Exact computation of the mobility of a diffusing particle in a defective lattice gas under an external field

2005 J. Phys.: Condens. Matter 17 S4165

(http://iopscience.iop.org/0953-8984/17/49/011)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **17** (2005) S4165–S4173 doi:10.1088/0953-8984/17/49/011

Exact computation of the mobility of a diffusing particle in a defective lattice gas under an external field

L F Perondi

Instituto Nacional de Pesquisas Espaciais, São José dos Campos, SP, Brazil

E-mail: perondi@dss.inpe.br

Received 4 July 2005, in final form 26 September 2005
Published 25 November 2005
Online at stacks.iop.org/JPhysCM/17/S4165

Abstract

We give a method for the exact computation of the mobility of a particle diffusing in a lattice gas with defects. We describe the method by considering its application to the computation of the mobility of a particle diffusing in a lattice with defects in the form of dead-ends. The mobility initially increases linearly with field intensity, then crosses over to a nonlinear behaviour and reaches a maximum. Beyond this point the mobility decreases with increasing field intensity, showing an anomalous behaviour which may be attributed to partial confinement imposed by the field. The proposed method is general and may be applied to the computation of arbitrary moments of the probability function of a single particle diffusing in a lattice gas with defects of arbitrary characteristics.

1. Introduction

Systems constituted by particles hopping in a lattice have been used extensively as simple models for studying both diffusion and transport phenomena in a variety of media. Applications include the study of atomic diffusion in solids (Allnatt and Lidiard 1993), the modelling of ionic motion in ionic conductors (Balkanski and Elliott 1998) and the study of growth phenomena in a variety of systems (Stanley and Ostrowsky 1986). A broad survey of applications is given by Bunde and Havlin (1991).

The properties of model systems with either single or many particles, moving in either perfect or disordered lattices, have been extensively studied (Hughes 1995, Bouchaud and Georges 1990, Havlin and Ben-Avraham 1987, Haus and Kehr 1987, Tahir-Kheli and Elliott 1983). Most of these studies have been concerned with the effect of static and dynamic disorder on the diffusion constant of individual particles. Transport properties have commonly been inferred from the Einstein relation between diffusion and conductivity, which is accepted to hold for small values of bias in systems far from a percolation threshold (Havlin and Ben-Avraham 1987 p 697, Bouchaud and Georges 1990 p 235).

Here we will restrict ourselves to single-particle systems with static disorder. A great deal of effort has been dedicated to the computation of the diffusion constant for a broad variety of models of disorder in such systems. Models in which the sites available for the diffusing particle are arranged in a regular lattice, and the disorder is caused by an irregular distribution of the transition rates, have been extensively investigated, with effort also dedicated to the study of systems in which the sites are randomly distributed in space (Perondi and Elliott 1993). Depending on the type of defect, the diffusing particle may display either normal or anomalous diffusive behaviour. While studies concerning the former case have been reviewed by Haus and Kehr (1987), studies concerning the latter have been reviewed by Bouchaud and Georges (1990). Systems in which the total probability is not conserved, such as those modelled with traps, have also received a great deal of attention (Barkema *et al* 2001, Giacometti and Murthy 1996).

Both numerical and analytical methods have been employed for the study of diffusion in disordered systems. While Monte Carlo simulations are by far the most well-known representative of the former category (Kehr and Binder 1984), examples of the latter category are varied and span a broad variety of techniques. In the case of single-particle disordered systems, effective medium approximations have been very much successful in computing diffusion properties for low concentrations of defects (Elliott *et al* 1974, Webman 1981, Hilfer 1991). Computing single-particle diffusion properties in structures near a percolation threshold or on incipient percolating clusters is still a very much open and challenging subject (Havlin and Ben-Avraham 1987).

As regards non-statistical numerical methods, a great deal of effort has been devoted to simple one-dimensional systems (Alexander *et al* 1981, Dyson 1953), mainly due to the difficulties in tackling higher-dimensional systems. Computing the one-particle distribution function and its moments exactly amounts to solving a coupled infinite set of differential equations, a task beyond the reach of current techniques in the absence of special symmetries.

The numerical solution of the rate equations requires, in general, two types of approximation. First, the infinite system is approximated by a finite system with the application of suitable boundary conditions. Second, numerically computed properties are averaged over a subset of the possible configurations of the disorder and over all possible initial conditions for the system. For self-averaging properties the averaging over different configurations of the disorder may be omitted. Both Monte Carlo and non-statistical numerical methods make use of these approximations.

Motivated by applications such as the study of ionic conduction in structures with special geometry, we have been developing and implementing a novel method for the computation of moments of the distribution function in disordered systems, which exhibits versatility and ease of implementation. The method is quite general and may be applied to lattices with arbitrary topology and to models of disorder with arbitrary characteristics. In the proposed approach, the computation of exact moments of the distribution function is reduced to a matrix multiplication algorithm, with clear advantages over either a direct numerical or a statistical solution of the rate equations. Similar approaches have already been considered for the study of diffusion in one-dimensional (Perondi and Binder 1993a) and two-dimensional (Perondi and Binder 1993b, Perondi 1993) many-particle systems. Our objective in this article is to present this new approach for single-particle systems and to illustrate its application to the study of the behaviour with field strength of the mobility of a diffusing particle in a lattice with defects in the form of dead-ends. We next briefly characterize the problem.

In single-particle systems, the field has the effect of making the diffusing particle move more likely in the field direction than against it. If the field is the same everywhere, i.e., there is a constant bias, and there are no defects in the form of dead-ends, the particle develops a drift

velocity which increases monotonically with field intensity, resulting in a constant mobility, the value of which is expected to depend on the concentration and shape of the defects. If the defects, otherwise, display a geometric form which favours confining the diffusing particle along the field direction, the field gives rise to two antagonistic effects on the motion of the particle. While movement is more likely along the field direction on normal sites, inside defects the field tends to trap the particle, thus delaying the progress of the particle along the field direction. The net result is a particle mobility that displays a highly nonlinear behaviour with field intensity.

It has been argued that, in systems with confining defects, the characteristic behaviour of the mobility will depend on the distribution $p(l)$ for the length l of the confining defects and on the system size (Bouchaud and Georges 1990 p 244). If $p(l)$ decays more slowly than exponentially, the system will display a time-dependent mobility which vanishes asymptotically with time. If $p(l)$ decays exponentially, a dynamic phase transition will take place in infinite systems, with the mobility initially increasing monotonically with field intensity and then abruptly vanishing for field intensities higher than a critical value E_c. For finite systems, the abrupt vanishing at E_c gives place to a maximum followed by an exponential decay. Finally, if $p(l)$ decays more quickly than exponentially, the mobility will display a non-zero value for any field intensity independently of system size, vanishing asymptotically for large values of the field intensity.

The model we investigate in this article may be classified in this latter category. We show that, also for this case, the mobility for large values of field intensity displays a behaviour that may be fitted to an exponential decay.

The article is organized as follows. Section 2 is devoted to a detailed description of the proposed method, and section 3 shows its application to the disordered lattice outlined above. Finally, section 4 gives the conclusions.

2. Description of the method

In a typical single-particle computer simulation the hopping rates $\{J_{il}\}$ are chosen so as to model the main physical characteristics of the system one wishes to study. A finite lattice is then generated and periodic boundary conditions are imposed on the model. The computed quantities, in general moments of the distribution function, are averages over a large number of history runs. The simulated situation is physically equivalent to that of a moving particle in an infinite lattice formed by the repetition of a basic pattern. When computing infinite-lattice related quantities, one is essentially keeping track of the number of times a particle crosses the boundaries of the basic pattern in a given direction.

The method we describe in this paper is essentially a formal extension of this procedure, in which a finite-lattice problem is solved while a bookkeeping of the number of times a given path crosses any of the boundaries is maintained. In this way one may establish a mapping of each path linking two sites in the finite lattice into a path linking two sites in the infinite lattice, and thus relate the probability functions of the two systems. We next discuss a way of formalizing this procedure.

For the sake of simplicity we consider a one-dimensional example. Extensions to higher dimensions are straightforward. Let N be the number of lattice sites in the basic segment from which the infinite lattice is generated by space translation. Once the hopping rates $\{J_{il}\}$ are defined and a total transition rate ϵ_0 has been chosen, we may construct the transition matrix A for the finite lattice, the elements of which are defined by

$$A_{lj} = p_{lj}, \qquad l, j \in [1, N], \tag{1}$$

where

$$p_{lj} = \frac{J_{lj}}{\epsilon_0}, \tag{2}$$

and the diagonal elements $\{J_{ii}\}$ are defined by

$$J_{ii} = \epsilon_0 - \sum_{l \neq i} J_{li}. \tag{3}$$

In order to classify paths according to the number of times a boundary is crossed in a given direction, we associate a phase factor $\exp(\mathrm{i}\theta)$ to the transition matrix element connecting site N to site 1 (p_{1N}). To the reverse transition we associate a phase $\exp(-\mathrm{i}\theta)$. We will denote the resulting matrix by $A(\theta)$. In terms of this matrix, the probability that a particle initially at site j reaches site l in n steps, with a net number of r boundary crossings, may be expressed as

$$P^r_{lj}(n) = \frac{1}{2\pi} \int_{-\pi}^{\pi} [A^n(\theta)]_{lj} \exp(-\mathrm{i}r\theta)\, \mathrm{d}\theta. \tag{4}$$

Since each path is formed by a succession of individual transitions and the probability associated with a path is given by the product of the probabilities of each individual transition, a path with a net number of r boundary crossings will exhibit a phase factor $\exp(\mathrm{i}r\theta)$. Since $[A^n(\theta)]_{lj}$ contains the sum of the probabilities of all paths of length n linking site j to site l, the integral filters out the corresponding quantity for r boundary crossings. In this way, the finite-lattice probability $P^r_{lj}(n)$ may be mapped into the infinite-lattice probability that the particle goes from site j to site $l + rN$ in n steps. Thus we may write

$$P_{l+rN,j}(n) = \frac{1}{2\pi} \int_{-\pi}^{\pi} [A^n(\theta)]_{lj} \exp(-\mathrm{i}r\theta)\, \mathrm{d}\theta, \tag{5}$$

where P, from now on, stands for the infinite-lattice probability function. By inverting the Fourier transform in equation (5) and taking derivatives one obtains

$$\sum_r r^k P_{l+rN,j}(n) = \left(-\mathrm{i}\frac{\partial}{\partial\theta}\right)^k [A^n(\theta)]_{lj}|_{\theta=0}. \tag{6}$$

By making use of equation (6), the first and second moments of the distribution function after n steps, for a particle beginning at site j at $n = 0$, may, correspondingly, be given by

$$\langle X\rangle_j(n) = \sum_{l=1}^{N}(l-j)(A^n(\theta))_{lj}|_{\theta=0} + N\sum_{l=1}^{N}\left(-\mathrm{i}\frac{\partial}{\partial\theta}\right)(A^n(\theta))_{lj}|_{\theta=0}, \tag{7}$$

$$\begin{aligned}\langle X^2\rangle_j(n) = {} & \sum_{l=1}^{N}(l-j)^2[A^n(\theta)]_{lj}|_{\theta=0} + 2N\sum_{l=1}^{N}(l-j)\left(-\mathrm{i}\frac{\partial}{\partial\theta}\right)[A^n(\theta)]_{lj}|_{\theta=0} \\ & + N^2\sum_{l=1}^{N}\left(-\mathrm{i}\frac{\partial}{\partial\theta}\right)^2[A^n(\theta)]_{lj}|_{\theta=0}.\end{aligned} \tag{8}$$

The mean displacement and the mean square displacement after n steps, averaged over all possible initial positions of the particle, may then be obtained from equations (7) and (8) in the form

$$\langle R\rangle(n) = \frac{1}{N}\sum_j(\langle X\rangle_j(n)), \tag{9}$$

$$\langle R^2\rangle(n) = \frac{1}{N}\sum_j(\langle X^2\rangle_j(n) - (\langle X\rangle_j(n))^2). \tag{10}$$

For sufficiently large n, one may obtain expressions for $\langle R(t)\rangle$ and $\langle R^2(t)\rangle$ by substituting $\epsilon_0 t$ for n in equations (9) and (10).

The drift velocity and the diffusion coefficient may then be obtained directly from

$$v_{\mathrm{d}} = \lim_{n\to\infty} \frac{\langle R(n)\rangle \epsilon_0}{n}, \tag{11}$$

$$D = \lim_{n\to\infty} \frac{\langle R^2(n)\rangle \epsilon_0}{2n}. \tag{12}$$

To carry through the calculations outlined above the derivatives in equations (7) and (8) have to be evaluated. From equation (6) we see that the knowledge of $A^n(\theta)$ up to order k in θ enables the calculation of all moments of P up to the kth order. A simple method for evaluating the first and second derivatives is as follows. By expanding the matrix A in powers of θ we obtain

$$A(\theta) = A + \mathrm{i}\theta B - \frac{\theta^2}{2} C + \mathrm{o}(\theta^3). \tag{13}$$

Squaring $A(\theta)$ and keeping terms up to second order yields

$$\begin{aligned} A^2(\theta) &= A^2 + \mathrm{i}\theta(AB + BA) - \frac{\theta^2}{2}(AC + CA + 2B^2) \\ &= A_2 + \mathrm{i}\theta B_2 - \frac{\theta^2}{2} C_2. \end{aligned} \tag{14}$$

The above procedure may be generalized to arbitrary n:

$$A^n(\theta) = A_n + \mathrm{i}\theta B_n - \frac{\theta^2}{2} C_n, \tag{15}$$

where

$$A_n = A_{n-1} A, \tag{16}$$

$$B_n = A_{n-1} B + B_{n-1} A, \tag{17}$$

$$C_n = A_{n-1} C + C_{n-1} A + 2 B_{n-1} B. \tag{18}$$

The first and second derivatives appearing in equations (7) and (8) are then directly given by the matrices B_n and C_n, respectively. Equations (16)–(18) define a simple iterative procedure for calculating these matrices. This procedure is easily generalized to the calculation of higher-order moments. The algorithm outlined above yields exact results for the one-particle probability function moments. Its computer implementation is quite straightforward.

3. Application to the computation of the mobility of a single particle

Next we apply the method described above to the study of the mobility displayed by a particle diffusing in a lattice with defects in the form of dead-ends, under the influence of an external bias. We consider a system in the form shown in figure 1. The finite lattice is a 7×7 lattice with defects as shown in figure 2, where the dashed segments represent forbidden transitions. The finite-lattice transition matrix has 49×49 elements, since each site reachable by the particle represents a possible state. A field is supposed to be applied in the x-direction, inducing a drift velocity in the positive x-direction. The elements of the transition matrix, for movement in the x-direction in the sense favoured by the bias, are given by $p_{il} = J_+/\epsilon_0$, for normal bonds, $p_{il} = 0$, for defective bonds, and $p_{il} = J_+ \exp(\mathrm{i}\theta_x)/\epsilon_0$, for transitions in the positive x-direction connecting sites at opposite edges of the finite lattice. The matrix elements associated to the

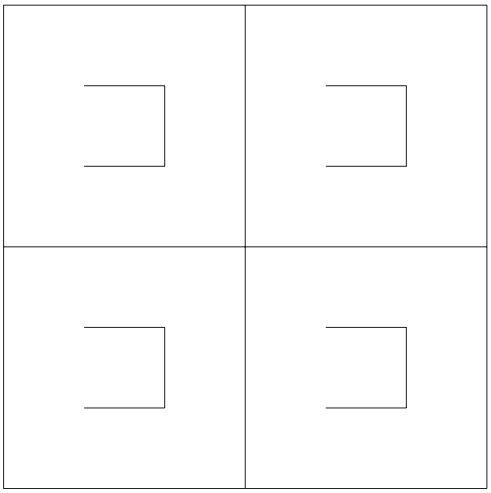

Figure 1. Model of the studied system. The system comprises an array of defects in the form of dead-ends. The figure shows four units of the finite lattice (*see text*).

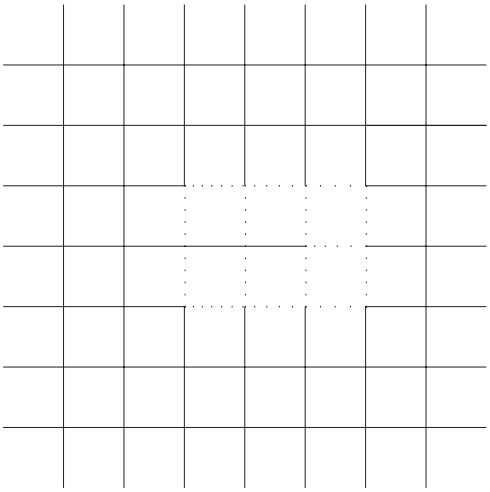

Figure 2. Model for the defect. The figure shows the structure of the defect and its position in the 7×7 lattice which by translations in the x- and y-directions forms the infinite lattice. The dashed segments indicate the forbidden transitions.

corresponding reverse transitions are given by the complex conjugate of these expressions, with J_+ replaced by J_-, which are defined as

$$J_+ = J_0 \exp(F_x), \tag{19}$$

$$J_- = J_0 \exp(-F_x), \tag{20}$$

where J_0 is the transition rate without bias, F_x is a dimensionless parameter related to the system physical variables by $F_x = E_x a/2K_\mathrm{b}T$, where E_x is the field intensity, a the lattice spacing and $K_\mathrm{b}T$ the usual thermal energy. The elements of the transition matrix in the y-direction have similar expressions, but with $F_y = 0$. Finally, we define the maximum transition rate off a site as $\epsilon_0 = J_0(2 + \exp(F_x) + \exp(-F_x))$.

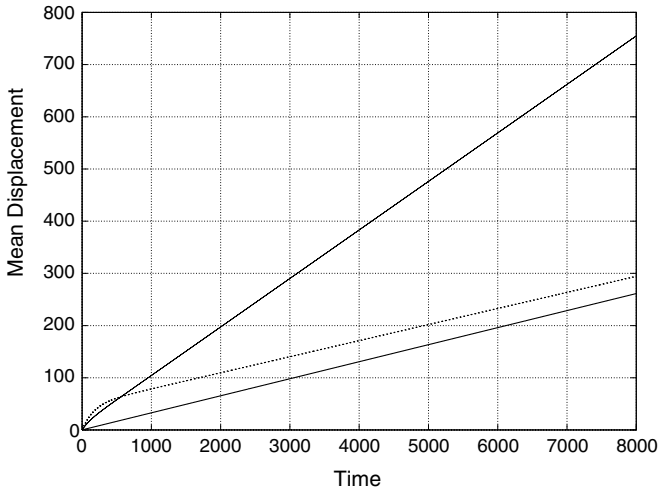

Figure 3. Computed mean displacements as a function of time. The figure shows the mean displacement for typical values of the external field. Field values are as follows: higher curve $F = 0.20$; middle curve $F = 0.55$; lower curve $F = 0.95$.

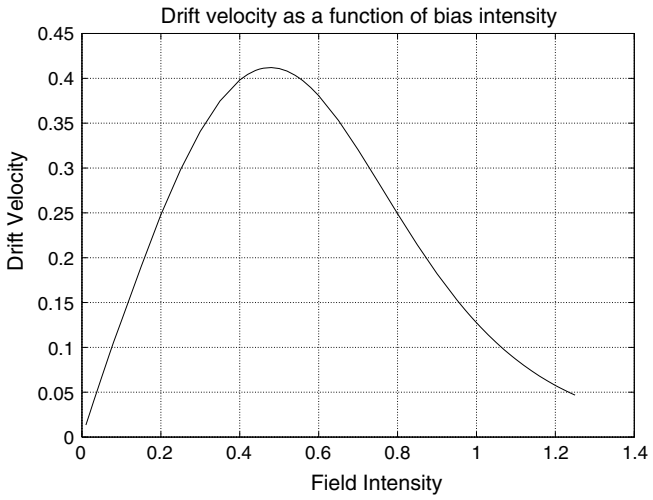

Figure 4. Average drift velocity. The figure shows the average drift velocity as a function of the field intensity.

The matrices A, B and C, defined in section 2, are then readily constructed, by following the procedure given therein. By implementing the iterative procedure also given there and making use of equations (9) and (10), we have computed the first and second moments of the one-particle distribution function. All results are given in units of J_0 and a. Typical computed mean displacements as a function of time, for particular values of bias, are shown in figure 3. The computed average drift velocity as a function of bias is given in figure 4. The connection between the discrete and continuous time pictures has been established by equating $n = \epsilon_0 t$.

The drift velocity for each value of bias has been obtained through a linear fitting of the mean displacement with time, for long times. It is seen that the drift velocity initially increases

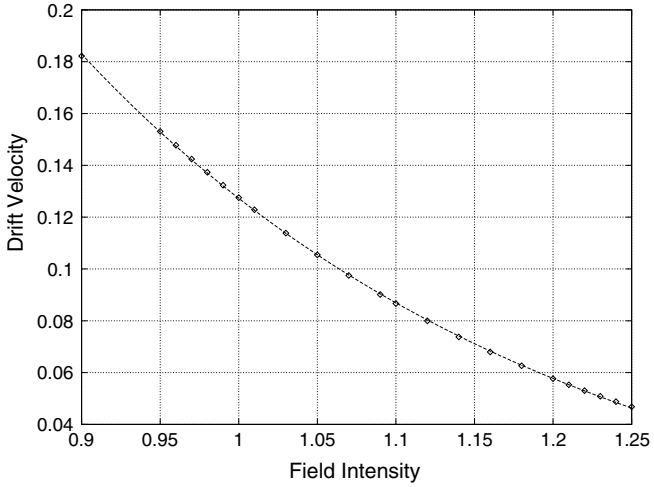

Figure 5. Average drift velocity as a function of field intensity for high values of the field intensity. The figure shows a comparison between the computed drift velocity (points) and the functional form $c_1 + c_2 \exp(-(x - c_3)/c_4)$ (line), where $c_1 = -0.018\,77$, $c_2 = 0.201\,75$, $c_3 = 0.900\,00$, $c_4 = 0.309\,36$.

linearly with bias, then crosses over to a nonlinear regime, reaches a maximum and then decays with further increase of the field intensity, indicating that the diffusing particle spends longer times in the traps with increasing bias, in plain agreement with previously published results and studies (Bouchaud and Georges 1990 p 127, Barma and Dhar 1982).

In the very low bias limit, the Einstein relation between diffusion constant and mobility is expected to hold. The diffusion constant, in the zero bias condition, has been obtained from the long-time behaviour of $\langle R^2 \rangle$ when $F = 0$, yielding $D = 0.633\,57$, a value, as expected, smaller than one, the perfect lattice value. By fitting a line $c_1 + c_2 F$ to the $v_d \times F$ curve in the limit of very low bias, the values $c_1 = 0.000\,01$ and $c_2 = 1.348\,01$ are obtained. In terms of the units and definitions we are working with we expect $v_d = 2DF$, hence yielding $D = 0.674\,01$, a value that differs by about 6% from the zero-bias result. Explaining this difference may require some further analysis. Possibly, the anisotropy introduced by the defects plays a role in this explanation.

Finally, we consider the behaviour of the drift velocity in the limit of large values of bias. It has been asserted that in a disordered system, with quenched defects, in the limit of large bias, when the relation between hopping transition rate and bias is as given above, the drift velocity decays exponentially with bias (Bouchaud and Georges 1990 p 244). We expect this relation to hold also for the case of the array of traps considered in our example. In figure 5 a comparison between the computed result and the result obtained by fitting to the functional form $c_1 + c_2 \exp(-(x - c_3)/c_4)$ shows remarkably good agreement, lending support to this conjecture.

4. Conclusions

A novel method for exactly computing the moments of one-particle distribution functions associated to a single particle diffusing in a lattice gas with defects of arbitrary characteristics, when periodic boundary conditions are imposed, has been presented. The method has been shown to be particularly suitable for studies concerning the mobility of a particle diffusing in a

lattice gas with confining defects. Since the results obtained are free from statistical errors and averaged over all initial possible positions of the particle in the lattice, the method seems to compare advantageously with Monte Carlo simulations in the study of phenomena governed by specific laws, such as in the cases of either anomalous mobility or anomalous diffusion, where very precise data are needed.

The method is general and, in principle, may be applied to any model system, even to those in which probability is not conserved, due to the presence of traps, for instance.

References

Alexander S, Bernasconi J, Schneider W R and Orbach R 1981 *Rev. Mod. Phys.* **53** 175

Allnatt A R and Lidiard A B 1993 *Atomic Transport in Solids* (Cambridge: Cambridge University Press)

Balkanski M and Elliott R J (ed) 1998 *Atomic Diffusion in Disordered Materials: Theory and Applications* (Singapore: World Scientific)

Barkema G T, Biswas P and van Beijeren H 2001 *Preprint* cond-mat/0105163v1

Barma M and Dhar D 1982 *J. Phys. C: Solid State Phys.* **16** 1451

Bouchaud J P and Georges A 1990 *Phys. Rep.* **195** 127

Bunde A and Havlin S (ed) 1991 *Fractals and Disordered Systems* (Berlin: Springer)

Dyson F J 1953 *Phys. Rev.* **92** 1331

Elliott R J, Krumhansel J A and Leath P L 1974 *Rev. Mod. Phys.* **46** 465

Giacometti A and Murthy K P N 1996 *Phys. Rev.* E **53** 5647

Haus J H and Kehr K W 1987 *Phys. Rep.* **150** 263

Havlin S and Ben-Avraham D 1987 *Adv. Phys.* **36** 263

Hilfer R 1991 *Phys. Rev.* B **44** 628

Hughes B D 1995 *Random Walks and Random Environments* (Oxford: Clarendon)

Kehr K W and Binder K 1984 *Applications of the Monte Carlo Method in Statistical Physicis* (*Topics in Current Physics* vol 36) ed K Binder (Berlin: Springer) p 181

Perondi L F 1993 *D Phil. Thesis* (Oxford: Oxford University Press)

Perondi L F and Binder P M 1993a *Phys. Rev.* B **47** 14221

Perondi L F and Binder P M 1993b *Phys. Rev.* B **48** 4136

Perondi L F and Elliott R J 1993 *J. Phys.: Condens. Matter* **5** 6857

Stanley H E and Ostrowsky N (ed) 1986 *On Growth and Form* (Dordrecht: Martinus Nijhoff)

Tahir-Kheli R A and Elliott R J 1983 *Phys. Rev.* B **27** 844

Webman I 1981 *Phys. Rev. Lett.* **47** 1496