Journal of Statistical Physics, Vol. 30, No. 2, 1983

Random Walks on Random Lattices with Traps

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A critical examination is presented of the continuous time random walk (CTRW) approximation and of frequency-dependent effective transition rate methods for calculating the configurational average of the Laplace transform of the probability $P(\mathbf{s}, t \mid \mathbf{s}_0)$ that a particle performing a random walk will be at site $\mathbf{s}$ time t after it reached the site $\mathbf{s}_0$. Some exact results are derived for the form of $P(\mathbf{s}, t \mid \mathbf{s}_0)$ at long times, and these indicate that the effective transition rate methods are the better approximation for systems with symmetric effective hopping rates, while the CTRW approximation is better for systems containing traps, i.e., states that are much easier to enter than to leave. The implications of these results for calculations of transient currents and of the ac conductivity for amorphous semiconductors are discussed.

KEY WORDS: Random walk; amorphous semiconductors; ac conductivity; transient currents.

1. INTRODUCTION

The analysis of the motion of a particle performing a random walk on a lattice with random transition rates between sites is extremely difficult. The most widely used approximation methods for calculating the average behavior of such a particle can be divided into two classes, according to whether they concentrate on the properties of sites or of bonds. While for motion with fixed transition rates there is a close correspondence between site percolation and bond percolation,[1] this is not the case when the transition rates are a random variable. Since we are interested in the transitions of particles along bonds between sites, the approaches based on bonds might seem the most appropriate. However, as we show in this paper, this is not always the case, especially for systems containing states

Presented at the Symposium on Random Walks, Gaithersburg, MD, June 1982.

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0022-4715/83/0200-0373$03.00/0

that are much more difficult to enter than to leave, which we refer to as traps.

The structure of this paper is as follows. In Section 2, we derive in matrix form exact equations for the particle's motion, using a continuous time random walk (CTRW) approach that is applicable to both Markovian and non-Markovian processes. The CTRW approximation of Scher, Lax, and Montroll,[2,3] which is essentially a single site approximation,[4] is shown to involve a decoupling of configurational averages in the matrix equation. The nature of the weighted average that this involves is examined for Markovian systems at short and long times. In Section 3 we outline two average bond methods for solving approximately the matrix equation, namely the average T-matrix approximation (ATA)[5] and the coherent potential approximation (CPA),[6] applied to homomorphic clusters of pairs of atoms.[7-11] Here, too, we examine the weighting of the averages used at short and long times. In Section 4, we derive some new exact results for the long time behavior of Markovian systems, and the consequences of these results for the correct weighting of averages are discussed in Section 5. We also discuss there the implications of our results for time-dependent transport in amorphous semiconductors, and our conclusions are summarized in Section 6.

2. THE CONTINUOUS TIME RANDOM WALK (CTRW) METHOD

We start our analysis with the exact CTRW approach to the hopping of particles between localized states. Let $P(\mathbf{s}, t \mid \mathbf{s}_0)$ be the probability that a particle is at site $\mathbf{s}$ time t after it reached $\mathbf{s}_0$, and $R(\mathbf{s}, t \mid \mathbf{s}_0)$ the probability density that is reaches $\mathbf{s}$ at such a time. In addition, let $\Phi_{\mathbf{s}'}(t)$ be the probability that a particle remains at site $\mathbf{s}'$ and is still there time t after it arrived there, and $\psi_{\mathbf{s}'}(t)$ and $\psi_{\mathbf{s}'}(\mathbf{s}-\mathbf{s}', t)$ the probability densities that it leaves $\mathbf{s}'$ and that it makes a transition through $\mathbf{s}-\mathbf{s}'$ to site $\mathbf{s}$, respectively, at this time t. Then P and R satisfy the equations

$$P(\mathbf{s}, t \mid \mathbf{s}_0) = \int_0^t R(\mathbf{s}, \tau \mid \mathbf{s}_0)\Phi_{\mathbf{s}}(t-\tau)\, d\tau \tag{1}$$

$$R(\mathbf{s}, t \mid \mathbf{s}_0) = \sum_{\mathbf{s}'} \int_0^t R(\mathbf{s}', \tau \mid \mathbf{s}_0)\psi_{\mathbf{s}'}(\mathbf{s}-\mathbf{s}', t-\tau)\, d\tau + \delta_{\mathbf{s},\mathbf{s}_0}\delta(t-0^+) \tag{2}$$

We take the Laplace transforms of these equations, denoting by $\hat{f}(u)$ the transform of $f(t)$. The resulting equations can be written in the simple matrix form

$$P = G_0 R \tag{3}$$

$$R = I + VG_0 R \tag{4}$$

where the matrices $R(u)$, $P(u)$, $G_0(u)$, and $VG_0(u)$ have for their $(\mathbf{s},\mathbf{s}')$ elements, respectively, $\hat{R}(\mathbf{s},u\,|\,\mathbf{s}')$, $\hat{P}(\mathbf{s},u\,|\,\mathbf{s}')$, $\hat{\Phi}_{\mathbf{s}}(u)\delta_{\mathbf{s},\mathbf{s}'}$ and $\hat{\psi}_{\mathbf{s}'}(\mathbf{s}-\mathbf{s}',u)$. It follows from equations (3) and (4) that

$$P = G_0 + G_0VP = G_0 + PVG_0 \tag{5}$$

The CTRW approximation of Scher, Lax, and Montroll[3,4] involves replacing $\Phi_{\mathbf{s}'}(t)$ and $\psi_{\mathbf{s}'}(\mathbf{s}-\mathbf{s}',t)$ by their configurational averages (denoted by $\langle\ \rangle$) over $\mathbf{s}'$,

$$\Phi(t) = \langle\Phi_{\mathbf{s}'}(t)\rangle, \qquad \psi(\mathbf{s}-\mathbf{s}',t) = \langle\psi_{\mathbf{s}'}(\mathbf{s}-\mathbf{s}',t)\rangle \tag{6}$$

Such a procedure corresponds to the decoupling of configurational averages in equation (5) to give

$$\langle P\rangle \simeq \langle G_0\rangle + \langle P\rangle\langle VG_0\rangle \tag{7}$$

In order to examine the nature of this approximation, it is convenient to restrict our attention to Markovian systems. For these, Eq. (5) is the Laplace transform of the master equation with $V_{\mathbf{s},\mathbf{s}'}$ the probability per unit time of a transition from $\mathbf{s}'$ to $\mathbf{s}$, and

$$G_0(u) = (uI + \Lambda)^{-1} \tag{8}$$

where Λ is a diagonal matrix whose $(\mathbf{s},\mathbf{s})$ element is

$$\lambda_{\mathbf{s}} = \sum_{\mathbf{s}'} V_{\mathbf{s}',\mathbf{s}} = \text{probability of a transition from } \mathbf{s} \text{ per unit time} \tag{9}$$

Thus, the averages in Eq. (7) give weight $(\lambda_{\mathbf{s}'} + u)^{-1}$ to transitions from site $\mathbf{s}'$ and $V_{\mathbf{s},\mathbf{s}'}/(\lambda_{\mathbf{s}'} + u)$ to a transition from $\mathbf{s}'$ to $\mathbf{s}$. For very large values of $|u|$, which determine the behavior of the system at very short times, this implies giving equal weight to each site. However, as $|u| \to 0$, which determines what happens as $t \to \infty$, the transitions from site $\mathbf{s}$ are given a relative weight $1/\lambda_{\mathbf{s}}$ inversely proportional to the transition rate from it, so that the averages are dominated by the sites that are most difficult to leave. The implications of such an averaging procedure will be discussed in Section 5.

3. AVERAGE T-MATRIX AND COHERENT MEDIUM APPROXIMATIONS

An alternative approach to the approximate calculation of $\langle P\rangle$ from Eq. (5) is to regard P as the Green's function of the operator $A = V - \Lambda$,

$$P = (uI - A)^{-1} = \left[uI - (V - \Lambda)\right]^{-1} \tag{10}$$

It is well known that for random alloys the average T-matrix approximation (ATA)[5] and coherent potential approximation (CPA)[6] provide excellent approximation for the calculation of $\langle P\rangle$. The basis of these

methods is to define an effective medium in terms of an operator A_e having translational symmetry, and express P in terms of the Green's function G_e of A_e by

$$P = G_e + G_e T G_e \tag{11}$$

If $A - A_e$ can be expressed as a sum of elements each associated with a given cluster of atoms, $A - A_e = \sum_k w_k$ say, a matrix t_k can be defined in terms of w_k and the matrix g_e of G_e between the sites of the cluster, and on writing $T = \sum_k T_k$ one finds[13] that

$$T_k = t_k\left(1 + G_e \sum_{l \neq k} T_l\right) \tag{12}$$

so that

$$\langle T_k \rangle = \langle t_k \rangle\left(1 + G_e \sum_{l \neq k} T_l\right) + \left\langle (t_k - \langle t_k \rangle) G_e \sum_{l \neq k} (T_l - \langle T_l \rangle)\right\rangle \tag{13}$$

The single-cluster approximations involve ignoring the second term in Eq. (13), i.e., in ignoring the correlation between fluctuations of A associated with different clusters. In that case, we readily find that

$$\langle P \rangle \simeq (z - A_e - S)^{-1} \tag{14}$$

where the matrix s of S between the sites of the cluster is given by

$$s = (I + \langle t_k \rangle g_e)^{-1} \langle t_k \rangle \tag{15}$$

with

$$\langle t_k \rangle = \langle (I - w_k g_e)^{-1} w_k \rangle \tag{16}$$

The ATA uses Eqs. (15) and (16) directly for a given A_e, while the CPA defines a coherent medium by the requirement that $\langle t_k \rangle = 0$.

In the original applications of this method, the clusters k were taken as single atoms, but for our problem a cluster consists of a pair of atoms with a bond between them, provided that only hopping between adjacent sites is allowed.[7–9] Simple calculations then show that, in our notation and with the diagonal and off-diagonal elements of g_e denoted by g_0 and g_1, respectively,

$$\langle t \rangle = t_a \begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}, \qquad t_a = \left\langle \frac{\tilde{V} - V_e}{1 + 2(g_0 - g_1)(\tilde{V} - V_e)} \right\rangle \tag{17}$$

Here, V_e is the value of V corresponding to A_e, and

$$\tilde{V} = \tfrac{1}{2}(V_{\mathbf{s},\mathbf{s}'} + V_{\mathbf{s}'\mathbf{s}}) \tag{18}$$

is the mean transition rate along a bond between adjacent sites $\mathbf{s}$ and $\mathbf{s}'$.

In order to examine the weighting of different bonds in this averaging procedure, we consider hypercubic lattices in d dimensions, with each site having $n = 2d$ nearest neighbors, in which case[7]

$$g_0 - g_1 = (1 - ug_0)/nV_e \tag{19}$$

As $|u| \to \infty$, $g_0 \sim 1/u$, and so t_a is proportional to $\langle \tilde{V} - V_e \rangle$, so that at short times all bonds contribute equally to the average. As $|u| \to 0$, $ug_0 \to 0$, and there is a difference between one-dimensional and multidimensional systems. In one dimension, t_a is proportional to $\langle 1 - V_e/\tilde{V} \rangle$, and so is dominated by bonds with small $\tilde{V}$, but if $n > 2$ the contribution to t_a from a bond with $\tilde{V} = 0$, for instance, is only $(n+2)/(n-2)$ times that from a bond with $\tilde{V} = 2V_e$. Such a result is physically very reasonable, since a particle can avoid difficult steps in two or three dimensions but not in one dimension.

4. SOME EXACT RESULTS FOR THE LONG-TIME BEHAVIOR

In the last two sections, we have seen that different methods of approximation give different weights to the various sites and transitions, especially in the limit $u \to 0$ which determines the behavior of the system at long times. We now derive some exact results for the simplest case, namely, that of a Markovian system, containing N sites $\mathbf{s}$, for which the N eigenvalues of A are all real and distinct. Our results can be generalized by methods parallel to those used by Feller[14] for finite Markov chains. In view of Gershgorin's theorem[15] and Eq. (9), the eigenvalues of $A = V - \Lambda$ are all nonpositive, and we denote them by $-\alpha^{(k)}$, with $\alpha^{(k)} < \alpha^{(k+1)}$. The corresponding right and left eigenvectors of A, $\mathbf{x}^{(k)}$ and $\mathbf{y}^{(k)}$, are defined by

$$A\mathbf{x}^{(k)} = -\alpha^{(k)}\mathbf{x}^{(k)}, \qquad \tilde{\mathbf{y}}^{(k)}A = -\alpha^{(k)}\tilde{\mathbf{y}}^{(k)} \tag{20}$$

and the Green's function of A can be written in the form

$$(uI - A)^{-1} = \sum_k c_k \mathbf{x}^{(k)}\tilde{\mathbf{y}}^{(k)}/(u + \alpha^{(k)}), \qquad c_k = 1/(\tilde{\mathbf{y}}^{(k)}\mathbf{x}^{(k)}) \tag{21}$$

It follows from equation (10) and inversion of the Laplace transform that

$$P(\mathbf{s}, t \mid \mathbf{s}') = \sum_k c_k x_{\mathbf{s}}^{(k)} y_{\mathbf{s}'}^{(k)} \exp(-\alpha^{(k)} t) \tag{22}$$

and at long times the terms with small α will dominate this sum.

Although A is a random matrix, we can find certain features of its eigenvectors for small α. From Eq. (9) and the fact that $A = V - \Lambda$ it follows that $\sum_{\mathbf{s}'} A_{\mathbf{s}',\mathbf{s}}$ vanishes. Hence $\alpha^{(0)} = 0$, and $\mathbf{y}^{(0)}$ has all its elements equal. If A is symmetric, $\mathbf{x}^{(k)} = \mathbf{y}^{(k)}$, and so, in view of Eqs. (22) and (21), all

states make comparable contributions to $P(\mathbf{s}, t \mid \mathbf{s}')$ for large t. However, this is not true for a system that contains trapping states. For instance, in a system containing a single trap state $\mathbf{s}$, and such that $A_{\mathbf{s},\mathbf{s}'} = hA_{\mathbf{s}',\mathbf{s}}$ with fixed h while $A_{\mathbf{s}'',\mathbf{s}'} = A_{\mathbf{s}',\mathbf{s}''}$ if $\mathbf{s}'$ and $\mathbf{s}''$ both differ from $\mathbf{s}$, we can find $\mathbf{x}^{(0)}$ exactly. If we choose $x_{\mathbf{s}}^{(0)} = h$, then $x_{\mathbf{s}'}^{(0)} = 1$ if $\mathbf{s}' \neq \mathbf{s}$, and this result can be generalized to systems containing a series of such traps with no direct transitions between them. It then follows from Eq. (22) that the relative weight of each trap state is approximately inversely proportional to the transition rate out of it. This result is very reasonable on physical grounds, since in systems containing traps a particle will spend most of its time in the traps.

Another type of system for which $\mathbf{x}^{(0)}$ can be found exactly is that originally considered by Scher and Lax,[3] in which $\psi_{\mathbf{s}'}(\mathbf{s} - \mathbf{s}', t) = p(\mathbf{s} - \mathbf{s}')\psi_{\mathbf{s}'}(t)$. This is a reasonable model for systems in which transitions between localized states take place via excitation to a band of extended states. For such a system, $A = MD$, where M is a symmetric translationally invariant matrix, i.e., $M_{\mathbf{s},\mathbf{s}'} = M(\mathbf{s} - \mathbf{s}')$, and has a right eigenvalue $\mathbf{y}^{(0)}$ with all its elements equal. Moreover, D is a diagonal matrix with $D_{\mathbf{s},\mathbf{s}} = \lambda_{\mathbf{s}}$, and so $x_{\mathbf{s}}^{(0)}$ is proportional to $1/\lambda_{\mathbf{s}}$. Thus, for this type of system the relative weight of each trap state as $t \to \infty$ is exactly proportional to the inverse of the transition rate out of it.

5. DISCUSSION

The results derived in the last section can be used to test the suitability of different approximation methods for the description of how different types of systems behave at long times or low frequencies. We are usually interested in the rate at which a system approaches its limiting state as $t \to \infty$, so that the requirement that an approximation give the correct limiting value as $t \to \infty$ is a necessary, but not a sufficient, condition for its suitability. The methods that we consider are the CTRW approximation described in Section 2, and effective bond approximations, including in particular the CPA method described in Section 3, which we call the coherent bond approximation (CBA).

For systems in which all the transition rates are symmetric, i.e., $V_{\mathbf{s},\mathbf{s}'} = V_{\mathbf{s}',\mathbf{s}}$, we found in Section 4 that all states contribute with similar weight to $P(\mathbf{s}, t \mid \mathbf{s}_0)$ at long times, and so an averaging procedure is required that gives all states a similar weighting. Thus, the CTRW approximation, which gives most weight to states that are difficult to leave even though these are also difficult to enter, cannot be expected to be accurate. Effective bond methods should be much better for this type of system, but even here a word of warning is required. As the frequency tends to zero, or $t \to \infty$, the

system's properties are expected to be dominated by states on the critical percolation path,[16] so that in multidimensional systems states not on this path should be excluded from the average. In the opposite extreme case of systems with all states fairly accessible, the analysis of Section 4 indicates that it is the states most difficult to leave, which can be regarded as traps, that dominate $P(\mathbf{s}, t \mid \mathbf{s}_0)$ at long times. In this case, it is the CTRW approximation that involves averages with approximately the correct weights, and so should provide a reasonable approximation. There are two basic reasons for the failure of the effective bond methods for these systems. Firstly, the CBA method neglects the correlations between fluctuations in the transition rates for different bonds, as noted after Eq. (13), while such correlations are an essential feature of the bonds from trap states. Secondly, in the CBA each bond is characterized by a symmetric average of the transition rates along it in the two directions, and such a procedure cannot take account of the distinctive properties of trap states. We note in passing that our conclusions about the range of validity of the CTRW approximation agree with those of Alexander,[17] who used rather different arguments and did not consider effective bond methods.

In the application of our results to time-dependent transport in amorphous semiconductors, a clear distinction must be made between the ac conductivity $\sigma(\omega)$ and the transient current $I(t)$ observed after the generation of a sheet of charge carriers. This distinction is often overlooked because there is a formal connection between these two quantities when they refer to the same system.[18] However, while $\sigma(\omega)$ refers to a system in which the occupancy of the different states is close to that in thermal equilibrium, the transient currents are often measured for systems very far from such equilibrium populations.

For the ac conductivity of a system at temperature T and with Fermi energy ϵ_F, if the states at $\mathbf{s}$ and $\mathbf{s}'$ have energies ϵ and ϵ', respectively, then according to Butcher's analysis[19] the ratio of the effective transition rates is

$$V_{\mathbf{s},\mathbf{s}'}/V_{\mathbf{s}',\mathbf{s}} = \cosh^2\left[\tfrac{1}{2}\beta(\epsilon' - \epsilon_F)\right]/\cosh^2\left[\tfrac{1}{2}\beta(\epsilon - \epsilon_F)\right] \tag{23}$$

where $\beta = 1/k_B T$. This ratio is close to unity if $\sigma(\omega)$ is dominated either by charge carriers close to ϵ_F or by those within a few $k_B T$ of the mobility edge of a band, for instance, and so for most real systems. Hence, the CBA method should be much more accurate than the CTRW approximation for the calculation of the low-frequency ac conductivity of amorphous semiconductors.

By contrast, a variety of different situations are possible for the transient currents $I(t)$ that follow the injection of a sheet of charge carriers. For the sake of definiteness, we consider systems in which $I(t)$ is due to the

motion of electrons, but our results can easily be generalized. If the injected electrons rapidly thermalize, and then have a quasiequilibrium distribution with constant effective Fermi level ϵ_{Fn} until they recombine, Eq. (23) will apply with ϵ_{Fn} replacing ϵ_F. Hence, provided that the electrons hop only between adjacent sites, the CBA method will be much more accurate in this case than the CTRW approximation. Another type of system for which this will be true is one in which the electrons are all in a band of localized states only a few $k_B T$ wide, with direct transitions between them. A different type of system, which has been extensively discussed recently,[20,22] is one where the electrons gradually sink lower and lower into the conduction band's tail of localized states, which they can only leave by thermal excitation to states above the mobility edge. For such systems, the occupation statistics of the states are far from equilibrium, and the deeper states behave as traps with strongly asymmetric transition probabilities. In this case, our analysis confirms the assumption[20–22] that the CTRW approximation should be fairly reliable in the long time limit, while effective bond methods will be quite inappropriate. Intermediate cases are also possible, such as systems in which the electrons occupy states in a band tail or impurity band that is more than a few $k_B T$ wide, and move by direct transitions between the localized states rather than by excitation to above a mobility edge. In this situation, the transition rates are not symmetric and traps will exist, but some of them are isolated in space and so also difficult to enter. Thus, neither the CTRW approximation, which gives too much weight to such isolated states, nor the CBA method, which ignores the correlation between the transition rates in different directions from a state near the bottom of the band, will be reliable approximations in this case.

6. CONCLUSIONS

From our comparison of the weightings used in the averages employed by the CTRW approximation and in the coherent band approximation (CBA) with those appropriate to the exact solution of the master equation at long times, we conclude that which method provides the better approximation depends on the details of the system considered. For systems in which the effective transition rate from state $\mathbf{s}$ to state $\mathbf{s}'$ approximately equals that from $\mathbf{s}'$ to $\mathbf{s}$, the CBA is much more accurate, but for systems whose behavior at long times is dominated by trap states $\mathbf{s}$ that are much more difficult to enter than to leave the CTRW approximation is the appropriate one, while there are systems for which neither type of method is reliable. It follows that the CBA method is preferable for calculations of the ac conductivity in most amorphous semiconductors and of transient currents if the charge carriers hop in a narrow band. On the other hand, the

CTRW approximation is much the more accurate one for calculating the transient currents if the charge carriers are spread over a wide band of localized states and can only move from one state to another by thermal excitation to states above a mobility edge.

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