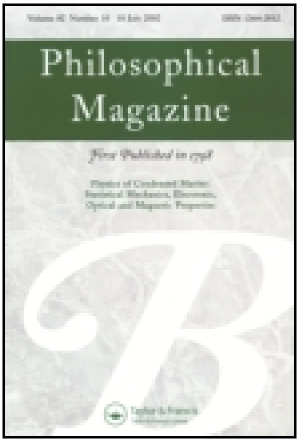

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A comment on the theory of excitation migration in disordered lattices

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A comment on the theory of excitation migration in disordered lattices

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ABSTRACT

The transport of an excitation on a lattice randomly occupied by guests is considered, emphasizing the dependence on the initial condition. Exact equations are derived for the transport, which can be written as a generalized master equation or as a continuous-time random-walk equation.

§ 1. INTRODUCTION

The theory of random walks on random lattices has been the subject of much study in recent years (see, for example, Butcher 1980). Recently, the present authors (Klafter and Silbey 1980) gave a formal derivation of the continuous-time random-walk equation (Scher and Lax 1973) for transport of excitations on a fractionally occupied lattice ; in that paper, we chose a simple initial condition. In the present paper, we discuss various initial conditions and make connections to other work on the subject.

Consider a lattice on which we put molecules capable of being excited and of transferring that energy to other such molecules (guests). The fractional occupation of the lattice by these guests is c $(0<c<1)$. There are of course many configurations consistent with a given value of c, and we focus attention on the average over all such configurations. Let $p(\mathbf{n}, t)$ be the probability of finding the excitation at lattice site n, in some particular configuration and $\langle p(\mathbf{n}, t)\rangle$ the average over all configurations.

First, we make a simple point : if

$$\langle p(\mathbf{n}, t)\rangle = \sum_{\mathbf{m}} G_{\mathbf{nm}}(t)\langle p(\mathbf{m}, 0)\rangle \tag{1}$$

then the equations of motion for $\langle p(\mathbf{n}, t)\rangle$ can be written as a generalized master equation (GME) or as a continuous-time random-walk (CTRW) equation. Note that the translational invariance of the averaged system is implied in the fact that $G_{\mathbf{nm}}$ is a function of $\mathbf{n}-\mathbf{m}$ only. We can then Fourier transform eqn. (1) to

$$\langle p(\mathbf{k}, t)\rangle = G(\mathbf{k}, t)\langle p(\mathbf{k}, 0)\rangle. \tag{2}$$

We now take the Laplace transform of eqn. (2) to find

$$\langle \tilde{p}(\mathbf{k}, z)\rangle = \tilde{G}(\mathbf{k}, z)\langle p(\mathbf{k}, 0)\rangle, \tag{3}$$

or, by rearrangement

$$z\langle \tilde{p}(\mathbf{k}, z)\rangle - \langle p(\mathbf{k}, 0)\rangle = [z\tilde{G}(\mathbf{k}, z) - 1]\langle p(\mathbf{k}, 0)\rangle \tag{4 a}$$

$$= [z - \tilde{G}^{-1}(\mathbf{k}, z)]\langle \tilde{p}(\mathbf{k}, z)\rangle \tag{4 b}$$

$$\equiv + \tilde{K}(\mathbf{k}, z)\langle p(\mathbf{k}, z)\rangle, \tag{4 c}$$

where $\tilde{G}(\mathbf{k}, z) = [z - \tilde{K}(\mathbf{k}, z)]^{-1}$, and by taking the inverse Laplace transform

$$\langle \dot{p}(\mathbf{k}, t)\rangle = + \int_0^t K(\mathbf{k}, t-\tau)\langle p(\mathbf{k}, \tau)\rangle \, d\tau. \tag{5}$$

Since in every configuration total probability is conserved,

$$G(\mathbf{k}=0, t) = \sum_{\mathbf{n}} G_{\mathbf{nm}}(t) = 1 \tag{6 a}$$

and so

$$K(\mathbf{k}=0, t) = \sum_{\mathbf{n}} K_{\mathbf{nm}}(t) = 0 \tag{6 b}$$

or

$$K_{\mathbf{nn}}(t) = -\sum_{\mathbf{m}\neq\mathbf{n}} K_{\mathbf{mn}}(t).$$

Equation (5) can be rearranged to the GME by inverting the Fourier transform

$$\langle \dot{p}(n, t)\rangle = \int_0^t d\tau \left\{ \sum_{\mathbf{m}\neq\mathbf{n}} K_{\mathbf{nm}}(t-\tau)\langle p(m, \tau)\rangle - \sum_{\mathbf{m}\neq\mathbf{n}} K_{\mathbf{mn}}(t-\tau)\langle p(n, \tau)\rangle. \right. \tag{7}$$

Finally, eqn. (4) or (7) can be rearranged to give the CTRW by defining (Klafter and Silbey 1980)

$$\tilde{\phi}(z) = [z - \tilde{K}_{\mathbf{nn}}(z)]^{-1}, \tag{8 a}$$

$$\tilde{\psi}_{\mathbf{n}-\mathbf{m}}(z) = \tilde{K}_{\mathbf{nm}}(z)\tilde{\phi}(z), \tag{8 b}$$

so that

$$\langle p(\mathbf{n}, t)\rangle = \phi(t)\langle p(\mathbf{n}, 0)\rangle + \sum_{\mathbf{m}\neq\mathbf{n}} \int_0^t d\tau \, \psi_{\mathbf{n}-\mathbf{m}}(t-\tau)\langle p(\mathbf{m}, \tau)\rangle \tag{9}$$

which is the CTRW equation (Scher and Lax 1973).

Finally, we point out that if the system is not translationally invariant so that $G_{\mathbf{nm}}(t)$ depends on n and m separately, then a GME still follows from eqn. (1) with the difference that $K_{\mathbf{nm}}$ is not simply a function of $\mathbf{n}-\mathbf{m}$. The equation corresponding to the CTRW will have $\psi_{\mathbf{nm}}(t)$ depending on $\mathbf{n}$ and $\mathbf{m}$ separately and a set of $\phi_{\mathbf{n}}(t)$ each depending on $\mathbf{n}$. Such cases will be described later.

From this discussion, it is clear that, at least formally, eqn. (2) implies the GME and the CTRW. Of course, the difficulties are all in deriving exact or good approximate forms for $G_{\mathbf{nm}}(t)$ and $K_{\mathbf{nm}}(t)$. Some progress has been made on this recently (Odagaki and Lax 1981, Webman 1981).

From eqn. (2), we can define a generalized diffusion function $\tilde{D}(\mathbf{k}, z)$ by (Haan and Zwanzig 1978)

$$\tilde{G}(\mathbf{k}, z) = [z + \tilde{D}(\mathbf{k}, z)]^{-1}, \tag{10}$$

so that $\tilde{D}(\mathbf{k}, z) = -\tilde{K}(\mathbf{k}, z)$.

The usual (i.e. long time) diffusion coefficient is given by

$$D = \lim_{z\to 0} \lim_{\mathbf{k}\to 0} \left[\frac{\partial^2 \tilde{D}(\mathbf{k}, z)}{\partial k^2}\right]. \tag{11}$$

§ 2. Initial conditions

We now specialize to a case in which the underlying equation for the probabilities in each configuration is the master equation,

$$\dot{p}(\mathbf{n}, t) = \sum_{\mathbf{m}}{}' \; W_{\mathbf{nm}} p(\mathbf{m}, t), \tag{12}$$

where

$$W_{nn} = - \sum_{\mathbf{n}\neq\mathbf{m}}{}' \; W_{nm}, \tag{13}$$

by conservation of probability.

The primed sum in eqn. (10) and (11) goes over *occupied* sites but we can sum over all sites by introducing the occupation variable ξ_n, which is 1 if site n is occupied and 0 if site $\mathbf{n}$ is not occupied (note : $\xi_n^2 = \xi_n$),

$$\dot{p}(\mathbf{n}, t) = \sum_{\mathbf{m}} W_{nm} \xi_n \xi_m p(\mathbf{m}, t) = \sum_{\mathbf{m}} V_{nm} p(\mathbf{m}, t), \tag{14}$$

where the sum is now over all sites in the lattice.

Klafter and Silbey (1980) solved this equation subject to the initial condition

$$p(n, 0) = \delta_{n0}\,; \quad \langle p(n, 0)\rangle = \delta_{n0} \tag{15}$$

independent of configuration. This may seem strange at first because at $t = 0$, the excitation is on site 0, *even if this site is unoccupied by a guest*. Obviously, if site 0 is unoccupied, the excitation cannot move and the diffusion constant is zero for all these configurations. In order to compute the true diffusion constant, D, we must exclude from the average those configurations for which site 0 is unoccupied. To do this, we first solve eqn. (12) subject to the initial condition, eqn. (15), to find

$$\left.\begin{aligned} \langle p(n, t)\rangle^{(0)} &= G_{n0}^{(0)}(t), \\ G_{nm}^{(0)}(t) &= (\exp(Vt))_{nm}, \end{aligned}\right\} \tag{16}$$

where the superscript denotes the use of this initial condition. Since this average is over *all* configurations, all sites are equivalent and so $G_{nm}^{(0)}(t)$ depends on $n - m$ only, and therefore eqns. (7)–(9) holds for this case. Let us denote the average probability of excitation at time *t for those configurations in which site* 0 *is unoccupied by a guest by* $\langle p(n, t)\rangle$. We can relate this to $\langle p(n, t)\rangle^{(0)}$ by

$$\langle p(n, t)\rangle^{(0)} = c\langle p(n, t)\rangle + (1 - c)\delta_{n0}, \tag{17}$$

because only a fraction, c, of the configurations have a guest on site 0. Therefore, using eqn. (14),

$$\langle p(n,t)\rangle = \frac{1}{c} G_{n0}{}^{(0)}(t) - \left(\frac{1-c}{c}\right)\delta_{n0}$$

$$= \sum_{\mathbf{m}} \left\{ \frac{1}{c} G_{nm}{}^{(0)}(t) - \left(\frac{1-c}{c}\right)\delta_{nm}\right\} \langle p(m,0)\rangle, \tag{18}$$

or, by Fourier transform

$$\langle p(k,z)\rangle = \tilde{G}(k,z)\langle p(k,0)\rangle, \tag{19}$$

where

$$\tilde{G}(k,z) = \frac{1}{c}\tilde{G}^{(0)}(k,z) - \left(\frac{1-c}{c}\right)\frac{1}{z}. \tag{20}$$

If we define

$$\tilde{G}^{(0)}(k,z) = [z + \tilde{D}^{(0)}(k,z)]^{-1} \tag{21}$$

then the true diffusion constant, D, is given in terms of the k independent part of $G^{(0)}$ by

$$D = \frac{1}{c} \lim_{z\to 0} \lim_{k\to 0} \left(\frac{\partial^2 \tilde{D}^{(0)}(k,z)}{\partial k^2}\right). \tag{22}$$

Thus, all the information for the calculation of $\langle p(n,t)\rangle$ and D is in $\tilde{G}^{(0)}$ and $\tilde{D}^{(0)}$.

We can derive eqn. (19) and (20) in another way by considering another initial condition,

$$p(\mathbf{n},0) = \xi_0 \delta_{\mathbf{n}0}, \tag{23 a}$$

$$\langle p(\mathbf{n},0)\rangle = c\delta_{\mathbf{n}0}. \tag{23 b}$$

Then,

$$\begin{aligned}\langle p(\mathbf{n},t)\rangle &= \langle [\exp(Vt)]_{\mathbf{n}0}\xi_0\rangle \\ &= \langle [\exp(Vt) - 1]_{\mathbf{n}0}\xi_0 + \xi_0\delta_{n0}\rangle \\ &= \langle [\exp(Vt) - 1]_{\mathbf{n}0}\rangle + c\delta_{\mathbf{n}0} \\ &= \langle [\exp(Vt)]_{\mathbf{n}0}\rangle - \delta_{\mathbf{n}0}(1-c),\end{aligned} \tag{24}$$

where we have noted that in the expansion of $(\exp(Vt) - 1)_{\mathbf{n}0}$ every term contains a ξ_0 and $\xi_0{}^2 = \xi_0$. We now rewrite this as

$$\langle p(\mathbf{n},t)\rangle = \left[\frac{1}{c}\langle[\exp(Vt)]\rangle_{\mathbf{n}0} - \delta_{\mathbf{n}0}\left(\frac{1-c}{c}\right)\right]c, \tag{25}$$

which differs from eqn. (18) only by a factor of c.

Note that had we considered a more general initial condition ($f(\mathbf{n})$ independent of configuration)

$$p(\mathbf{n},0) = \xi_{\mathbf{n}} f(\mathbf{n}), \tag{26 a}$$

$$\langle p(\mathbf{n},0)\rangle = cf(\mathbf{n}), \tag{26 b}$$

then

$$\langle p(\mathbf{n}, t)\rangle = \sum_{\mathbf{m}} \langle [\exp(Vt)]_{\mathbf{nm}} \xi_{\mathbf{m}} \rangle f(\mathbf{m})$$

$$= \sum_{\mathbf{m}} \left\{ \frac{1}{c} \langle [\exp(Vt)]_{\mathbf{nm}} \rangle - \delta_{\mathbf{nm}} \left(\frac{1-c}{c} \right) \right\} \langle p(\mathbf{m}, 0) \rangle, \tag{27}$$

so that

$$G_{\mathbf{nm}}(t) = \frac{1}{c} G_{\mathbf{nm}}{}^{(0)}(t) - \delta_{\mathbf{nm}} \left(\frac{1-c}{c} \right), \tag{28}$$

or

$$G(\mathbf{k}, t) = \frac{1}{c} G^{(0)}(\mathbf{k}, t) - \left(\frac{1-c}{c} \right). \tag{29}$$

Equations (28) and (29) belong to the translational invariant case in eqn. (1), where one can define the matrix $\mathbf{G}$,

$$\tilde{\mathbf{G}} = \frac{1}{c} (z + \tilde{\mathbf{D}}^{(0)})^{-1} + \frac{1}{z} \left(\frac{c-1}{c} \right) \mathbf{1}. \tag{30}$$

We have shown that the probabilities $\langle p(\mathbf{n}t)\rangle$ depend on the initial conditions. However, if one is interested in the diffusion coefficient, the information needed is included in $\langle p(\mathbf{n}, \dot{t})\rangle^{(0)}$ for which the initial condition of Klafter and Silbey (1980) holds and also all the derivations that appear there.

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