_i \rangle - \langle \Sigma_{ii} \rangle\big) \tag{4.1a}$$

$$\langle G_{mi} \rangle = \langle \Gamma_{mi}^{(i)} \rangle \langle G_{ii} \rangle \tag{4.1b}$$

$$\langle \Sigma_{ii} \rangle = n \int J_{il} \langle G_{ll}^{(i)} \rangle J_{li} \, \mathrm{d}\boldsymbol{R}_l + n^2 \int\int J_{il} \langle G_{ll}^{(i,l_1)} \rangle J_{ll_1} \langle G_{l_1 l_1}^{(i)} \rangle J_{l_1 i} \, \mathrm{d}\boldsymbol{R}_l \, \mathrm{d}\boldsymbol{R}_{l_1} + \ldots \tag{4.1c}$$

$$\langle \Gamma_{mi}^{(i)} \rangle = J_{mi} \langle G_{mm}^{(i)} \rangle + n \int \langle G_{mm}^{(i,l)} \rangle J_{ml} \langle G_{ll}^{(i)} \rangle J_{li} \, \mathrm{d}\boldsymbol{R}_l + n^2 \int\int \langle G_{mm}^{(i,l,l_1)} \rangle J_{ml} \langle G_{ll}^{(i,l_1)} \rangle J_{ll_1} \langle G_{l_1 l_1}^{(i)} \rangle J_{l_1 i} \, \mathrm{d}\boldsymbol{R}_l \, \mathrm{d}\boldsymbol{R}_{l_1} + \ldots \tag{4.1d}$$

where n is the concentration of allowed sites. In the above expressions it is implicit that all the averages are conditional ones, in which some sites are maintained fixed during the averaging procedure. Within the notation we are using they coincide with the sites denoted by the subscript and superscript indices. For example, $\langle G_{mi}^{(i)} \rangle$ is defined by

$$\langle G_{mi}^{(i)} \rangle = \prod_{l \neq m,i} \int \frac{\mathrm{d}\boldsymbol{R}_l}{\Omega} G_{mi}^{(i)}(\boldsymbol{R}_1, \boldsymbol{R}_2, \ldots).$$

In the derivation of equations (4.1), decoupling approximations were used. We expect these approximations to be of reasonable accuracy in the high-concentration regime, when

fluctuations in the considered stochastic variables are in general small when compared to their average values.

According to the discussion of section 3, we can interpret the limit

$$\lim_{s\to 0^+} \langle \varepsilon_i \rangle \langle G_{ii} \rangle \tag{4.2}$$

as the average number of returns to site i for a random walk that begins at this same site. In three dimensions for the cubic Bravais lattices SC, BCC and FCC this limit has the approximate value 1.51, 1.39 and 1.34, respectively. We note that this value approachs unity with increasing number of nearest neighbours. For a disordered lattice in the high concentration regime, when an infinite percolating cluster is present, we expect the corresponding quantity to have a value very close to unity. The restricted Green functions, on the other hand, satisfy the following inequalities:

$$\langle G_{ii}^{(i,l_1,\ldots)} \rangle < \langle G_{ii} \rangle \tag{4.3a}$$

$$\langle \varepsilon_i \rangle \langle G_{ii}^{(i,l_1,\ldots)} \rangle \geqslant 1 \tag{4.3b}$$

in the limit $s \to 0^+$. Therefore, in this limit and for large concentrations all restricted Green functions have the same order of magnitude, their values being spread over a narrow band between the values of $\langle G_{ii} \rangle$ and $1/\langle \varepsilon_i \rangle$. Taking this fact into account we expect that the approximation of considering all the restricted Green functions to be equal to the same site-independent value will not substantially affect series (4.1*c*) and (4.1*d*). This common value will be determined, following the example in section 2, by requiring that the normalization equation (2.4) is satisfied. Within this approximation, series (4.1*c*) and (4.1*d*) are easily summed by Fourier transformation. The resulting set of equations is

$$\langle G_{ii} \rangle = 1/\big(s + \varepsilon_0 - \langle \Sigma_{ii} \rangle\big) \tag{4.4a}$$

$$\langle \Gamma_{mi}^{(i)} \rangle = \frac{G}{(2\pi)^3} \int \exp(\mathrm{i}\boldsymbol{K} \cdot \boldsymbol{R}_{mi}) \frac{J(\boldsymbol{K})}{1 - nGJ(\boldsymbol{K})} \, \mathrm{d}\boldsymbol{K} \qquad (m \neq i) \tag{4.4b}$$

$$\langle G_{mi} \rangle = [\langle \Gamma_{mi}^{(i)} \rangle (1 - \delta_{im}) + \delta_{im}] \langle G_{ii} \rangle \tag{4.4c}$$

$$\langle \Sigma_{il} \rangle = \frac{nG}{(2\pi)^3} \int \frac{J(\boldsymbol{K})^2}{1 - nGJ(\boldsymbol{K})} \mathrm{d}\boldsymbol{K} \tag{4.4d}$$

where G is the common value attributed to the restricted Green functions and

$$J(\boldsymbol{K}) = \int J(\boldsymbol{R}) \exp(-\mathrm{i}\boldsymbol{K} \cdot \boldsymbol{R}) \mathrm{d}\boldsymbol{R} \tag{4.4e}$$

$$\varepsilon_0 = \langle \varepsilon_l \rangle = nJ(\boldsymbol{K} = 0) = nJ(0). \tag{4.4f}$$

Rigorously, after the averaging procedure we would have to work with probability densities, since the positions are now continuous. The density corresponding to a given quantity is obtained by multiplying its value by the concentration n. For the sake of economy of notation, we will continue to work in a discrete space making the following replacements

$$\sum_m \to n \int \mathrm{d}\boldsymbol{R}_m \qquad \delta_{mi} \to (1/n)\delta(\boldsymbol{R}_m - \boldsymbol{R}_i)$$

wherever necessary. Another observation concerns the hopping rates. It is assumed that there is no possibility of the random walker making a transition to the same site, i.e., the

element J_{ii} is considered to be zero. In order to be consistent with this fact, the definition (1.2) should be interpreted as

$$J_{ij} = \begin{cases} J_0 & \text{if } \epsilon < |\boldsymbol{R}_i - \boldsymbol{R}_j| \leqslant a_0 \\ 0 & \text{otherwise} \end{cases}$$

with the limit $\epsilon \to 0$ implicit in all the calculations. From equations (4.4) and taking into account the above remarks, the requirement of probability conservation, equation (2.4), assumes the form

$$\left[1/(1 - G\varepsilon_0) - G\langle\Sigma_{ii}\rangle\right]\langle G_{ii}\rangle = 1/s. \tag{4.5}$$

Equations (4.5), (4.4*a*) and (4.4*d*) constitute a closed set of equations, the solution of which yields all the quantities of interest. In the remaining part of this section we derive the expressions for the mean square displacement and the diffusion constant and discuss qualitatively their behaviours in the long-time regime. We reserve the next section for a more detailed discussion.

The mean square displacement can be obtained from the Fourier transform of $\langle G_{mi}\rangle$

$$G_K(s) = \int \langle G_{mi}\rangle \exp(-\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}_{mi})\mathrm{d}\boldsymbol{R}_{mi} \tag{4.6a}$$

noting that

$$\nabla_K^2 G_K|_0 = -\int |\boldsymbol{R}_{mi}|^2\langle G_{mi}(s)\rangle \mathrm{d}\boldsymbol{R}_{mi}. \tag{4.6b}$$

On the other hand, from the definition of the mean square displacement we have

$$\langle R^2(s)\rangle = \sum_m |\boldsymbol{R}_{mi}|^2\langle G_{mi}\rangle = n\int |\boldsymbol{R}_{mi}|^2\langle G_{mi}\rangle \mathrm{d}\boldsymbol{R}_{mi}. \tag{4.7}$$

Comparing equations (4.6*b*) and (4.7) it follows that

$$\langle R^2(s)\rangle = -n\nabla_K^2 G_K|_0. \tag{4.8}$$

The Fourier transform of the hopping rate defined by equation (1.2) is given by

$$J(\boldsymbol{K}) = \left(4\pi J_0/K^2\right)\left[\sin(Ka_0)/K - a_0\cos(Ka_0)\right]. \tag{4.9}$$

From equations (4.4), (4.5), (4.8) and (4.9) it can be shown that

$$\langle R^2(s)\rangle = 6G\langle G_{ii}\rangle\left(1/s\langle G_{ii}\rangle - G\langle\Sigma_{ii}\rangle\right)^2 D_0 \tag{4.10}$$

where D_0 is the high-concentration-limit value of the diffusion constant given by equation (1.3). The time derivative of the long-time mean square displacement is then given by

$$\left.\frac{\mathrm{d}\langle R^2\rangle}{\mathrm{d}t}\right|_\infty = \lim_{s\to 0^+} s^2\langle R^2(s)\rangle = 6\lim_{s\to 0^+}\left(\frac{G}{\langle G_{ii}\rangle}\right)D_0 \tag{4.11}$$

since the product $G\langle\Sigma_{ii}\rangle$ tends to a finite value for $s \to 0^+$. The diffusion constant is hence given by

$$D = \lim_{s\to 0^+}\left(\frac{G}{\langle G_{ii}\rangle}\right)D_0. \tag{4.12}$$

In order to obtain a first impression of the results, we can solve equation (4.5) approximately for G, by noting that in the limit $s \to 0^+$ the product $G\Sigma_{ii}$ can be disregarded since, as observed above, it tends to a finite value in this limit. Within this approximation we have

$$G = \big(1 - \langle\Sigma_{ii}(0)\rangle/\varepsilon_0\big)\langle G_{ii}\rangle \tag{4.13}$$

and consequently

$$D = \big(1 - \langle\Sigma_{ii}(0)\rangle/\varepsilon_0\big)D_0. \tag{4.14}$$

According to the interpretative scheme introduced in section 3, $\langle\Sigma_{ii}\rangle/\varepsilon_0$ is interpreted as the probability of return to the origin. Equation (4.14) hence expresses the plausible result that in a disordered 3D lattice the diffusion constant is proportional to the probability of the random walker 'escaping' from the origin.

5. Discussion

Equations (4.4) and (4.5) define a self-consistent equation for the quantity $\langle\Sigma_{ii}\rangle$. In order to investigate the solutions of this equation it is convenient to introduce the variable

$$m = 1/G\varepsilon_0 - 1.$$

In terms of this variable, the self-consistent equation for $\langle\Sigma_{ii}(s)\rangle$ assumes the form

$$\langle\Sigma_{ii}(s)\rangle = \left(nJ(0) - \frac{s}{m}\right)\left(\frac{(1+m)nJ(0)}{(1+m)nJ(0) - s}\right) = \frac{1}{(2\pi)^3}\int\frac{J(\boldsymbol{K})^2}{(1+m)J(0) - J(\boldsymbol{K})}\mathrm{d}\boldsymbol{K}. \tag{5.1}$$

We note that since

$$J(0) \geqslant J(\boldsymbol{K})$$

the integrand in equation (5.1) is non-singular for $m > 0$. Furthermore, for a spherically symmetrical hopping rate $J(\boldsymbol{R})$, the behaviour of $J(\boldsymbol{K})$ for small $|\boldsymbol{K}|$ is proportional to $|\boldsymbol{K}|^2$ and the integrand is also non-singular for $m = 0$. The integral attains its maximum value for $m = 0$. Let us define a concentration value n_c such that

$$n_c J(0) = \frac{1}{(2\pi)^3}\int\frac{J(\boldsymbol{K})^2}{J(0) - J(\boldsymbol{K})}\mathrm{d}\boldsymbol{K}. \tag{5.2}$$

For $n < n_c$, it can be shown that the solutions of equation (5.1) for $s = 0$ are such that $m > 0$ and consequently

$$\langle\Sigma_{ii}(0)\rangle = nJ(0) \qquad (n < n_c). \tag{5.3}$$

For $n > n_c$, the solutions have the form

$$s/m = C(s)$$

where $C(s)$ is such that $C(0)$ is finite. It is easily checked that

$$C(0) = (n - n_c)J(0)$$

and consequently

$$\langle \Sigma_{ii}(0) \rangle = n_c J(0) \qquad (n > n_c). \tag{5.4}$$

In terms of the variable m, we also have that

$$G/\langle G_{ii} \rangle = \left[s + nJ(0) - \langle \Sigma_{ii}(s) \rangle \right] / (1 + m) nJ(0). \tag{5.5}$$

Introducing these results into equation (4.12) we obtain

$$D = \begin{cases} 0 & n < n_c \\ [(n - n_c)/n] D_0 & n > n_c. \end{cases} \tag{5.6}$$

From this result we conclude that the value n_c defined by equation (5.2) has the interpretation of a critical concentration below which there is no diffusion. Later, it will be shown that according to the present formalism the diffusion is anomalous only at $n = n_c$. We note that in the limit of high concentrations $n \gg n_c$, the predicted diffusion coefficient reduces to the continuum limit D_0. From equation (5.2) it can easily be seen that the critical concentration n_c is independent of the amplitude J_0 of the hopping rates. This result is consistent with the fact that n_c should depend only on the geometrical characteristics of the underlying lattice.

Both the concentration n of allowed sites and the range a_0 of the hopping rates are independent parameters of the model. On physical grounds, one expects that, for a fixed concentration of allowed sites, there should exist a critical value of the hopping range above which the system has a finite diffusion constant and vice versa. Hence, we expect equation (5.2) to define a curve in the parameter space separating a 'diffusive' region from a 'non-diffusive' one, which resembles a critical curve in a two-phase system. From equations (4.9) and (5.2) it can be shown that such a 'critical' curve is given by

$$n_c \tfrac{4}{3}\pi (a_0)_c^3 = \frac{2}{\pi} \int_0^\infty \frac{\tilde{J}(k)^2}{\frac{1}{3}k^2 - \tilde{J}(k)} \mathrm{d}k \tag{5.7a}$$

$$\tilde{J}(k) = \sin(k)/k - \cos(k). \tag{5.7b}$$

The quantity on the left-hand side of equation (5.7*a*) can be interpreted as the average number of nearest neighbours Z_c along the critical curve. Hence the two 'phases' can be characterized by a single parameter, namely the average number of nearest neighbours—the system displaying a diffusive behaviour for $Z > Z_c$. Numerical evaluation of the integral on the right-hand side of equation (5.7*a*) leads to the value $Z_c \sim 4.47$ for the present model. More precise calculations of the percolation limit in this model by Pike and Seager (1974) give $Z_c \sim 2.9$ using computer simulation and those by Haan and Zwanzig (1977) give $Z_c \simeq 3.05$ from series expansion. Some comparisons can also be made with ordered lattices. The probabilities of return to the origin for SC, BCC and FCC lattices are approximately given by 0.34, 0.28 and 0.26 (Montroll 1964), respectively. The corresponding quantities

for disordered lattices which have on average the same number of nearest neighbours are in this approximation 0.74, 0.56 and 0.37, respectively. Hence, as one would expect, disorder has the effect of confining the random walker, the effect being more accentuated the lower the coordination number.

We next investigate the long-time behaviour of the probability $\langle P_{ii}(t)\rangle$ of the random walker being at the origin and the mean square displacement for $Z < Z_c$, $Z = Z_c$ and $Z > Z_c$. A connection with percolation theory is made. One remarkable feature of the formalism is that although the hypotheses used in deriving the principal equations apply rigorously to the limit $Z \gg Z_c$, the picture that emerges from extrapolation to the region $Z < Z_c$ is consistent with what one would physically expect. We therefore present the results for this region, with the warning that a strictly formal justification for them has not been established. In order to simplify the presentation, the following equations, unless explicitly stated, will be presented in a dimensionless form, J_0^{-1} and a_0 being used as the unities of time and distance, respectively. Most of the results are based on the fact that for three dimensions, in the limit $m \to 0^+$, equation (5.1) can be rewritten as

$$\langle \Sigma_{ii}(s)\rangle = (Z - s/m)(1+m)Z/[(1+m)Z - s] = Z_c - A\sqrt{m}. \tag{5.8}$$

where $A = \frac{10}{3}\sqrt{10}$. The derivation of this result is presented in appendix A. From this result it is possible to obtain the behaviour of the solutions for various limits.

From the previous results, it can be shown that for $Z < Z_c$, the long-time behaviour of the conditional probability $\langle P_{ii}\rangle$ is finite and given by

$$\langle P_{ii}\rangle = \lim_{s\to 0^+} s\langle G_{ii}(s)\rangle = \frac{m_0(m_0+1)}{(m_0+1)m_0+1} \tag{5.9}$$

where $m_0(Z)$ is the solution of equation (5.8) for $s \to 0^+$. A finite value of $\langle P_{ii}\rangle$ for $t \to \infty$, means that for $Z < Z_c$ the random walker is on average confined to a finite cluster. Furthermore, since the hopping rates are symmetrical and to the level of approximation in which we are working fluctuations in the number of nearest neighbours are neglected, we can interpret $\langle P_{ii}\rangle$ as the inverse of the average number of sites in the cluster. Within this interpretation, the quantity

$$N(Z) = \big[(m_0+1)m_0+1\big]/m_0(m_0+1) \qquad (Z < Z_c) \tag{5.10}$$

is the average number of sites in a cluster to which a randomly selected site belongs, since the origin is arbitrary. Since for $Z \to Z_c$ from below $m_0(Z)$ approaches zero, $N(Z)$ diverges at the critical value Z_c. This result provides a connection with percolation theory, Z_c being interpreted in this context as the critical number of nearest neighbours for percolation in the present system. From equation (5.8), it is easily seen that in the limit $Z \to Z_c$, $m_0(Z)$ has the asymptotic behaviour

$$m_0(Z) = \big[(Z - Z_c)/A\big]^2. \tag{5.11}$$

Hence $N(Z)$ diverges with an exponent of two for $Z \to Z_c$. From equation (5.8) it can be shown that up to the first correction in s, we have

$$m = m_0 + 2s/\sqrt{m_0}A \tag{5.12}$$

where m_0 is given by equation (5.11). From this result and equation (4.10) it can be shown that the mean square displacement has the following long-time behaviour for Z near Z_c:

$$\langle R^2(t)\rangle = R_\infty^2[1-\exp(-t/T)] \tag{5.13a}$$

where

$$R_\infty^2 = \tfrac{3}{5}\big[A/(Z_c - Z)\big]^2 \tag{5.13b}$$

$$T = (2/A)\big[A/(Z_c - Z)\big]^3. \tag{5.13c}$$

Hence, the mean square displacement of the random walker also diverges with an exponent of two as Z approaches Z_c. The quantity $\xi = \sqrt{R_\infty^2}$ can be interpreted as a measure of the average size of the finite cluster to which the origin is linked. Hence, near the percolation threshold this quantity diverges with an exponent of one. In appendix B, some aspects of the extension of the formalism to the region $Z < Z_c$ are discussed.

Right at the percolation threshold, the solution of equation (5.8) for $s \to 0^+$ has the asymptotic behaviour

$$m_c \simeq (s/A)^{2/3}$$

implying that

$$\langle \Sigma_{ii}(s)\rangle \simeq Z_c - A(s/A)^{1/3}.$$

As a consequence we obtain

$$\langle G_{ii}\rangle \simeq s^{-1/3} \qquad \langle R^2(s)\rangle \simeq s^{-5/3}$$

showing that

$$\langle P_{ii}\rangle \simeq t^{-2/3} \tag{5.14a}$$

$$\langle R^2(t)\rangle \simeq t^{2/3} \tag{5.14b}$$

for long times. Therefore at $Z = Z_c$ the random walker is not confined in a finite cluster but, on the other hand, its mean square displacement increases with an exponent $\frac{2}{3}$ in time instead of the exponent of one that characterizes normal diffusion. Hence at $Z = Z_c$ the diffusion is anomalous.

For $Z > Z_c$, the solution to equation (5.8) has the following asymptotic behaviour in the limit $s \to 0^+$:

$$m = s/(Z - Z_c). \tag{5.15}$$

From this result it is readily shown that in this limit

$$\langle G_{ii}(s)\rangle \simeq 1/\big\{(Z - Z_c) + A\big[s/(Z - Z_c)\big]^{1/2}\big\}$$

$$\langle R^2(s)\rangle \simeq (6/s^2)\big\{1 - (Z_c/Z) + (1/Z)\big[s/(Z - Z_c)\big]^{1/2}\big\} D_0.$$

The corresponding long-time behaviours are given by

$$\langle P_{ii}(t)\rangle = \big[(Z - Z_c)^{1/2}/A\big]\Big[1/\sqrt{(\pi t)} - a\exp(a^2 t)\,\mathrm{ERFC}\big(at^{1/2}\big)\Big] \tag{5.16a}$$

$$\langle R^2(t)\rangle = \tfrac{6}{10}(Z - Z_c)t + \big[12A/10(Z - Z_c)^{1/2}\big]t^{1/2}/\sqrt{(\pi)} \tag{5.16b}$$

where $a = (Z-Z_c)^{3/2}/A$ and ERFC is the complementary error function. A noteworthy point is the prediction of a contribution to the long-time mean square displacement proportional to $t^{1/2}$ that becomes increasingly important as $Z \to Z_c$. By expanding the ERFC function in equation (5.16*a*) it is shown that the dominant contribution in the long-time regime is expressed by

$$\langle P_{ii}(t)\rangle = \left[Z/n(Z-Z_c)\right]1/(4\pi Dt)^{3/2} \tag{5.17}$$

where D is the dimensionless diffusion constant

$$D = \tfrac{1}{10}(Z-Z_c). \tag{5.18}$$

Therefore the dominant contribution to $\langle P_{ii}\rangle$ is proportional to $t^{-3/2}$ as is usual in normal diffusion.

As a final point, we investigate the long-time behaviour of the conditional probabilities. From equations (4.4*c*), (4.13), (5.1) and (5.7*b*) the following expression is obtained for the off–diagonal Green-function elements:

$$\langle G_{mi}\rangle = \frac{4\pi}{3Z}\frac{m}{s}\frac{1}{(2\pi)^3}\int \frac{\exp(\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}_{mi})}{m+[1-(3/k^2)\tilde{J}(K)]}\mathrm{d}\boldsymbol{K}. \tag{5.19}$$

In the derivation of this result, equation (5.1) was approximated by

$$\langle \Sigma_{ii}\rangle = Z - s/m. \tag{5.20}$$

This equation is asymptotically correct in the limit of small values of m and s. For small values of m and large values of $|\boldsymbol{R}|$, the main contribution to the integral in equation (5.19) comes from the region $|\boldsymbol{K}| \simeq 0$. Expanding $\tilde{J}(K)$ up to fourth order and performing the integral, the following result is obtained:

$$\langle G_{mi}\rangle = (1/s4\pi n)K_0^3\left[\exp(-K_0|\boldsymbol{R}_{mi}|)\right]/K_0|\boldsymbol{R}_{mi}| \tag{5.21a}$$

where

$$K_0 = \sqrt{10m}. \tag{5.21b}$$

Using the previous results for m in the regions $Z < Z_c$, $Z = Z_c$ and $Z > Z_c$ the following expressions are obtained:

$$\langle G_{mi}\rangle = (1/s4\pi n)10\left[(Z_c-Z)/A\right]^2\left[\exp\left[-\sqrt{10}\left[(Z_c-Z)/A\right]|\boldsymbol{R}_{mi}|\right]\right]/|\boldsymbol{R}_{mi}| \qquad (Z<Z_c) \tag{5.22a}$$

$$\langle G_{mi}\rangle = (1/4\pi n)\left(10/A^{2/3}\right)\left\{\exp\left[-\sqrt{10}(s/A)^{1/3}|\boldsymbol{R}_{mi}|\right]\right\}/s^{1/3}|\boldsymbol{R}_{mi}| \qquad (Z=Z_c) \tag{5.22b}$$

$$\langle G_{mi}\rangle = (1/4\pi n)\left\{\exp\left[-(s/D)^{1/2}|\boldsymbol{R}_{mi}|\right]\right\}/D|\boldsymbol{R}_{mi}| \qquad (Z>Z_c). \tag{5.22c}$$

We note that equation (5.22*c*) leads to the well known result

$$\langle P_{mi}\rangle = (1/n)\left[\exp(-|\boldsymbol{R}_{mi}|^2/4Dt)\right]/(4\pi Dt)^{3/2}$$

for a free particle diffusing with an effective diffusion constant given by equation (5.18).

6. Concluding remarks

A first remark concerns the failure of the formalism in dealing with the two-dimensional (2D) case. Direct application of the formalism, as it stands, leads to the result that in a 2D disordered lattice there is no diffusion, the random walker being confined in a finite cluster for any value of Z. This result clearly contradicts physical expectations and indicates a breakdown of the approximations adopted in arriving at equation (4.14). A peculiarity of random walks in 2D ordered lattices is that the average number of visits to a given site is infinite, independent of the number of nearest neighbours. Assuming that this is also the case for random walks in disordered lattices, we see that, contrary to the 3D and higher-dimensional cases, there is no upper bound for the restricted Green functions discussed in section 4. In this case, therefore, the approximation of considering all restricted Green functions to be equal to a constant site-independent value is clearly not justifiable and, consequently, series (4.1*c*) and (4.1*d*) cannot be approximated by a geometrical series, invalidating all the subsequent results. The 2D case has, therefore, to be handled by a different method.

It is generally accepted that the cluster properties near and at the percolation threshold associated with the site and bond percolation problems in ordered lattices are only affected by dimensionality. This universality concept asserts that critical exponents and the shape of the scaling functions are dimensional invariants, being independent of the peculiarities of the lattice. If this universality concept holds, the percolation problem in, say, an SC lattice, should yield the same exponents as the percolation problem in that lattice when second, third and subsequent neighbours are taken into account. In the case of an SC lattice, if we characterize the sites linked to any particular site by a length parameter a_0, such that all sites inside a sphere of radius a_0 centred at a given site are considered to be linked to this site, then the model we are investigating is equivalent to the corresponding site percolation problem in the limit in which a_0 is very large when compared to the lattice parameter. Hence it seems that the model under consideration should belong to the same universality class as the site and bond percolation problems in ordered lattices.

We next compare our results with equivalent results for percolation in ordered lattices. Using the standard notation for the critical exponents and making use of the usual scaling and hyperscaling relations (Grimmett 1989a, Stauffer 1979, 1991), we obtain the following values for three dimensions: $\gamma = 2$, $\nu = 1$, $\beta = \frac{1}{2}$, $\delta = 5$, $\Delta = \frac{5}{2}$, $\eta = 0$, $\rho = 2$ and $\alpha = -1$. There is some scatter in the published data for ordered lattices; the best results given by Stauffer (1986) are $\gamma = 1.76$, $\nu = 0.88$, $\beta = 0.44$, $\delta = 5.00$, $\Delta = 2.20$, $\eta = 0$, $\rho = 2$ and $\alpha = -0.64$. Our approximation gives results in good qualitative agreement. For dimensions greater than four, it is shown in appendix A that equation (5.1), in the limit $m \to 0^+$, assumes the form

$$(Z - s/m)(1+m)Z/[(1+m)Z - s] = Z_c - Bm \tag{6.1}$$

where B is a constant. Following the procedure outlined for the 3D case, the values $\gamma = 1$ and $\nu = \frac{1}{2}$ are obtained. For $d = 4$, the correction on the right-hand side of equation (6.1) has the form $m \ln(m)$ and it can be shown that

$$\langle N \rangle \propto \left[1/(Z_c - Z)\right] \ln\left[1/(Z_c - Z)\right] \tag{6.2a}$$

$$\xi \propto \left[1/(Z_c - Z)^{1/2}\right] \left\{\ln\left[1/(Z_c - Z)\right]\right\}^{1/2}. \tag{6.2b}$$

Therefore, in our approximation, the upper dimension, beyond which the critical exponents attain mean field values, is $d = 4$. The discrepancy between this result and the widely

accepted one (Stauffer 1979), that for percolation problems the upper critical dimension is $d = 6$, remains to be understood. A brief analysis of the preceding results reveals that the present model yields the same critical exponents as an n-component vector model with symmetry O(n) in the limit $n \to \infty$, or as the spherical model (Itzykson and Drouffe 1991) for the treatment of thermal phase transitions in magnetic systems (see appendix A). Here, as in these models, the lower critical dimension, below which there is no transition, is $d = 2$, while the upper dimension, beyond which mean field results hold, is $d = 4$.

Gefen and co-workers (1983) discussed the features of a random walk near and at the percolation threshold. Based on arguments of self-similarity they arrive at the result that the mean square displacement of a random walker on a cluster at the percolation threshold should behave as

$$\langle r^2(t)\rangle \propto t^{2/(2+\theta)}. \tag{6.3}$$

Arguing that both finite and infinite clusters near the percolation threshold should also be self-similar in scales L which are much smaller than the correlation length ξ, they conclude that equation (6.3) should also hold for finite and infinite clusters near the percolation threshold for times such that $\langle r(t)\rangle \ll \xi$. They assert that the exponent θ is related to the conductivity exponent μ through the relation

$$\theta = (\mu - \beta)/\nu \tag{6.4}$$

and by straightforward arguments show that the diffusion constant in an infinite cluster above the percolation threshold should behave as

$$D \propto \xi^{-\theta}. \tag{6.5}$$

They propose a general scaling form for the mean square displacement from which these results would be derived:

$$\langle r^2(t)\rangle \propto t\xi^{-\theta} f_{\pm}(t/\xi^{2+\theta}) \tag{6.6}$$

where (+) and (−) denote above and below the percolation threshold, respectively. Comparing equations (6.3) and (5.14b) we see that the present formalism reproduces equation (6.3) with the exponent $\theta = 1$. Identifying the correlation length with

$$\xi = (Z - Z_c)^{-\nu}$$

we note that equation (6.5) is also reproduced. Equations (5.13a) and (5.16b) can be cast, respectively, in the form

$$\langle R^2(t)\rangle \propto \left[t\xi^{-\theta}\left(t/\xi^{2+\theta}\right)^{-1}\right]\left[1 - \exp\left(-t/\xi^{2+\theta}\right)\right] \tag{6.7a}$$

$$\langle R^2(t)\rangle \propto t\xi^{-\theta}\left[1 + \left(2A/\sqrt{\pi}\right)\left(t/\xi^{2+\theta}\right)^{-1/2}\right] \tag{6.7b}$$

showing that the functional form (6.6) is also reproduced. Recent simulation results suggest that θ for 3D lies in the range $1.626 \leqslant \theta \leqslant 1.897$ (Roman 1990, Duering and Roman 1991).

The Laplace transformed version of equation (6.6) is equivalent to a general functional form previously proposed by Straley (1980). In its essential form it is written as

$$\langle R^2(s)\rangle = \left(\epsilon^x/s^2\right) F\left(s\epsilon^{-y}\right) \tag{6.8}$$

with $\epsilon = |p - p_c|$. It is assumed that the function F depends explicitly on p and is such that $F(0) = 0$ for $p < p_c$ and $F(0) \neq 0$ for $p > p_c$. Straley also proposed asymptotic explicit functional forms. For $p < p_c$, a form previously suggested by Mitescu and Roussenq (1983) was assumed:

$$\langle R^2(t)\rangle = R_\infty^2[1 - a\exp(-t/T)] \tag{6.9a}$$

while for $p > p_c$ the following form was conjectured:

$$\mathrm{d}\langle R^2(t)\rangle/\mathrm{d}t = 2D[1 + c\exp(-t/\tau)]. \tag{6.9b}$$

In the above equations, a and c are constants of order unity. By comparing the Laurent series of equations (6.9a) and (6.9b) with that corresponding to equation (6.8) the following relations are obtained:

$$R_\infty^2 \propto \epsilon^{x-y} \tag{6.10a}$$

$$D \propto \epsilon^x \tag{6.10b}$$

$$T \propto \epsilon^{-y} \tag{6.10c}$$

$$\tau \propto \epsilon^{-y}. \tag{6.10d}$$

If we replace ϵ by $|Z - Z_c|$, it is easily checked that the Laplace transformations of equations (6.7a) and (6.7b) satisfy equation (6.8) with the exponents $x = 1$ and $y = 3$. By comparing equations (6.7a) and (6.7b) with equations (6.9a) and (6.9b), it is seen that the explicit functional form (6.9a) is exactly reproduced while (6.9b) is not. In the latter case, instead of a dampened exponential, an inverse square root in t/τ is obtained, implying a much longer saturation time. The relations (6.10) are all satisfied.

We now consider the geometrical properties of the incipient infinite cluster predicted by the present approximation. It has been established that the diagonal element of the self-correlation function at the critical concentration (Alexander and Orbach 1982) should scale according to

$$\langle P_{ii}\rangle \propto t^{-d_f/d_w} \qquad Z = Z_c$$

where d_f is the fractal dimension of the incipient infinite cluster and $d_w = 2 + \theta$ is the anomalous diffusion exponent. From equation (5.14a) it is seen that $d_f = 2$, since $\theta = 1$ as has been seen above. On the other hand, it is a well established result that $d_f = d - \beta/\nu$ (Kapitulnik *et al* 1983). According to the values of γ and ν obtained from the analysis of the region $Z < Z_c$, we would then have that $d_f = \frac{5}{2}$. The present approach therefore fails in the description of the geometrical properties of the incipient infinite cluster. We interpret this fact as a direct consequence of the approximation of considering the restricted Green functions to be equal to a constant, independent of the sites with which they are associated. This simplification establishes an equivalence between sites, which should hold, for instance, for the backbone sites but not for the sites belonging to ramifications, particularly thin dendrites. We therefore consider that the exponents obtained for $Z = Z_c$ are more appropriate to the backbone than to the whole of the incipient infinite cluster. The backbone of the incipient infinite cluster is itself a fractal object with fractal dimension $d_B = d - \beta_B/\nu$ (Kirkpatrick 1978). Assuming $d_B = 2$ and $\nu = 1$ we obtain $\beta_B = 1$. These results are in reasonable agreement with the simulation results $d_B = 1.77 \pm 0.07$ (Hermmann *et al* 1984) and $\beta_B = 0.9 \pm 0.1$ (Kirkpatrick 1978). Also, according to Grimmett (1989b)

$d_B = d - 2\beta/\nu$, which yields $d_B = 2$ if we use the previous results for β and ν. These results lend some support to the above interpretation.

From equations (5.22) other results concerning the subcritical phase as well as the incipient infinite cluster can be derived. From equation (5.22*a*), the self-correlation function for $Z < Z_c$, apart from unimportant numerical factors, is seen to have the form

$$\langle P(\boldsymbol{R})\rangle \propto |Z_c - Z|^2\big[\exp\big(-|Z_c - Z||\boldsymbol{R}|\big)\big]/|\boldsymbol{R}|. \tag{6.11}$$

This expression can be related to static distribution functions such as the probability density that there is an open path connecting the origin to a site at $\boldsymbol{R}$, $\tau(\boldsymbol{R})$, in the following way. Let $f(N, \boldsymbol{R})$ be the number of sites in the element of volume $d\boldsymbol{R}$ at $\boldsymbol{R}$ of a cluster with N sites, where $\boldsymbol{R}$ is measured from the centre of gravity of the cluster. If $\rho(N)dN$ is the probability that the cluster to which the origin belongs has a number of sites between N and $N + dN$, then the averaged self-correlation function can be expressed by

$$\langle P(\boldsymbol{R})\rangle = \int \frac{f(N, \boldsymbol{R})\rho(N)}{N} \mathrm{d}N \tag{6.12}$$

since the steady-state probability of occupation of any site in a finite cluster with N sites is $1/N$. In the spirit of the approximations adopted in section 4, this expression can be approximated by

$$\langle P(\boldsymbol{R})\rangle \simeq f(\langle N\rangle, \boldsymbol{R})/\langle N\rangle \tag{6.13}$$

where $\langle N\rangle$ is the average number of sites in the cluster to which the origin belongs. Identifying $f(\langle N\rangle, \boldsymbol{R})$ with $\tau(\boldsymbol{R})$ and by comparing equation (6.13) with equation (6.11) the following result is obtained:

$$\tau(\boldsymbol{R}) \propto [\exp(-|\boldsymbol{R}|/\xi)]/|\boldsymbol{R}| \tag{6.14}$$

where we have made use of equations (5.10), (5.11) and (5.13*b*). It is generally hypothesized that $\tau(\boldsymbol{R})$ obeys the scaling form (Grimmett 1989b)

$$\tau(\boldsymbol{R}) \propto g(|\boldsymbol{R}|/\xi)/|\boldsymbol{R}|^{d-2+\eta} \tag{6.15}$$

where $g(x) \to 0$ faster than any power of x^{-1} as $x \to \infty$. Equation (6.14) satisfies this scaling *ansatz* with $\eta = 0$. The value of η thus obtained is consistent with the value obtained from the normal scaling and hyperscaling relations with $\gamma = 2$ and $\nu = 1$. Also, $g(x)$ is believed to be a negative exponential (Grimmett 1989c). At $Z = Z_c$, starting from equation (5.22*b*) and using the steepest-descent method for the approximate evaluation of the inverse Laplace transform, the following asymptotic expressions for the time-dependent self-correlation function are obtained:

$$\langle P(\boldsymbol{R}, t)\rangle \propto \big(1/t^{2/3}|\boldsymbol{R}|\big)h(|\boldsymbol{R}|/t^{1/3}) \qquad |\boldsymbol{R}|/t^{1/3} \ll 1 \tag{6.16a}$$

$$\langle P(\boldsymbol{R}, t)\rangle \propto \big(1/t^{2/3}|\boldsymbol{R}|\big)\big(|\boldsymbol{R}|/t^{1/3}\big)^{1/4}\exp\big[-\big(|\boldsymbol{R}|/t^{1/3}\big)^{3/2}\big] \qquad |\boldsymbol{R}|/t^{1/3} \gg 1 \tag{6.16b}$$

where

$$h(x) = \sum_{n=0}^{\infty} \Gamma\left(\frac{n+2}{3}\right) x^n \frac{(-1)^n}{n!}.$$

These are asymptotic results valid for large t and large $|\boldsymbol{R}|$. It is expected that the self-correlation function at the percolation threshold obeys the general scaling form (Havlin and Ben-Avraham 1987)

$$\langle P(\boldsymbol{R},t)\rangle \propto \left(|\boldsymbol{R}|^{d_f-d}/t^{d_f/d_w}\right)\Pi\left(|\boldsymbol{R}|/t^{1/d_w}\right) \tag{6.17}$$

where $\Pi(x) \to 0$ faster than any power of x^{-1} as $x \to \infty$. Equations (6.16) are consistent with equation (6.17) provided that $d_f = 2$. Equation (6.16*b*), in particular, is quite similar to an expression obtained by Guyer (1984), through a numerical renormalization method, for the Sierpinski gasket

$$\langle P(\boldsymbol{R},t)\rangle \propto \left(|\boldsymbol{R}|^{d_f-d}/t^{d_f/d_w}\right)\exp\left[-\left(|\boldsymbol{R}|/t^{1/d_w}\right)^u\right] \tag{6.18a}$$

where

$$u = \left(1-1/d_w\right)^{-1}. \tag{6.18b}$$

We note that the value of u in equation (6.16*b*) is in accordance with equation (6.18*b*).

We conclude by noting that the proposed method, despite some shortcomings, yields results that comply with the minimum requirements for the description of the diffusion phenomenon in a disordered system. Specifically, a percolation threshold is predicted, separating a non-diffusive regime from a diffusive one, with the self-correlation function and the mean square displacement assuming scaling forms which are believed to hold near and at a critical point. The actual critical exponents obtained are only approximate. This is in part due to the fact that the model, in averaging over sites, does not fully reproduce the special geometry of the clusters close to the percolation threshold. However, it does give an overall description of the properties of diffusion for a specific form of spatially disordered lattice.

Appendix A. Small-m expansion

We consider the expansion of

$$I(m) = \frac{A_d}{(2\pi)^d}\int \frac{J(K)^2}{(1+m)J(0)-J(K)}K^{d-1}\mathrm{d}K \tag{A1}$$

for small m in general dimension d. The constant A_d is the area of the unit sphere in d dimensions and is given by

$$A_d = 2\pi^{d/2}/\Gamma(d/2). \tag{A2}$$

The normalized Fourier transform of the hopping rate has the following small-$|\boldsymbol{K}|$ expansion:

$$J(K) \simeq J(0) - AK^2 \tag{A3}$$

where

$$J(0) = A_d/d \tag{A4a}$$

$$A = A_d/2d(d+2). \tag{A4b}$$

For $m = 0$ and $K = 0$ the integrand in equation (A1) is singular and hence cannot be expanded in powers of m for general K. We consider the following partition of the interval of integration:

$$\int_0^\infty = \int_0^{xK_0} + \int_{xK_0}^{\Lambda} + \int_{\Lambda}^{\infty} \tag{A5}$$

where

$$K_0 = \sqrt{2(d+2)m}$$

and Λ is a parameter small enough for the expansion (A3) to be valid in the interval $(0, \Lambda)$. x is an arbitrary parameter that satisfies the relations

$$x > 1 \tag{A6a}$$

$$xK_0 < \Lambda. \tag{A6b}$$

In the interval $(0, xK_0)$ we have

$$M_1 \simeq \int_0^{xK_0} \frac{J(0)^2}{mJ(0) + AK^2} K^{d-1} \mathrm{d}K = \frac{J(0)^2}{A} K_0^{d-2} \int_0^{\tan^{-1}(x)} \tan(\theta)^{d-1} d\theta. \tag{A7}$$

In the interval (xK_0, Λ), the integrand can be expanded in powers of K_0. For odd d the following result is obtained:

$$\begin{aligned} M_2(K_0, \Lambda) &\simeq \int_{xK_0}^{\Lambda} \frac{J(0)^2}{mJ(0) + AK^2} K^{d-1} \mathrm{d}k \\ &\simeq \frac{J(0)^2}{A} \sum_{p=0}^{\infty} \left(\frac{\Lambda^{d-2-2p}}{d-2-2p} K_0^{2p} - \frac{x^{d-2-2p}}{d-2-2p} K_0^{d-2} \right) (-1)^p \\ &\simeq M_2(0, \Lambda) - \sum_{p=0}^{\infty} \frac{J(0)^2}{A} \frac{x^{d-2-2p}}{d-2-2p} (-1)^p K_0^{d-2} + o(m). \end{aligned} \tag{A8}$$

For even d there are logarithmic corrections. In particular for $d = 4$ one obtains

$$M_2(K_0, \Lambda) = M_2(0, \Lambda) + \left[J(0)^2/A \right] 6m \ln(m) + o(m). \tag{A9}$$

The integral over the interval (Λ, ∞) has only corrections of order m:

$$M_3(K_0, \infty) = M_3(0, \infty) + o(m). \tag{A10}$$

Putting together these results, and noting that by definition

$$Z_c = \left[A_d/(2\pi)^d \right] \left[M_2(0, \Lambda) + M_3(0, \infty) \right]$$

we obtain for $2 < d < 4$

$$I(m) = Z_c - \left[A_d/(2\pi)^d \right] \left[J(0)^2/A \right] [2(d+2)]^{(d-2)/2} f_d m^{(d-2)/2} + o(m) \tag{A11}$$

where the constant f_d is defined by the expansion

$$\int_0^{\tan^{-1}(x)} \tan(\theta)^{d-1} d\theta = -f_d + \sum_{p=0}^{\infty} \frac{x^{d-2-2p}}{d-2-2p}(-1)^p. \tag{A12}$$

For $d = 3$, this constant assumes the value $f_d = \pi/2$ and the result

$$I(m) = Z_c - \tfrac{10}{3}\sqrt{10}m^{1/2} \tag{A13}$$

is obtained. For $d = 4$, using the result (A9) we obtain

$$I(m) = Z_c + \tfrac{9}{2}m \ln m + o(m). \tag{A14}$$

For $d > 4$ the correction is $o(m)$ as can be checked from the previous results.

From the results of section 4 we have that below Z_c, the number of sites in the average cluster behaves as

$$\langle N \rangle \propto 1/m \propto 1/(Z_c - Z)^{2/(d-2)} \tag{A15a}$$

while the correlation length behaves as

$$\xi \propto 1/m^{1/2} \propto 1/(Z_c - Z)^{1/(d-2)}. \tag{A15b}$$

For $2 < d < 4$ the exponents γ and ν are hence respectively given by $2/(d-2)$ and $1/(d-2)$, which are similar to the corresponding results for the spherical model.

Appendix B. Approximations in the region $Z \lesssim Z_c$

In this appendix we discuss some aspects of the approximation involved in the treatment of the region $Z < Z_c$.

From the results of section 5, we have that for $Z < Z_c$ the long-time average value of the restricted Green functions is given by

$$G = 1/(m_0 + 1)\varepsilon_0 \tag{B1}$$

where m_0 is given by

$$m_0 = [(Z - Z_c)/A]^2. \tag{B2}$$

We note that equation (B1) contradicts equation (4.3*b*). This is a consequence of the fact that the series for $\langle \Gamma_{mi} \rangle$ and $\langle \Sigma_{ii} \rangle$, for $Z < Z_c$, have been approximated by an infinite series. According to the rearrangements (2.9) and (2.10) the corresponding series should have a finite number of terms in this region. In formal terms the finite series

$$\langle \Gamma_{mi} \rangle = \frac{1}{(2\pi)^3} \int \frac{n^{N-1}[G'J(\boldsymbol{K})]^N - G'J(\boldsymbol{K})}{nG'J(\boldsymbol{K}) - 1} \exp(i\boldsymbol{K} \cdot \boldsymbol{R}_{mi}) d\boldsymbol{K} \tag{B3}$$

where N is the number of sites in the average finite cluster and G' is the actual value of the average of the restricted Green functions, has been replaced by the infinite series (4.4*b*).

The value of G in the latter series is therefore an effective value. If we use equation (B3), the long-time normalization equation reads

$$\langle G_{ii}\rangle\left\{1-\left[nG'J(0)\right]^N\right\}/\left[1-nG'J(0)\right]=1/s. \tag{B4}$$

From this result, the following relationship between G' and G is obtained:

$$\left\{1-\left[nG'J(0)\right]^N\right\}/\left[1-nG'J(0)\right]=1/[1-nGJ(0)]=\left(m_0+1\right)/m_0. \tag{B5}$$

If we assume that $nG'J(0)\rightarrow$ to 1 for $s\rightarrow 0^+$ as in the case when the infinite percolating cluster exists, equation (B5) implies that

$$N\simeq\left(m_0+1\right)/m_0. \tag{B6}$$

This condition is equivalent to equation (5.10). We conclude, therefore, that for $Z<Z_c$ and large N the actual value of G tends to unity and hence condition (4.3*b*) is not violated.

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