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Abstract. A concentration c of particles undergo correlated random walks on a lattice. The random walks are constrained by only allowing the lattice sites to be singly occupied. This leads to the particles being 'dynamically' correlated. In addition to the dynamic correlations the hopping rates of the particles are disordered. The random hopping rates give rise to 'static' correlations. The resultant model is a many-body problem with disorder.

Of principal interest are the new correlations that arise between a disordered random walk and a correlated random walk (CRW) and the effect these correlations have on the self-diffusion constant. The CRW is represented by a non-linear master equation from which the diffusion constant is obtained by means of classical many-body Green functions. The dynamic correlations are represented by a two-particle Green function. The disorder is studied by means of the bond coherent potential approximation (BCPA). The disorder gives rise to a vertex correction to the two-particle Green function. The vertex correction is obtained by using the BCPA.

1. Introduction

The correlated random walk (CRW) problem has been studied as a model of the statistical effects of high densities of ions on the ionic diffusivity of superionic conductors. We are concerned with the effects of disorder, in particular random hopping rates, on the CRW diffusion constant. Random hopping rates are expected to occur in glassy ionic conductors (Brak and Elliott 1989) which are of considerable technological importance.

A review of the early work on CRWs may be found in LeClaire and Lidiard (1956), more recent results were obtained by Sankey and Fedders (1980) (see this paper for earlier references) who used diagrammatic methods to obtain the self-diffusion response function. Another interesting approach has been used by Nakazato and Kitahara (1980). An important series of papers (Tahir-Kheli and Elliott 1983, Tahir-Kheli 1983a, b, c, Holdsworth *et al* 1986) beginning with the paper by Tahir-Kheli and Elliott (1983) (TKE) used Green function techniques to obtain the diffusion response function for a tracer particle which had a hopping rate which was different to the background particles. The other papers in the series generalised the method to multicomponent systems, to systems with two sublattices, and to the case where the background particles are stationary. Monte Carlo simulations of CRWs (Richards 1977, Kehr *et al* 1980, Murch and Rothman 1981, Kutner *et al* 1982, Murch 1984 and Tahir-Kheli *et al* 1986) are a convenient test of the, unfortunately necessary, approximations made in the various calculations. A more recent review is given by Allnatt and Lidiard (1987).

We consider the CRW model in a little more detail. In its simplest form the model consists of a concentration c of particles hopping between nearest-neighbour sites of a lattice. However the random walk motion of each particle is constrained in that two particles are not allowed to occupy a lattice site at the same time. Thus a particle can only hop onto a site if that site is vacant. This gives rise to a 'blocking' effect on the motion of the particles. In order to determine the diffusion constant of a particle one of the particles, the 'tracer' particle, must be picked out and its motion followed in the remaining 'background' particles. If the tracer has the same hopping rate as the background particles then the diffusion constant is the self-diffusion constant. However, it is a feature of the TKE method that the tracer particle can have a different hopping rate to the background particles as may be the case in some experiments where the tracer particles may be different isotopes.

The single occupancy constraint can have a marked effect on the tracer diffusion constant. The simplest approximation (MFA) is to assume that the only effect of the background particles is to reduce the probability of the tracer jumping onto a site by the vacancy concentration $v = 1 - c$. This modifies the tracer diffusion constant by the factor v. However, this only takes into account the 'local' effect of the background particles, the diffusion constant depends on the entire *path* of the tracer. This can be seen by the following argument (LeClaire and Lidiard 1956). At any time step the tracer can only hop onto a vacant nearest-neighbour site. Let a_i be the (stochastic) nearest-neighbour vector taken by the tracer on the ith step t, assuming the tracer started at some initial site. Then after n steps the net displacement of the tracer is $X = \sum_{i=1}^{n} a_i$ and hence the diffusion constant, which is defined by $\lim_{n\to\infty}\langle X^2\rangle_P/2n$, is given by

$$\mathbb{D} = \lim_{n\to\infty} \left(\left\langle \sum_i a_i^2 \right\rangle_P + 2\left\langle \sum_{i>j} a_i a_j \right\rangle_P \right) \bigg/ 2n$$

$$= \lim_{n\to\infty} \frac{\langle \sum_i a_i^2 \rangle_P}{2n} \left(1 + \frac{2\langle \sum_{i>j} a_i a_j \rangle_P}{\langle \sum_i a_i^2 \rangle_P} \right) \tag{1.1}$$

which is generally written in the form

$$\mathbb{D} = \mathbb{D}_0 f_0 \tag{1.2}$$

where $\mathbb{D}_0 = \lim_{n\to\infty}\langle \sum_i a_i^2 \rangle_P/2n$ and the 'correlation factor' f_0 is the remaining factor in (1.1). The average $\langle \ldots \rangle_P$ uses the probability of each n-step path occurring i.e. sum over all n-step paths, multiplied by the probability of the path occurring. Note that $\mathbb{D}_0$ just depends on products of 'local' steps and, in the absence of disorder, is given by

$$\mathbb{D}_0 = va^2 J_A \tag{1.3}$$

where J_A is the tracer hopping rate. This is the MFA mentioned above. We shall assume that the hopping rate is given by the Arrhenius form

$$J_A = \Omega_A e^{-\beta E} \tag{1.4}$$

where β is the inverse temperature and E the height of the energy barrier the particle has to jump over. Equation (1.1) clearly shows that the MFA must be modified by the correlation factor, which (1.1) shows depends on the average of steps at two different times i.e. $\langle \sum_{i>j} a_i a_j \rangle_P$. It will be seen below that in the Green function formalism $\mathbb{D}_0$ is always given by the *one*-particle Green function whilst the correlation factor is related to a non-interacting of 'free' *two*-particle Green function.

In the presence of disorder and for a particular configuration of bonds the tracer may or may not be able to diffuse depending on the particular values of the nearest-neighbour

hopping rates. However, *on average* the tracers motion is diffusive, although the diffusion constant may be zero or anomalous. It is the average diffusion constant $\bar{\mathbb{D}}$ that we are concerned with. For the CRW with disorder the average diffusion constant retains the same *form* as (1.2) with $\mathbb{D}_0$ replaced by $\bar{\mathbb{D}}_0$ and f_0 replaced by the average correlation factor $\bar{f}_0$. The argument is the same as that leading to (1.1) except that the probability of a given path occurring, for a given bond configuration, depends on the particular sequence of hopping rates encountered on each step of the walk. This only changes the averaging procedure and *not* the form of (1.2).

The diffusion constant is obtained from the continuum limit of the CRW. As shown in § 2 we use a master equation to represent the CRW. The master equation is then used to obtain equations of motion for various moments of the stochastic variables. The equations of motion of the moments, when supplemented with initial conditions, give rise to an inhomogeneous term and thus the moments are classical Green functions. These equations of motion of the various moments are coupled to equations of motion of higher order moments. This hierarchy of equations is characteristic of a many-body problem. If the same decoupling approximation of TKE is used a closed set of equations is obtained which may be solved and the diffusion constant extracted.

In the presence of disorder these equations of motion are averaged over the disorder to obtain an equation of motion for the *average* Green function from which the average diffusion constant may be extracted. The disorder average cannot be done exactly and must be approximated. The approximation we use is the coherent potential approximation (Elliott *et al* 1974) as applied to bond disorder (BCPA). This is a self-consistent effective medium approximation and is discussed in detail in § 3.

The CRW in a disordered medium is essentially a problem of correlations. The CRW in a non-disordered medium has correlations which arise from the blocking effect of the particles. We will refer to these correlations as 'dynamic' correlations. It is these correlations which are approximated by the TKE decoupling scheme. If we consider a 'simple' random walk (i.e. only one particle performing a random walk in an *empty* lattice), then when disorder is added to the simple random walk additional correlations arise when averaging over the disorder. It is these correlations that are approximated by the BCPA. We will refer to the disorder correlations as 'static' correlations. When disorder is added to the CRW *new* correlations arise. There are new static correlations which arise when averaging the two-particle Green function used to obtain f_0. These two-particle static correlations give rise to a 'vertex' function which is obtained by using the BCPA in § 4. There are additional correlations which arise between the particle interactions and the disorder averaging. These static-dynamic correlations are more complicated than the two-particle static correlations. As an initial study we neglect these correlations.

The additional complexity of the static-dynamic correlations has its origin in the nature of the mathematical representation of the problem. There is a fundamental difference in the way the effect of disorder is represented and the way the particle interactions are represented. The interactions between the particles manifest themselves in the coupling of *differential* equations. This is the analogue of the Zubarov method in many-body quantum mechanics. The differential equations are solved by decoupling approximations. By contrast, in the simple random walk, the disorder manifests itself through an implicit *integral* equation for the Green function. The integral equation is then solved by iteration, leading to a Dyson's type equation. This is analogous to a path integral or field theory method, which is characterised by Feynman diagrams. A problem then arises when the CRW and the disorder are combined. In order to solve the problem

it seems necessary to use only one of the two types of representation. As the disorder cannot be expressed in differential form, it is necessary to use the integral representation. This presents little problem for the one-particle diffusion constant $\mathbb{D}_0$ and, as is seen in § 5, it is also possible to express the *free* two-particle Green in a form convenient for the integral representation required by the disorder. This enables the effect of the new two-particle static correlation to be obtained. However, to go further, it appears to be necessary to reformulate the CRW in an integral form. We do not consider this problem and thus neglect the static–dynamic correlations. Unfortunately an explicit expression cannot be obtained for the average of the two-particle Green function and some numerical integration has to be done to determine $\bar{f}_0$. The numerical work is discussed in § 6.

We only consider two types of hopping rate probability distribution, however the calculation is easily modified for different distributions. The first distribution considered is the percolation or binary distribution, where the hopping rate is 0 with probability p and some value J with probability $1 - p$. The second distribution considered is the uniform barrier height distribution. Here the height of the energy barrier E is considered to be random (with uniform distribution). The distribution of barrier heights in turn induces a distribution of hopping rates through (1.4).

2. Equations of motion

When including disorder in the CRW it is more convenient to reformulate the CRW in terms of a master equation and use the Laplace transform in place of the Fourier transform (in time) used by TKE. The details of the master equation and results that will be needed below may be found in Brak (1989). We briefly outline the method principally to establish the notation and reduce the necessity of constant referral to TKE. Let the concentration of the background particles be c. Then the state of the system at any particular time is given by the stochastic vector

$$pn = \{p_1, p_2, \ldots, p_N, n_1, n_2, \ldots, n_N\} \tag{2.1}$$

where

$$p_j = \begin{cases} 1 & \text{if the tracer particle occupies site } j; \\ 0 & \text{otherwise} \end{cases} \tag{2.2a}$$

and

$$n_j = \begin{cases} 1 & \text{if a background particle occupies site } j, \\ 0 & \text{otherwise.} \end{cases} \tag{2.2b}$$

and N is the size of the lattice. Let the single tracer particle hop with rate J_A and the background particles hop with rate J_B. The master equation is an equation of motion for the conditional probability $\mathbb{P}(pn, t)$ where $\mathbb{P}(pn; t)$ is the probability of the system being in the state pn at time t, given that it was in some initial state at time $t = 0$. The master equation is

$$\frac{\partial}{\partial t} \mathbb{P}(pn; t) = \sum_{p'n'} \sum_j \left(W_j(pn \leftarrow p'n') \mathbb{P}(p'n'; t) - W_j(p'n' \leftarrow pn) \mathbb{P}(pn; t) \right)$$

$$\tag{2.3}$$

where $\Sigma_{p'n'}$ is a sum over all states $p'n'$ and Σ_j is a sum over all lattice sites. The transition rate is given by

$$W_j(pn \leftarrow p'n') = \sum_a (J_A p'_{j+a}(1 - p'_j - n'_j)\delta_{p_j,p'_j}\bar{\delta}_{p_{j+a},p'_{j+a}}\delta_{n_j,n'_j}\delta_{n_{j+a},n'_{j+a}}$$

$$+ J^B n'_{j+a}(1 - p'_j - n'_j)\delta_{p_j,p'_j}\delta_{p_{j+a},p'_{j+a}}\bar{\delta}_{n_j,n'_j}\bar{\delta}_{n_{j+a},n'_{j+a}})$$

$$\times \prod_{l\notin\{j,j+a\}} \delta_{p_l,p'_l}\delta_{n_l,n'_l}. \tag{2.4}$$

where δ_{p_j,p'_j} is one if p_j equals p'_j and zero otherwise, $\bar{\delta}_{p_j,p'_j} = 1 - \delta_{p_j,p'_j}$ and Σ_a is a sum over nearest-neighbour lattice vectors.

As shown explicitly in Brak (1989) the diffusion constant is the coefficient of k^2 in the expansion of the characteristic function

$$G_k(t) = \sum_l \exp(-i\,kl)\langle p_l \rangle. \tag{2.5}$$

Here averages $\langle \ldots \rangle$ are taken using the conditional probability distribution $\mathbb{P}(pn, t)$ and in addition averaging over all initial configurations of background particles with the tracer fixed on site g. If the Laplace transform of $G_k(t)$,

$$G_k(s) = \int_0^\infty \exp(-st)G_k(t)\,\mathrm{d}t \tag{2.6}$$

can be obtained then the diffusion constant $\mathbb{D}$ is given by

$$1/\mathbb{D} = \lim_{k\to 0}\lim_{s\to 0} k^2 G_k(s). \tag{2.7}$$

Thus we see it is not necessary to solve (2.3) completely but only to find $\langle p_l \rangle$. Using the master equation it can be shown that

$$\frac{\partial}{\partial t}\langle p_l \rangle = J_A \sum_a \langle v(p_{l+a} - p_l + p_l u_{l+a} - p_{l+a}u_l)\rangle \tag{2.8}$$

where $u_l = n_l - c$ has been used. Equation (2.8) is not closed and requires averages of the form $\langle p_l u_j \rangle$. Once again using the master equation as well as the decoupling scheme of TKE it can be shown that

$$\frac{\partial}{\partial t}\langle p_l u_j \rangle = \sum_a \langle v J_A(p_{l+a}u_j - p_l u_j) + J_B(p_l u_{j+a} - p_l u_j)\rangle(1 - \delta_{l,j})$$

$$- \sum_a c J_A \langle p_l u_{l+a} - p_{l+a}u_l + v(p_{l+a} - p_l)\rangle\delta_{l,j}$$

$$+ \langle J_A((v-c)p_l u_j + cp_j u_l + vcp_l) + J_B(p_l u_j + cp_l)\rangle\delta_{\langle l,j\rangle}. \tag{2.9}$$

where $v = 1 - c$ and $\delta_{\langle l,j\rangle}$ is one if l and j are nearest neighbours and zero otherwise. Let the Laplace transform of $\langle p_l u_j \rangle$ be denoted by

$$G_{l,g}^{j,g}(s) = \int_0^\infty \exp(-st)\langle p_l u_j \rangle\,\mathrm{d}t. \tag{2.10}$$

Note, for notational convenience only, subscripts have been used to denote the tracer

labels and superscripts used to label the background 'particle'. The Laplace transform of equations (2.8) and (2.9) then give

$$sG_{l,g} = \delta_{l,g} + vJ_A \sum_a (G_{l+a,g} - G_{l,g}) + J_A \sum_a (G_{l,g}^{l+a,g} - G_{l+a,g}^{l,g}) \quad (2.11a)$$

and

$$sG_{l,g}^{j,g} = -c\delta_{l,g}\delta_{j,g} + \sum_a [vJ_A(G_{l+a,g}^{j,g} - G_{l,g}^{j,g}) + J_B(G_{l,g}^{j+a,g} - G_{l,g}^{j,g})](1 - \delta_{l,j})$$

$$- \sum_a cJ_A[G_{l,g}^{l+a,g} - G_{l+a,g}^{l,g} + v(G_{l+a,g} - G_{l,g})]\delta_{l,j}$$

$$+ \{J_A[(v-c)G_{j,g}^{l,g} + cG_{l,g}^{l,g} + vcG_{l,g}] + J_B(G_{l,g}^{l,g} + cG_{l,g})\}\delta_{\langle l,j\rangle}. \quad (2.11b)$$

The average of the background variable u_j satisfies an equation of motion

$$H^{j,g} = -c\delta_{j,g} + J_B \sum_a (H^{j+a,g} - H^{j,g}) + J_B \sum_a (G_{j\mp a,g}^{j,g} - G_{j,g}^{j+a,g}) \quad (2.12)$$

where

$$H^{j,g}(s) = \int_0^\infty \exp(-st)\langle u_j\rangle \, dt. \quad (2.13)$$

Despite there being more than one background particle it can be shown (Brak 1989) that $H^{j,g}$ can be interpreted as representing a single 'hole' undergoing a correlated random walk. Equations (2.11a) and (2.12) both have inhomogeneous terms arising from the initial conditions $\langle p_l\rangle(t=0) = \delta_{l,g}$ and $\langle u_j(t=0)\rangle = -c\delta_{j,g}$ and thus $G_{l,g}$ and $H^{j,g}$ are classical one-particle Green functions. Similarly $G_{l,g}^{j,g}$ is a classical two-particle Green function.

Equations (2.11a, b) are the same results obtained by TKE. They find that the correlation factor for cubic lattices is given by

$$f_0 = [1 - 2cJ_B \overline{\cos}\,\theta/(vJ_A + J_B)(1 + \overline{\cos}\,\theta)]^{-1} \quad (2.14)$$

where for the case of the simple cubic lattice

$$\overline{\cos}\,\theta = (vJ_A + J_B)(\hat{P}_0(0; 2a) - \hat{P}_0(0; 0)) \quad (2.15)$$

and

$$\hat{P}_0(s; r) = \frac{1}{N} \sum_\lambda \frac{\exp(-i\lambda r)}{s + vJ_A\Gamma_\lambda + J_B\Gamma_\lambda} \quad (2.16)$$

where

$$\Gamma_\lambda = \sum_a (1 - e^{i\lambda a}). \quad (2.17)$$

The sum over the wavevector λ in (2.16) is over the Brillouin zone of the simple cubic lattice.

3. One-particle BCPA

Previous methods (Elliott and Pepper 1973, Chakrabarti *et al* 1982, Kanehisa and Elliott 1987, Webman 1981, Odagaki and Lax 1981) of implementing the BCPA using one-particle Green function methods do not conveniently generalise to the two-particle case.

Hence an alternative formulation of the BCPA has been developed which can be used for the two-particle Green function. We present the method for the *simple* random walk (i.e. only one particle on the lattice) with disordered bonds. The equation of motion is given by (2.11a) but without the two-particle terms. Let the hopping rate of the particle be J. In the presence of random hopping rates (or disordered bonds) the equation for a given configuration of bonds can be written in the form

$$sG_{l,g} = \delta_{l,g} + J \sum_a (G_{l+a,g} - G_{l,g}) + \sum_\gamma K^{(\gamma)}(\delta_{l,d_\gamma} - \delta_{l,d'_\gamma})(G_{d'_\gamma,g} - G_{d_\gamma,g}) \tag{3.1}$$

where Σ_γ is a sum over all bonds of the lattice, d_γ and d'_γ are the two sites adjacent to the γ bond. Note, the hopping rate is made up of two components, J the non-random hopping rate representing an unperturbed system and $K^{(\gamma)}$ a random hopping rate. Thus, for a given bond configuration, the hopping rate of the bond γ is $J + K^{(\gamma)}$. If $K^{(\gamma)}$ is non-zero then the bond γ will be referred to as a 'defect' bond. In terms of the non-random system whose Green function $\hat{G}_{l,g}$ is given explicitly by

$$\hat{G}_{l,g}(s) = \frac{1}{N} \sum_\lambda \frac{e^{i\lambda(l-g)}}{s + J\Gamma_\lambda} \tag{3.2}$$

equation (3.1) can be written in the form

$$G_{l,g} = \hat{G}_{l,g} + \sum_{m,n} \hat{G}_{l,m} W_{m,n} G_{n,g} \tag{3.3}$$

where $W_{m,n}$ is the disorder matrix

$$W_{m,n} = \sum_\gamma K^{(\gamma)}(\delta_{m,d_\gamma} - \delta_{m,d'_\gamma})(\delta_{d'_\gamma,n} - \delta_{d_\gamma,n}). \tag{3.4}$$

The above Green functions are indexed by the sites of the lattice. We now change to bond indexed Green functions. This is done by partitioning the sites of the lattice into disjoint pairs. The sites of any pair must be nearest neighbours. Each pair, e.g. $\{l_1, l_2\}$, now uniquely labels a bond $\gamma = \{l_1, l_2\}$, and no two labelled bonds have any sites in common. Bond indexes will be denoted by Greek characters. As the bond partitioning is disjoint any site indexed matrix is partitioned into disjoint 2×2 submatrices. Each submatrix is uniquely labelled by a pair of bond indexes. Because the bond submatrices are disjoint the equation of motion for the 2×2 matrix Green function $G_{\mu,\nu}$ is the same as (3.3) but with the site indexes replaced by bond indexes, that is

$$G_{\mu,\nu} = \hat{G}_{\mu,\nu} + \sum_{\rho_1,\rho_2} \hat{G}_{\mu,\rho_1} W_{\rho_1,\rho_2} G_{\rho_2,\nu} \tag{3.5}$$

where each sum in $\Sigma_{\rho_1,\rho_2} \equiv \Sigma_{\rho_1}\Sigma_{\rho_2}$ is over all the bonds in the above partitioning.

With the equation of motion for G in bond index form we can continue with the conventional BCPA method. The average diffusion constant $\bar{\mathbb{D}}_0$ is obtained from the averaged Green function $\langle\!\langle G \rangle\!\rangle$. Here $\langle\!\langle \ldots \rangle\!\rangle$ is used to denote averaging over the bond disorder. The average Green function is obtained by means of the CPA. The CPA is a self-consistent approximation method and as such consists of two stages, first a self-consistent effective medium is constructed and the second, the self-consistency is implemented by means of an approximation. The construction of the effective medium is as follows. Instead of considering the disorder to be a perturbation away from a medium where the hopping rate is J, a non-random medium is introduced where the hopping rate is $J + \sigma$. If this is done then $\hat{G}$ in (3.5) must be replaced by the non-random effective medium Green function $\bar{G}$ and W replaced by $W - \Sigma$ (the relation between Σ and σ is given

below). Finally, the self-energy Σ (and hence σ) is determined self-consistently by requiring that when the Green functions equation of motion for G i.e. (3.5) is averaged over all disorder configurations we must have $\langle\!\langle G \rangle\!\rangle = \bar{G}$. We summarise the CPA replacements:

$$J \rightarrow \bar{J} = J + \sigma \tag{3.6a}$$

$$W \rightarrow \bar{W} = W - \Sigma \tag{3.6b}$$

$$\hat{G} \rightarrow \bar{G}. \tag{3.6c}$$

This construction is well defined and makes no approximations, however in order to proceed approximations are necessary. The essential approximation of the CPA is to neglect the correlations that arise because of clustering of defect bonds. The implementation of the CPA for *bond* disorder is more complex than for the case of *site* disorder, this is because the bond matrix W (i.e. the matrix whose matrix elements are $W_{\mu,\nu}$) is not diagonal whilst the corresponding matrix for site disorder is diagonal. The bond matrix W is however diagonal in the particular situation where two conditions are met (i) if there are only *isolated* defects (i.e. no defect clusters) and (ii) if the disjoint partitioning is done in such a way that each isolated defect is labelled by a single bond of the partitioning i.e. the two sites adjacent to the defect form a bond of the disjoint partitioning. If the first condition is met (e.g. very low defect concentrations) the second condition can always be met by a suitable choice of the partitioning.

Thus in the case of only isolated defects W is bond diagonal and (3.4) gives the 2×2 matrix $W_{\mu,\nu}$ as

$$W_{\mu,\nu} = -\delta_{\mu,\nu} K^{(\mu)} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \tag{3.7}$$

In the BCPA the approximation has to be implemented in two steps. Firstly, the bond matrix W (and Σ) are assumed to be diagonal. However, because of the nature of the bond partitioning and the diagonal approximation, symmetries of the lattice can be lost when converting from bond indexes back to site indexes. This problem is circumvented when it is necessary to convert from the bond indexes back to the site indexes if the following correspondence is used

$$\sum_{\gamma} \sum_{m_1 \in \gamma} \sum_{m_2 \in \gamma} \rightarrow \sum_{m_1} \sum_{m_2} (z\delta_{m_1,m_2} + \delta_{\langle m_1,m_2\rangle}) \tag{3.8}$$

where the sums on the right-hand side are over all the lattice sites and z is the coordination number of the lattice. Using (3.7) the equation of motion for $G_{\mu,\nu}$ then becomes

$$G_{\mu,\nu} = \bar{G}_{\mu,\nu} + \sum_{\rho} \bar{G}_{\mu,\rho} \bar{W}_{\rho,\rho} G_{\rho,\nu} \tag{3.9}$$

where $\bar{W}_{\rho,\rho} = W_{\rho,\rho} - \Sigma_{\rho,\rho}$ and $\Sigma_{\rho,\rho}$ is the bond diagonal non-random self-energy given by

$$\Sigma_{\rho,\rho} = -\sigma \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}. \tag{3.10}$$

Furthermore, $\bar{G}_{\mu,\nu}$ satisfies the equation

$$\bar{G}_{\mu,\nu} = \hat{G}_{\mu,\nu} + \sum_{\rho} \hat{G}_{\mu,\rho} \Sigma_{\rho,\rho} \bar{G}_{\rho,\nu}. \tag{3.11}$$

Equation (3.11) can be converted back to site indexes using (3.8). The resultant equation

has the full symmetry of the lattice and hence can be solved by Fourier transforming to give

$$\bar{G}_{l,g}(s) = \frac{1}{N} \sum_{\lambda} \frac{e^{i\lambda(l-g)}}{s + (J + \sigma)\Gamma_{\lambda}}. \tag{3.12}$$

Equation (3.9) may be formally solved by introducing the 'multiple scattering' T-matrix:

$$G_{\mu,\nu} = \bar{G}_{\mu,\sigma} + \sum_{\rho_1,\rho_2} \bar{G}_{\mu,\rho_1} \bar{T}_{\rho_1,\rho_2} \bar{G}_{\rho_2,\nu} \tag{3.13}$$

where $\bar{T}$ can be written in terms of the bond diagonal single *bond* t-matrix $\bar{t}$, where $\bar{T}$ and $\bar{t}$ are given by

$$\bar{T}_{\rho_1,\rho_2} = \bar{t}_{\rho_1,\rho_1}(1 - \bar{G}^F \bar{t})^{-1}_{\rho_1,\rho_2} \tag{3.14a}$$

$$\bar{t}_{\rho,\rho} = (W_{\rho,\rho} - \Sigma_{\rho,\rho})(1 - \bar{G}_{\rho,\rho} \bar{W}_{\rho,\rho})^{-1} \tag{3.14b}$$

and where $\bar{G}^F_{\rho_1,\rho_2} = \bar{G}_{\rho_1,\rho_2}(1 - \delta_{\rho_1,\rho_1})$ i.e. the bond off-diagonal part of $\bar{G}$. The 2×2 matrix $\bar{t}_{\rho,\rho}$ is given by

$$\bar{t}_{\rho,\rho} = t^{(\rho)} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \qquad t^{(\rho)}(s) = \frac{-(K^{(\rho)} - \sigma)}{1 + 2(K^{(\rho)} - \sigma)\Delta\bar{G}} \tag{3.15}$$

where $\Delta\bar{G} = \bar{G}_{0,0} - \bar{G}_{1,0}$ with $\bar{G}_{0,0}$ and $\bar{G}_{1,0}$ given by (3.12) with $l - g = 0$ and $l - g = a$ respectively.

The effective medium is determined by $\langle\langle G \rangle\rangle = \bar{G}$. Averaging (3.13) and putting $\langle\langle G \rangle\rangle = \bar{G}$ requires, for self-consistency, that $\langle\langle \bar{T} \rangle\rangle = 0$. The principal approximation of the CPA is to neglect, when averaging $\bar{T}$ over all configurations, correlations between $\bar{t}_{\rho,\rho}$ matrices labelled by different bonds. With this approximation $\langle\langle \bar{T} \rangle\rangle = 0$ becomes

$$\langle\langle \bar{t}_{\rho,\rho} \rangle\rangle = 0, \tag{3.16}$$

which is equivalent to $\langle\langle t^{(\rho)}(s) \rangle\rangle = 0$. Having obtained the average Green function using the BCPA the average single-particle diffusion constant $\mathbb{D}_0$, is obtained using (2.7) but with $G_k(s)$ replaced by $\bar{G}_k(s)$.

We consider the results for the two distributions discussed in the introduction. The percolation distribution has total hopping rates J or 0. This requires that the distribution of K be given by

$$K = \begin{cases} -j & \text{with probability } p \\ 0 & \text{with probability } 1 - p. \end{cases} \tag{3.17}$$

Thus p is the concentration of *missing* bonds. The uniform distribution for the height of the energy barriers E is given by

$$\text{Prob}\{E \in E + dE\} = \begin{cases} dE/2\Theta & \text{if } E_0 - \Theta \leqslant E \leqslant E_0 + \Theta \\ 0 & \text{otherwise} \end{cases} \tag{3.18}$$

where 2Θ is the width of the distribution and E_0 its mean. The total hopping rate $J + K$ is required to have the uniform barrier distribution, thus (3.18) induces a distribution in K where $K = J[\exp(\beta(E - E_0)) - 1]$ and (1.4) has been used.

Using the above formalism for the BCPA and equation (2.7) the following results are obtained for the diffusion constant when the disorder has a percolation distribution

$$
\bar{\mathbb{D}}_0 = \begin{cases} a^2 J/(1 - p/p_c) & \text{for } p \leqslant p_c, \text{ where } p_c = 1 - 2/z \\ 0 & \text{for } p > p_c. \end{cases} \qquad \text{(BCPA)} \qquad (3.19)
$$

and for the uniform distribution the diffusion constant is

$$
\bar{\mathbb{D}}_0 = a^2 J \frac{2}{z - 2} \frac{\sinh(\beta \Theta (1 - 2/z))}{\sinh(2\beta \Theta / z)}. \qquad (3.20)
$$

These results are shown in figure 3 and figure 8. It can be seen that the BCPA correctly obtains the diffusion constant vanishing at the percolation threshold p_c. This result agrees very well with Monte Carlo results (Kirkpatrick 1971) over the whole range of p except in the immediate region of the threshold where the diffusion is known to be anomalous. These results can be compared with the very simplest approximation, the virtual crystal approximation (VCA), where the diffusion constant is obtained from (1.3) with J replaced by its average, $\langle\!\langle J \rangle\!\rangle$. For the percolation distribution

$$
\bar{\mathbb{D}}_0 = a^2 J (1 - p) \qquad \text{(VCA)} \qquad (3.21)
$$

and for the uniform distribution

$$
\bar{\mathbb{D}}_0 = a^2 J \frac{\sinh(\beta \Theta)}{\beta \Theta} \qquad \text{(VCA)}. \qquad (3.22)
$$

It is clear that the VCA percolation $\bar{\mathbb{D}}_0$ is a very poor approximation failing to vanish at the percolation threshold. This also shows how much better a self-consistent approximation can be.

4. Two-particle BCPA

It will be shown below that the two-particle static correlations discussed in the introduction require the evaluation of an average of the form

$$
\langle\!\langle G_{l,g}(s_1) H^{j,h}(s_2) \rangle\!\rangle
$$

where G and H refer to two *non*-interacting particles. Such averages frequently occur when calculating transport coefficients in the presence of disorder, and are thus of interest beyond the diffusion problem considered here.

In § 3 a single particle was considered. There are now two independent particles A and B. The hopping rate of particle A has a non-random component J_A and a random component K_A. The A particles Green function $G_{l,g}$ satisfies (3.1). The hopping rate of particle B has a non-random component J_B and a random component K_B. The B particles Green function also satisfies an equation similar to (3.1) but the particles Green function will be denoted $H^{j,h}$ and has initial condition $\delta_{j,h}$. Note this is a different initial condition to that of (2.12).

Velický (1969) has studied this average, and evaluated it using the CPA for the case of *site* disorder. His results cannot be applied directly as the disorder here is *bond* disorder. Thus we consider the application of the CPA to the general two-particle bond disorder problem and specialise to the CRW model after obtaining the general result.

In the presence of disorder and within the CPA we have the general correspondence given by equations (3.6) for both the A and B hopping rates and Green functions.

Carrying out the correspondence for a *given* bond configuration means that G and H satisfy an equation of the form of (3.9) and $\bar{G}$ and $\bar{H}$ satisfy an equation of the form (3.11). Thus the two-particle average is given by (in site index form)

$$\langle\!\langle G_{l,g}H^{j,h}\rangle\!\rangle = \langle\!\langle(\bar{G}_{l,g} + \sum_{m,n}\bar{G}_{l,m}\bar{T}_{m,n}\bar{G}_{n,g})(\bar{H}^{j,h} + \sum_{u,w}\bar{H}^{j,u}\bar{T}^{u,w}\bar{H}^{w,h})\rangle\!\rangle$$

$$= \bar{G}_{l,g}\bar{H}^{j,h} + \bar{G}_{l,g}\sum_{u,w}\bar{H}^{j,u}\langle\!\langle\bar{T}^{u,w}\rangle\!\rangle\bar{H}^{w,h}$$

$$+ \sum_{m,n}\bar{G}_{l,m}\langle\!\langle\bar{T}_{m,n}\rangle\!\rangle\bar{G}_{n,g}\bar{H}^{j,h}$$

$$+ \sum_{m,n}\sum_{u,w}\bar{G}_{l,m}\langle\!\langle\bar{T}_{m,n}\bar{G}_{n,g}\bar{H}^{j,u}\bar{T}^{u,w}\rangle\!\rangle\bar{H}^{w,h}. \tag{4.1}$$

Now, the site indexed average T-matrix elements $\langle\!\langle\bar{T}_{m,n}\rangle\!\rangle$ do not vanish but the bond indexed average T-matrix elements $\langle\!\langle\bar{T}_{\rho_1,\rho_2}\rangle\!\rangle$ do vanish because of the BCPA self-consistency. It is for this reason that the bond indexes were introduced. Thus if (4.1) is written in bond index form it simplifies to

$$\langle\!\langle G_{\mu,\nu}H^{\alpha,\tau}\rangle\!\rangle = \bar{G}_{\mu,\nu}\bar{H}^{\alpha,\tau} + \sum_{\rho_1,\rho_2}\sum_{\rho_3,\rho_4}\bar{G}_{\mu,\rho_1}\langle\!\langle\bar{T}_{\rho_1,\rho_2}\bar{G}_{\rho_2,\nu}\bar{H}^{\alpha,\rho_3}\bar{T}^{\rho_3,\rho_4}\rangle\!\rangle\bar{H}^{\rho_4,\tau}. \tag{4.2}$$

The $\bar{T}_{\rho_1,\rho_2}$ matrix can be expanded in an infinite series using (3.14a) which gives

$$\bar{T}_{\rho_1,\rho_2} = \bar{t}_{\rho_1,\rho_1}\delta_{\rho_1,\rho_2} + \bar{t}_{\rho_1,\rho_1}\bar{G}^F_{\rho_1,\rho_2}\bar{t}_{\rho_2,\rho_2} + \sum_{\rho_3}\bar{t}_{\rho_1,\rho_1}\bar{G}^F_{\rho_1,\rho_3}\bar{t}_{\rho_3,\rho_3}\bar{G}^F_{\rho_3,\rho_2}\bar{t}_{\rho_2,\rho_2} + \dots .$$

$$\tag{4.3}$$

If (4.3) and a similar equation for $\bar{T}^{\rho_3,\rho_4}$ are substituted into (4.2) then the resultant expression contains a sum of averages of products of $\bar{t}$-matrices and $\bar{G}^F$-matrices. Following the BCPA, single bond $\bar{t}$-matrices or products of single bond $\bar{t}$-matrices labelled by the *same* bond are assumed uncorrelated with single bond $\bar{t}$-matrices labelling *different* bonds e.g. $\langle\!\langle\bar{t}_{\rho_1,\rho_1}\bar{t}_{\rho_2,\rho_2}\bar{t}^{\rho_1,\rho_1}\bar{t}^{\rho_3,\rho_3}\rangle\!\rangle \simeq \langle\!\langle\bar{t}_{\rho_1,\rho_1}\bar{t}^{\rho_1,\rho_1}\rangle\!\rangle\langle\!\langle\bar{t}_{\rho_2,\rho_2}\rangle\!\rangle\langle\!\langle\bar{t}^{\rho_3,\rho_3}\rangle\!\rangle$ where ρ_1, ρ_2 and ρ_3 are different bonds. However, the self-consistency of the BCPA requires that $\langle\!\langle\bar{t}_{\rho_1,\rho_1}\rangle\!\rangle = 0$ thus any products containing an average of a single $\bar{t}$-matrix will vanish. Only terms containing products of averages of products of two (or more) $\bar{t}$-matrices, labelled by the same bond, will not vanish e.g.

$$\langle\!\langle\bar{t}_{\rho_1,\rho_1}\bar{t}_{\rho_2,\rho_2}\bar{t}^{\rho_1,\rho_1}\bar{t}^{\rho_2,\rho_2}\rangle\!\rangle \simeq \langle\!\langle\bar{t}_{\rho_1,\rho_1}\bar{t}^{\rho_1,\rho_1}\rangle\!\rangle\langle\!\langle\bar{t}_{\rho_2,\rho_2}\bar{t}^{\rho_2,\rho_2}\rangle\!\rangle \neq 0.$$

This reduces (4.2) to

$$\langle\!\langle G_{\mu,\nu}H^{\alpha,\tau}\rangle\!\rangle = \bar{G}_{\mu,\nu}\bar{H}^{\alpha,\tau} + \sum_{\rho_1,\rho_2}\bar{G}_{\mu,\nu}\bar{H}^{\alpha,\rho_1}(\langle\!\langle\bar{t}_{\rho_1,\rho_1}\bar{t}^{\rho_1,\rho_1}\rangle\!\rangle\delta_{\rho_1,\rho_2}$$

$$+ \langle\!\langle\bar{t}_{\rho_1,\rho_1}\bar{t}^{\rho_1,\rho_1}\rangle\!\rangle\bar{G}^F_{\rho_1,\rho_2}\langle\!\langle\bar{t}_{\rho_2,\rho_2}\bar{t}^{\rho_2,\rho_2}\rangle\!\rangle\bar{H}^{\rho_1,\rho_2}_F + \dots)\bar{G}_{\rho_2,\nu}\bar{H}^{\rho_2,\tau}. \tag{4.4}$$

Equation (4.4) defines a two-particle T-matrix $\bar{\Pi}^{\rho_1,\rho_2}_{\rho_1,\rho_2}(s_1,s_2)$ through

$$\langle\!\langle G_{\mu,\nu}H^{\alpha,\tau}\rangle\!\rangle = \bar{G}_{\mu,\nu}\bar{H}^{\alpha,\tau} + \sum_{\rho_1,\rho_2}\bar{G}_{\mu,\rho_1}\bar{H}^{\alpha,\rho_1}\bar{\Pi}^{\rho_1,\rho_2}_{\rho_1,\rho_2}\bar{G}_{\rho_2,\nu}\bar{H}^{\rho_2,\tau} \tag{4.5}$$

as well as a 'vertex function' $\bar{\Lambda}^{\rho_1,\rho_2}_{\rho_1,\rho_2}(s_1,s_2)$ through

$$\langle\!\langle G_{\mu,\nu}G^{\alpha,\tau}\rangle\!\rangle = \bar{G}_{\mu,\nu}\bar{H}^{\alpha,\tau} + \sum_{\rho_1,\rho_2}\bar{G}_{\mu,\rho_1}\bar{H}^{\alpha,\rho_1}\bar{\Lambda}^{\rho_1,\rho_2}_{\rho_1,\rho_2}\langle\!\langle G_{\rho_2,\nu}H^{\rho_2,\tau}\rangle\!\rangle. \tag{4.6}$$

The vertex function is related to $\bar{\Pi}$ by the equation

$$\bar{\Pi}_{\rho_1,\rho_2}^{\rho_1,\rho_2} = \bar{\Lambda}_{\rho_1,\rho_2}^{\rho_1,\rho_2} + \sum_{\rho_3,\rho_4} \bar{\Lambda}_{\rho_1,\rho_3}^{\rho_1,\rho_3} \bar{G}_{\rho_3,\rho_4} \bar{H}^{\rho_3,\rho_4} \bar{\Pi}_{\rho_4,\rho_2}^{\rho_4,\rho_2}. \tag{4.7}$$

Comparing (4.4) and (4.5) shows that $\bar{\Pi}$ can be expresed in terms of the single-bond $\bar{t}$-matrices

$$\bar{\Pi}_{\rho_1,\rho_2}^{\rho_1,\rho_2} = \left[\delta_{\rho_1,\rho_2} \delta^{\rho_1,\rho_2} + \sum_{\rho_3} \bar{\Pi}_{\rho_1,\rho_3}^{\rho_1,\rho_3} \bar{G}_{\rho_3,\rho_2}^{F} \bar{H}_{F}^{\rho_3,\rho_2} \right] \langle\!\langle \bar{t}_{\rho_2,\rho_2} \bar{t}^{\rho_2,\rho_2} \rangle\!\rangle. \tag{4.8}$$

Substituting (4.8) into (4.7) and rearranging results in the following equation for $\bar{\Lambda}$:

$$\bar{\Lambda}_{\rho_1,\rho_2}^{\rho_1,\rho_2}[1 + \bar{G}_{\rho_2,\rho_2} \bar{H}^{\rho_2,\rho_2} \langle\!\langle \bar{t}_{\rho_2,\rho_2} \bar{t}^{\rho_2,\rho_2} \rangle\!\rangle] = \delta_{\rho_1,\rho_2} \delta^{\rho_1,\rho_2} \langle\!\langle \bar{t}_{\rho_1,\rho_1} \bar{t}^{\rho_1,\rho_1} \rangle\!\rangle, \tag{4.9}$$

which shows that $\bar{\Lambda}$ is bond diagonal. If an object is bond diagonal then the diagonal elements (submatrices) can be explicitly represented by a site matrix if the rows and columns are suitably labelled. Thus the 4×4 submatrix $\bar{\Lambda}_{\rho,\rho}^{\rho,\rho}$ can be written in the form

$$\bar{\Lambda}_{\rho,\rho}^{\rho,\rho} = \Lambda_{\mathrm{AB}} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \otimes \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix} \tag{4.10}$$

where $\otimes$ is a direct product, $\Lambda_{\mathrm{AB}}(s_1, s_2)$ is the scalar

$$\Lambda_{\mathrm{AB}} = \langle\!\langle t_A t_B \rangle\!\rangle / (1 + 4 \langle\!\langle t_A t_B \rangle\!\rangle \Delta \bar{G} \Delta \bar{H}) \tag{4.11}$$

and $t_A(s_1)$ and $t_B(s_2)$ are given by (3.15) but with $K \to K_A$, K_B and $J \to J_A$, J_B respectively. Also, $\Delta \bar{H}$ is the same expression as $\Delta \bar{G}$ but with $\bar{H}$ replacing $\bar{G}$. Converting (4.5) back to site representation gives

$$\langle\!\langle G_{l,g} H^{j,h} \rangle\!\rangle = \bar{G}_{l,g} \bar{H}^{j,h} + \sum_{\rho_1,\rho_2} \sum_{\substack{m_1 \in \rho_1 \\ m_2 \in \rho_1}} \sum_{\substack{m_3 \in \rho_2 \\ m_4 \in \rho_2}} \bar{G}_{l,m_1} \bar{H}^{j,m_2} \bar{\Pi}_{m_1,m_4}^{m_2,m_3} \bar{G}_{m_4,g} \bar{H}^{m_3,h} \tag{4.12}$$

where $l \in \mu$, $g \in \nu$, $j \in \alpha$ and $h \in \tau$. Using (3.8) enables (4.12) to be written in the form

$$\langle\!\langle G_{l,g} H^{j,h} \rangle\!\rangle = \bar{G}_{l,g} \bar{H}^{j,h} + \sum_{m_1,m_2} \sum_{\substack{b_1 \in \{0,a\} \\ b_2 \in \{0,a'\}}} \bar{G}_{l,m_1+b_1} \bar{H}^{j,m_1} \bar{\Pi}_{m_1+b_1,m_2+b_2}^{m_1,m_2} \bar{G}_{m_2+b_2,g} \bar{H}^{m_2,h}. \tag{4.13}$$

where each of the sums over b_1 and b_2 are over the set $\chi = \{0, a_n; n = 1, \ldots, z\}$ where a_n is a nearest-neighbour lattice vector. An equation similar to (4.13) may be obtained for (4.7). Fourier transforming (4.13) and the corresponding equation for (4.7) gives

$$\langle\!\langle Q_k(j - l + g - h) \rangle\!\rangle = \bar{Q}_k(j - l + g - h)$$
$$+ \sum_{b_1,b_2} \bar{Q}_k(j - l - b_1) \bar{\Pi}_k(b_1 - b_2) \bar{Q}_k(b_2 + g - h) \tag{4.14a}$$

and

$$\bar{\Pi}_k(m_2 - m_1 + m_4 - m_3) = \bar{\Lambda}_k(m_2 - m_1 + m_4 - m_3)$$
$$+ \sum_{b_1,b_2} \bar{\Lambda}_k(m_2 - m_1 - b_1) \bar{Q}_k(b_1 - b_2) \bar{\Pi}_k(b_2 + m_4 - m_3) \tag{4.14b}$$

where the Fourier transforms are given by

$$\langle\!\langle Q_k(s_1, s_2; r) \rangle\!\rangle = \frac{1}{N} \sum_l e^{-ikl} \langle\!\langle G_{l,0}(s_1) H^{l-r,0}(s_2) \rangle\!\rangle \tag{4.15a}$$

$$\bar{\Pi}_k(s_1, s_2; r) = \frac{1}{N} \sum_\lambda e^{-i\lambda r} \bar{\Pi}_{k-\lambda}^{\lambda}(s_1, s_2) \tag{4.15b}$$

$$\bar{\Pi}_{k-\lambda}^{\lambda}(s_1, s_2) = \sum_{r_1, r_2} \exp\{-[i(k - \lambda)r_1 + i\lambda r_2]\}\bar{\Pi}_{r_1, 0}^{r_2, 0}(s_1, s_2) \qquad (4.15c)$$

and similarly for $\bar{Q}_k(s_1, s_2; r)$ and $\bar{\Lambda}_k(s_1, s_2; r)$. Using (3.8) and (4.10) and explicit expression may be obtained for $\bar{\Lambda}_k(r)$ which is given by

$$\bar{\Lambda}_k(r) = \Lambda_{AB} \sum_{\lambda} e^{-i\lambda r} \Gamma_\lambda \Gamma_{k-\lambda} = \Lambda_{AB} \sum_{a, a'} (\delta_{r, 0} - \delta_{r, a} - e^{ika'}\delta_{r, -a'} + e^{ika'}\delta_{r, a - a'}).$$

$$(4.16)$$

Equation (4.14b) forms a set of $z + 1$ simultaneous linear equations and thus can be solved to obtain $\bar{\Pi}_k(r)$. Substituting $\bar{\Pi}_k(r)$ into (4.14a) gives $\langle\!\langle Q_k(r) \rangle\!\rangle$. Inverse transforming equation (4.15a) one finally obtains $\langle\!\langle G_{t-g, 0}H^{j-h, 0} \rangle\!\rangle$. However, in many cases the full $\langle\!\langle GH \rangle\!\rangle$ matrix is not required.

5. The correlation factor and BCPA

In § 3 we considered the effect of disorder on a simple random walk within the BCPA. In this section we return to the CRW and consider the effect of disorder on the diffusion constant $\mathbb{D}$. The CRW diffusion is defined to be of the form $\mathbb{D}_0 f_0$ as discussed in the introduction. This form of the diffusion constant splits $\mathbb{D}$ into a factor $\mathbb{D}_0$, which is the diffusion constant of a tracer which is *independent* of the background particles and a second factor f_0 which contains all the many-body dynamics arising from the blocking effect of the background particles on the tracer particle. This form of $\mathbb{D}$ is retained even in the presence of disorder. This is because the path averages of (1.1) just change from all paths of the same length being equally likely (with no disorder), to each path occurring with a probability determined by exactly which random bonds occur for that path for each particular bond configuration. This change does not affect the form of the expression. Thus we have that

$$\bar{\mathbb{D}} = \bar{\mathbb{D}}_0 \bar{f}_0 \qquad (5.1)$$

is generally valid. This means that $\bar{\mathbb{D}}_0$ can be obtained from the one-particle disorder problem, and in particular the BCPA of § 3. In this section we consider the evaluation $\bar{f}_0$.

In principle $\langle\!\langle f_0 \rangle\!\rangle$ should be determined by averaging the CRW Green function G given by equations (2.11). This would then take account of the static-dynamic correlations that arise between the particles interactions and the disorder. However we consider here a simpler, but non-trivial, approximation. We neglect the static-dynamic correlations and consider only the static correlations using the BCPA. This is done by replacing the correlation factor by its average i.e. $\bar{f}_0 \rightarrow \langle\!\langle f_0 \rangle\!\rangle$. As the BCPA is being used we must first consider the effective medium by making the replacements (3.5), thus

$$f_0 \rightarrow f_0(J_A + \sigma_A, J_B + \sigma_B, \overline{\cos}\,\theta). \qquad (5.2)$$

We then approximate $\langle\!\langle f_0 \rangle\!\rangle$ by replacing all configuration dependent quantities by their averages. In the effective medium the only remaining configuration dependent quantity is $\overline{\cos}\,\theta$, thus

$$\langle\!\langle f_0 \rangle\!\rangle \approx f_0(J_A + \sigma_A, J_B + \sigma_B, \langle\!\langle\overline{\cos}\,\theta\rangle\!\rangle). \qquad (5.3)$$

As σ_A and σ_B are already given by the one-particle BCPA we consider $\langle\!\langle\overline{\cos}\,\theta\rangle\!\rangle$ which is given by the average of (2.15).

As shown by TKE $\hat{P}_k(s; r)$ represents the free propagation of a pair of particles. This dependence on two particles can be made more explicit as follows. Equation (2.16) can be written in the equivalent form

$$\hat{P}_k(s; r) = \frac{1}{N} \sum_l e^{-i\lambda l} \int_0^\infty \exp(-st) \langle p_l u_{l-r} \rangle_0 \, dt \tag{5.4}$$

where $\langle p_l u_j \rangle_0$ satisfies the equation

$$\frac{\partial}{\partial t} \langle p_l u_j \rangle_0 = \sum_a [v J_A (\langle p_{l+a} u_j \rangle - \langle p_l u_j \rangle) + J_B (\langle p_l u_{j+a} \rangle - \langle p_{l+a} u_j \rangle)] \tag{5.5}$$

with initial condition $\delta_{l,g} \delta_{j,h}$.

It can be shown (Brak 1989) that for independent particles

$$\langle p_l u_j \rangle_0 = \langle p_l \rangle_0 \langle u_j \rangle_0. \tag{5.6}$$

where $\langle p_l \rangle_0$ satisfies (2.8) but without the second order moments, similarly for $\langle u_j \rangle_0$. As the Laplace transform of a product of two functions of time is the convolution of the Laplace transform of each function, the Laplace transform of (5.6)

$$\hat{P}_{l,g}^{j,h}(s) = \int_0^\infty \exp(-st) \langle p_l \rangle_0 \langle u_j \rangle_0 \, dt \tag{5.7}$$

becomes

$$\hat{P}_{l,g}^{j,h}(s) = \frac{1}{2\pi i} \int_{x-i\infty}^{z+i\infty} \hat{G}_{l,g}(s') \hat{H}^{j,h}(s - s') \, ds' \tag{5.8}$$

where $\hat{G}_{l,g}$ is the Laplace transform of $\langle p_l \rangle_0$ and is given by (3.2) $(J \to J_A)$ and $\hat{H}$, which is the Laplace transform of $\langle u_j \rangle_0$ and represents a free 'hole', is given by

$$\hat{H}_{j,h}(s - s') = \frac{1}{N} \sum_\lambda \frac{e^{i\lambda(j-h)}}{s - s' + J_B \Gamma_\lambda}. \tag{5.9}$$

The value of x determines the position of the Bromwich contour of (5.8) and must be chosen so that all the poles (in the s' complex plane) of $\hat{G}$ are to the left of x and all the poles of $\hat{H}$ are to the right of x.

Thus we see that

$$\hat{P}_k(s; r) = \frac{1}{N} \sum_l \exp(-ikl) \hat{P}_{l,0}^{l-r,0}$$

is related, by a convolution, to a product of two one-particle Green functions

$$\hat{Q}_{l,g}^{j,h}(s', s - s') = \hat{G}_{l,g}(s') \hat{H}^{j,h}(s - s').$$

When averaging this product over the disorder, section § 4 showed that additional correlations arise between the two Green functions. These are what we call static two-particle correlations. In the presence of disorder $\hat{Q} \to Q$, $\hat{P} \to P$, $\hat{G} \to G$ and $\hat{H} \to H$ and thus we may use the results of § 4 to obtain $Q_k(s', s - s'; r)$ and hence, through the convolution, $P_k(s; r)$. Furthermore only the linear combination $P_0(0; 2a) - P_0(0; 0)$ is required to determine $\langle\langle \overline{\cos \theta} \rangle\rangle$. This will prove to be a considerable simplification. Additional simplifications arise because only the limit $k = 0$ is required, in particular

$\bar{Q}_0(s', s - s'; r) = \bar{Q}_0(s', s - s'; -r)$ and similarly for $\bar{\Lambda}_0$ and $\bar{\Pi}_0$. Using this enables (4.14a, b), for $k = 0$ and $s = 0$, to be written in the form

$$Q_0(m + n) = \bar{Q}_0(m + n) + \sum_{a,a'} \sum_{b_1, b_2} \bar{Q}_0(m + b_1)\bar{\Pi}_0(b_1 + b_2)\bar{Q}_0(b_2 + n) \tag{5.10a}$$

and

$$\bar{\Pi}_0(m + n) = \bar{\Lambda}_0(m + n) + \sum_{a,a'} \sum_{b_1, b_2} \bar{\Lambda}_0(m + b_1)\bar{Q}_0(b_1 + b_2)\bar{\Pi}_0(b_3 + n) \tag{5.10b}$$

where $m \equiv m_2 - m_1$ and $n \equiv m_3 - m_4$. Equations (5.10) are then conveniently written in 7×7 matrix form (for the simple cubic lattice)

$$Q_0 = \bar{Q}_0 + \bar{Q}_0\bar{\Pi}_0\bar{Q}_0 \tag{5.11a}$$

$$\bar{\Pi}_0 = \bar{\Lambda}_0 + \bar{\Lambda}_0\bar{Q}_0\bar{\Pi}_0 \tag{5.11b}$$

where the matrix elements are $(Q_0)_{m,n} \equiv Q_0(m + n)$ (similarly for the other matrices in (5.11)) with m and n taken from the set $\{0, a_n; n = 0, \ldots, z\}$, where a_n is a nearest-neighbour lattice vector. Equations (5.11) may be solved for Q_0 which is given by

$$\langle\!\langle Q_0 \rangle\!\rangle = \bar{Q}_0(1 - \bar{\Lambda}_0\bar{Q}_0)^{-1}. \tag{5.12}$$

In order to obtain explicit expressions for the matrix elements of Q_0 it appears to be necessary to invert a 7×7 matrix, however it is possible to block diagonalise the matrices in (5.12) by a similarity transformation using a unitary matrix (Wolfram and Callaway 1963†). The block diagonal matrices have two 2×2 blocks and a *diagonal* 3×3 'p-wave' block. The diagonal elements of the p-wave block are conveniently the linear combination required for (2.15). Thus we obtain

$$\bar{\Pi}_0(2a_x) - \bar{\Pi}_0(0) = \frac{\bar{\Lambda}_0(2a_x) - \bar{\Lambda}_0(0)}{1 - (\bar{\Lambda}_0(2a_x) - \bar{\Lambda}_0(0))(\bar{Q}_0(2a_x) - \bar{Q}_0(0))} \tag{5.13}$$

Using (4.16) gives $\bar{\Lambda}_0(2a_x) - \bar{\Lambda}_0(0) = -41\Lambda_{AB}$, and hence

$$Q_0(2a_x) - Q_0(0) = \frac{\bar{Q}_0(2a_x) - \bar{Q}_0(0)}{1 + 41\Lambda_{AB}(\bar{Q}_0(2a_x) - \bar{Q}_0(0))}. \tag{5.14}$$

Thus we have that, in conjunction with (5.14),

$$\langle\!\langle \overline{\cos}\,\theta \rangle\!\rangle = [v(J_A + \sigma_A) + (J_B + \sigma_B)] \lim_{\eta \to 0} \int \frac{ds'}{2\pi i}\, (Q_0(s' + \eta, \eta - s'; 2a_x)$$

$$- Q_0(s' + \eta, \eta - s'; 0)) \tag{5.15}$$

where η is used to shift the poles off the Bromwich contour.

6. Numerical analysis

The previous section reduced $\langle\!\langle \overline{\cos}\,\theta \rangle\!\rangle$ as far as possible and further progress has only been made by numerical methods. The computation necessary to obtain a numerical result for $\langle\!\langle \overline{\cos}\,\theta \rangle\!\rangle$ consists of three parts: (i) the BCPA self-energies σ_A and σ_B must be determined for arbitrary s'; (ii) the two-particle Green function Q_0 ($s' + \eta, \eta - s'; r)$

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† One of the matrix elements has the wrong sign.

must be determined for arbitrary s' and for $r = 0$, $2a$ and (iii) the Bromwich contour integral must be done numerically.

The difficulty with the Bromwich integral is the infinite range of integration. This can be overcome by a simple trick. The range is first split into two semi-infinite ranges $0 \to \infty$ and $0 \to -\infty$. Each semi-infinite range is then split at an arbitrary point s_0 and the integral transformed as follows:

$$\int_0^\infty f(s) \, ds = \int_0^{s_0} f(s) \, ds + \int_0^{1/s_0} f(1/s) \frac{ds}{s^2}$$

which reduces the range of integration to two finite domains. The numerical integration was carried out using the Rombert algorithm (Numerical Recipes 1986).

Although the BCPA self-energies can be determined analytically for $s' = 0$, as was required to obtain (3.19) and (3.20), it is not possible for general s' and thus they must be determined numerically. The self-consistent iteration method used is the IATA method given by Chen (1973) which is always convergent (Ducastelle 1974) to a unique solution.

The effective medium two-particle Green function $\bar{Q}_0(s' + \eta, \eta - s'; r)$ is more difficult to evaluate. It can be written in the form

$$\bar{Q}_0(s' + \eta, \eta - s'; r) = \frac{1}{N} \sum_\lambda \frac{e^{i\lambda r}}{[s' + \eta + (J_A + \sigma_A)\Gamma_\lambda][\eta - s' + (J_B + \sigma_B)\Gamma_\lambda]}.$$

(6.1)

This form suggests that $\bar{Q}$ can be determined numerically by summing over the Brillouin zone. This takes more computer time than say evaluating (5.9) by Brillouin zone summation because, for $r = 2a$, the irreducible part of the zone is much larger than that required for (5.9). This is not much of a problem if only $\bar{Q}$ is required, however $\bar{Q}$ as well as the BCPA iteration to determine σ_A and σ_B are required for each point in the numerical integration of the Bromwich integral which increases the amount of computer time required enormously. We can however reduce (6.1) from a product of one-particle Green functions to a sum of one-particle Green functions by a partial fraction expansion, in particular

$$\bar{Q}_0(s' + \eta, \eta - s'; r) = [s'(\bar{J}_A + \bar{J}_B)$$
$$+ \eta(\bar{J}_B - \bar{J}_A)]^{-1}(\bar{J}_B \bar{H}_{r,0}(\eta - s') - \bar{J}_A \bar{G}_{r,0}(\eta + s')).$$

(6.2)

This simple identity will prove to be of considerable help. Equation (6.2) reduces the numerical work to the numerical integration (5.15), the BCPA iteration and the evaluation of $\bar{G}_{r,0}$ and $\bar{H}_{r,0}$ for $r = 0, a, 2a$.

The lattice Green functions $\bar{G}_{r,0}(s)$ (and $\bar{H}$) may be evaluated very efficiently by using the complete elliptic functions of the first and second kinds. We consider only the simple cubic lattice. There exist several publications on the simple cubic lattice Green functions and their relation to elliptic integrals. Elliptic functions possess a considerable advantage over Brillouin zone summation in that they can be evaluated numerically orders of magnitude quicker (for the same accuracy) using the arithmetic-geometric mean algorithm (Bulirsch 1965, Morita and Horiguchi 1973). Early publications (Watson 1939, Joyce 1972, Joyce 1973) only related $\bar{G}$ to elliptic functions for $r = 0$ and for fixed s or a limited range of s. Later publications (Morita 1971, Morita and Horiguchi 1974) used recurrence relations to relate $\bar{G}$, for arbitrary r and s, to $\bar{G}$ along certain axes. These axis Green functions were expressed in terms of an integral over elliptic functions. The integral has to be done numerically. This reduces the numerical work required to
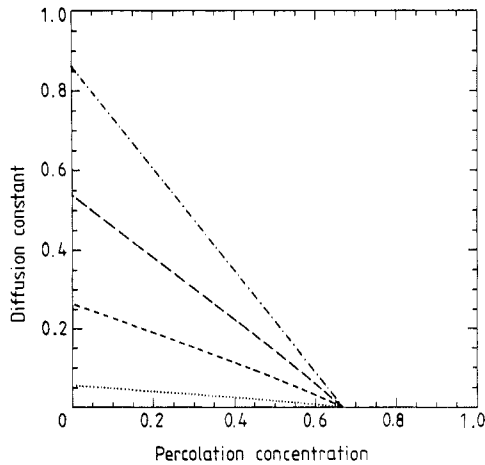
Figure 1. Diffusion constant as a function of the percolation concentration for a range of particle densities, $c = 0.1$ (chain curve), $c = 0.366$ (long-dashed curve), $c = 0.633$ (short-dashed curve) and $c = 0.9$ (dotted curve), for $J_A = 1.0$, and $J_B = 5.0$.
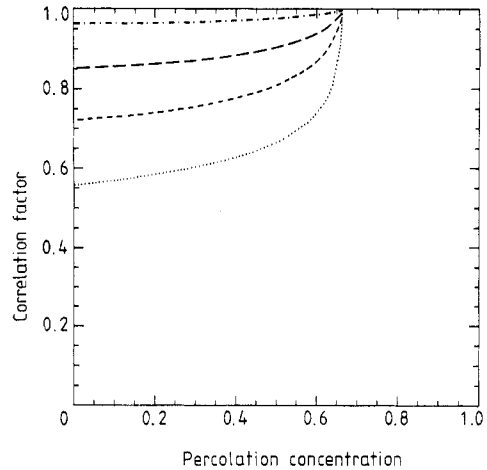
Figure 2. Correlation factor as a function of percolation concentration for a range of particle densities, $c = 0.1$ (chain curve), $c = 0.366$ (long-dashed curve), $c = 0.633$ (short-dashed curve) and $c = 0.9$ (dotted curve) ($J_A = 1.0, J_B = 5.0$).

obtain $\bar{G}$, from three numerical integrations (Brillouin zone summations in 3d), to one numerical integration and the evaluation of the elliptic functions.

A final set of papers (Horiguchi and Morita 1975†, Morita 1975) managed to relate $\bar{G}$ for all r to the Green functions for $r = (0, 0, 0)$, $r = (0, 0, 1)$ and $r = (0, 0, 2)$. More importantly, these three Green functions where expressed entirely in terms of elliptic functions. Without this final result the numerical evaluation of $\langle\!\langle \overline{\cos}\,\theta \rangle\!\rangle$ would have been impractical. If the arithmetic-geometric mean method is carried out using complex variables it gives the values of the two elliptic functions only in the region of the real axis between their branch points, whilst we require them for the whole complex plane. However, in the above mentioned publications analytic continuation expressions are provided expressing the elliptic functions in parts of the complex plane in terms of the elliptic functions near the real axis. Only one expression is omitted which is required for $r = (0, 0, 2)$ and may be found elsewhere (Bateman 1953). The importance of the identity (6.2) is now evident.

7. Results and discussion

The results of the computations for the percolation distribution are as follows. Figure 1 shows the diffusion constant $\bar{\mathbb{D}} = \bar{\mathbb{D}}_0 \bar{f}_0$ as a function of the percolation concentration for a range of particle densities. The percolation concentration is the concentration of *missing* bonds, thus as the concentration of missing bonds increases the diffusion constant decreases until the concentration of missing bonds reaches the percolation threshold when there is no longer an infinite cluster of *present* bonds and the diffusion constant

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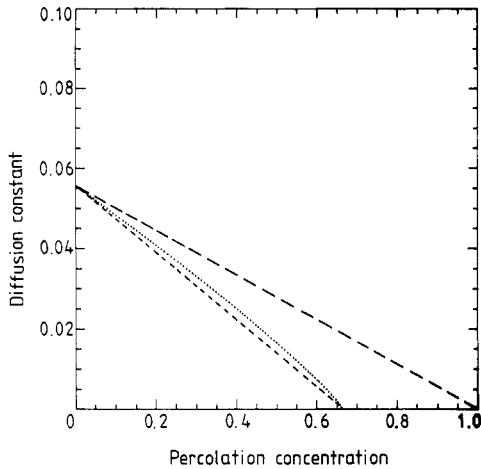† There are two typing errors in equation (12).

Figure 3. Diffusion constant as a function of percolation concentration for the various approximations, VCA (long-dashed curve), BCPA without two-particle disorder correlations (short-dashed curve) and BCPA with two-particle disorder correlations (dotted curve) ($J_A = 1.0$, $J_B = 5.0$, $c = 0.9$).
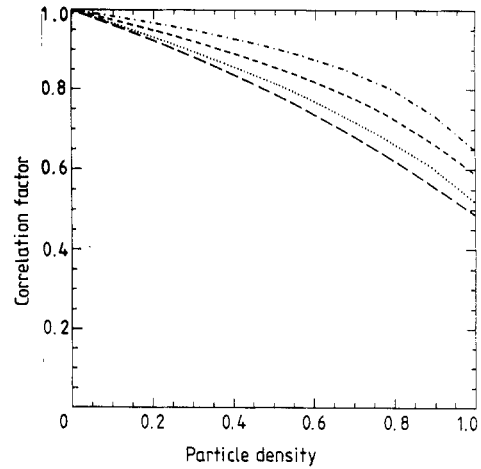

Figure 4. Correlation factor as a function of particle density for various percolation concentrations, $p = 0$ (long-dashed curve), $p = 0.3$ (dotted curve), $p = 0.5$ (short-dashed curve) and $p = 0.6$ (chain curve) ($J_A = 1.0, J_B = 5.0$).
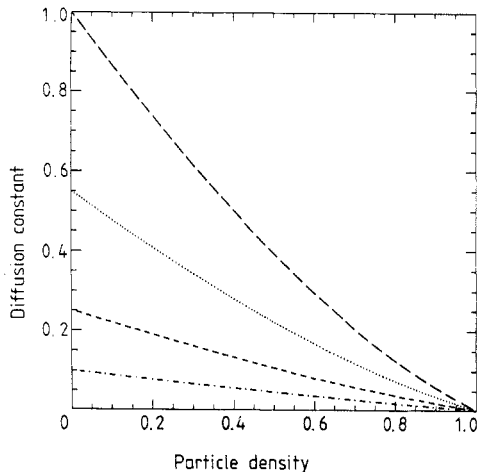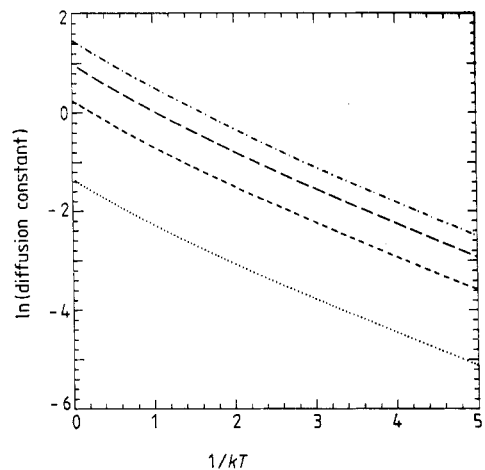

Figure 5. Diffusion constant as a function of particle density for various percolation concentrations, $p = 0$ (long-dashed curve), $p = 0.3$ (dotted curve), $p = 0.5$ (short-dashed curve) and $p = 0.6$ (chain curve) ($J_A = 1.0, J_B = 5.0$).

Figure 6. Logarithm of the diffusion constant (uniform distribution) as function of inverse temperature for various particle densities, $c = 0.1$ (chain curve), $c = 0.366$ (long-dashed curve), $c = 0.633$ (short-dashed curve) and $c = 0.9$ (dotted curve), for $\Omega_A = 5.0, \Omega_B = 2.0, E_0 = 1.0$ and $\Theta = 1.0$.
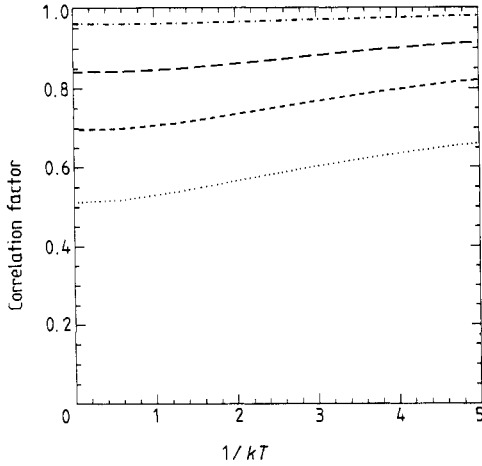
Figure 7. Correlation factor (uniform distribution) as a function of inverse temperature for various particle densities, $c = 0.1$ (chain curve), $c = 0.366$ (long-dashed curve), $c = 0.633$ (short-dashed curve) and $c = 0.9$ (dotted curve). Same parameters as figure 6.
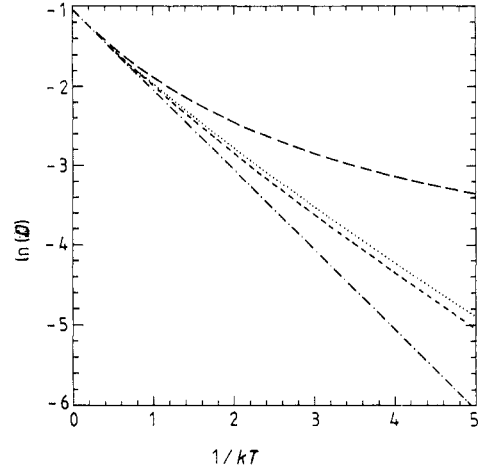
Figure 8. Logarithm of the diffusion constant (uniform distribution) as function of inverse temperature comparing the different approximations, VCA (long-dashed curve), BCPA with two-particle disorder correlations (dotted curve), BCPA without two-particle disorder correlations (short-dashed curve) and the result when there is no disorder (chain curve), for $\Omega_A = 5.0$, $\Omega_B = 5.0$, $E_0 = 1.0$ and $\Theta = 1.0$.

vanishes. The higher the particle density the lower the initial value (i.e. at $p = 0$) of the diffusion constant, which is determined by the factor $1 - c$ in $\bar{\mathbb{D}}_0$ and by $\bar{f}_0$. When $c = 0$ (where only the tracer is present) the diffusion constant decreases linearly with percolation concentration, however as c increases the p dependence is no longer linear. The non-linearity is more pronounced the greater the particle concentration, as is more clearly seen in figure 3 (where $c = 0.9$). The origin of the deviation from linearity is the dependence of the correlation factor on the percolation concentration as is shown in figure 2. The p dependence of the correlation factor arises entirely from the p dependence of the average cosine $\langle\!\langle \overline{\cos}\,\theta \rangle\!\rangle$, which we have seen is attributable to the new static correlations which arise when the two-particle Green function is averaged over the disorder. Figure 3 compares the results obtained for $\bar{\mathbb{D}}$ by the various approximations. The VCA result is clearly very poor, failing to predict a percolation threshold. The figure also shows the effect of the two-particle correlations compared to the one-particle BCPA (where $\bar{f}_0 \approx f_0$). Figure 4 and figure 5 show the dependence of the correlation factor and diffusion constant on the particle density for a range of percolation concentrations. The correlation factor is again responsible for the departure of the diffusion constants linear dependence on particle density. But in this case the dynamic correlations are responsible.

In the absence of disorder the temperature dependence of the diffusion constant is of the same Arrhenius form (1.4) as the hopping rate. This form is retained when the disorder has a percolation distribution, however for the uniform distribution of barrier heights there is a strong departure from the Arrhenius form. This is shown in figure 6 where the logarithm of the diffusion constant is plotted against inverse temperature for the distribution given in (3.18). The deviation from a straight line shows clearly. For the results presented here we have assumed that the tracer and background particles have the *same* barrier height distribution and only differ in their attempt frequencies. If the

tracer and background particles have different mean barrier heights then the correlation factor already has a temperature dependence due to the hopping rate factors, J_A and J_B (see (2.14)) and then acquires an addition temperature dependence from the $\langle\!\langle \overline{\cos}\ \theta \rangle\!\rangle$ factor.

With both the tracer and the background particles having the same distribution the correlation factors temperature dependence, shown in figure 7, is only due to the temperature dependence of $\langle\!\langle \overline{\cos}\ \theta \rangle\!\rangle$. For this particular distribution the effect of the disorder is to counteract the reducing effect (on the diffusion constant) of the correlation factor, particularly at low temperatures (compared with u_0). For figures 6 to 8 $E_0 = 1$ and $\Theta = 1$. As Θ is reduced all the results tend smoothly to the non-random results (i.e. straight lines). Figure 8 compares the results obtained for the diffusion constant by the various approximations, showing that the VCA over estimates the diffusion constant. The figure also shows clearly the effect of the disorder on the diffusion constant.

The principle result obtained by this work is the effect of the disorder on the correlation factor. In the absence of disorder the $\langle\!\langle \overline{\cos}\ \theta \rangle\!\rangle$ factor is independent of the percolation concentration and independent of the temperature. When the hopping rates become random the two-particle static correlations result in a deviation from this simple behaviour. When the disorder has a percolation distribution the $\langle\!\langle \overline{\cos}\ \theta \rangle\!\rangle$ factor, and hence the correlation factor, develops a strong dependence on the percolation concentration and vanishes at the percolation threshold. When the energy barrier height distribution is uniform the $\langle\!\langle \overline{\cos}\ \theta \rangle\!\rangle$ factor develops a clear temperature dependence. It can thus be seen that the overall result of the disorder is to couple the dynamic and static correlations together, resulting in a disorder dependent correlation factor.

Acknowledgment

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