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Derivation of the Continuous-Time Random-Walk Equation

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The transport of electrons or excitations on a lattice randomly occupied by guests is considered. The equation governing the transport in any configuration is assumed to be the master equation. A projection operator technique is used to derive the exact equation governing the transport averaged over all configurations, which can be written as either a generalized master equation or the continuous-time random-walk equations (CTRW), establishing the correctness of the CTRW for these problems.

Recently there has been considerable interest in various aspects of dispersive incoherent transport in condensed disordered media.[1-9] Both charge transport[4-8] and electronic energy transfer[1-3,10] have been extensively studied, resulting in interesting short-time (ac limit) and long-time (dc limit) behaviors. Two main approaches have been adopted in order to investigate the dispersive nature of transport in disordered systems: (A) The Green's function, or self-energy (SE) method,[1,2,11] (B) the continuous-time random walk (CTRW)[4-6,9,12] which was originally based on an approximate equivalence between the problem of an incoherent, random-walk migration on a disordered lattice and the CTRW on an ordered lattice.[4-6,12] The CTRW is found to be an attractive approach to tackle these problems because it is mathematically tractable and it contains all the information of the disorder in the system in a hopping-time distribution function. The theory accounts very well for the transport behavior in a broad class of materials.[3,4-7]

The CTRW ideas were first suggested by Montroll and Weiss,[12] who introduced the distribution function $\psi(t)$ into the usual random-walk formalism to discuss a random walk with random jump times. This approach was elaborated later by Scher and Lax,[4] who were the first to introduce the equations for the CTRW, the generalization of $\psi(t)$ to $\psi_{\vec{n}-\vec{m}}(t)$ and the applications to transport in disordered systems. Application of a decoupled scheme of the CTRW was also proposed and studied by Scher and Montroll.[5,6] The connection of the CTRW to the master equation (ME) was discussed by Bedeaux, Lakotos-Lindenberg, and Schuler,[13] and the connection to the generalized master equation (GME) was pointed out by Schlesinger, Kenkre, and Montroll[14] and by Kenkre and Knox.[15] This latter connection was studied only in a decoupled scheme which corresponds to the Scher-Montroll approximation.[5,7] There has been recently much discussion in the literature on the point of whether the CTRW is exact and, if it is not exact, to what approximation it does correspond.[7,8,11,16,17] In this Letter we derive the CTRW for transport on a lattice which is fractionally occupied by impurities. We show that both the CTRW equation and the GME are equivalent and *exact* equations for the dynamics of the system. This exact derivation should provide the justification to the approach which has been recently subjected to some criticism.[7,8,16]

The argument proceeds in the following way. Assuming that the equation governing the migration in each configuration is a ME, we average

over all possible configurations to arrive at an exact GME. We then rework the equations so that they are identical to the CTRW equations for transport on a translationally invariant lattice. We also comment on the approximations which have been used for the hopping-time distribution functions in the CTRW and their connection to the exact relations with the GME.

Consider a lattice on which there are two kinds of sites: those containing a guest (or impurity) molecule and those containing a host molecule. The host molecules are *incapable of participating in the transport*, so that migration can occur only among the guests. There is an enormous number of configurations consistent with the fractional concentration of quests (= c). The equation of motion of the probability $P_{\vec{n}}(t)$ of an electron (or an excitation) being on site n at time t is, for *each configuration*,

$$\dot{P}_{\vec{n}}(t)=\sum_{\substack{\vec{m}\\ \text{guests}\\ \vec{m}\neq\vec{n}}}(W_{\vec{n},\vec{m}}P_{\vec{m}}-W_{\vec{m},\vec{n}}P_{\vec{n}}), \tag{1}$$

where the sum is over the guest sites only. $W_{\vec{m},\vec{n}}$ is assumed to be a function only of $R_{\vec{n}}-R_{\vec{m}}$, and for convenience symmetric, i.e., $W_{\vec{n},\vec{m}}=W_{\vec{m},\vec{n}}$, which is the usual high-T limits. This symmetry is not necessary for the formal development which follows; however, we assume hopping rates which do not depend on site-energy fluctuation.[4,7,8,16] Define

$$W_{\vec{n},\vec{m}}'=(1-\delta_{\vec{n},\vec{m}})W_{\vec{n},\vec{m}}-\delta_{\vec{n},\vec{m}}\sum_{\vec{r}\neq\vec{n}}W_{\vec{r},\vec{n}}, \tag{2}$$

then

$$\dot{P}_{\vec{n}}(t)=\sum_{\substack{\vec{m}\\ \text{guests}}}W_{\vec{n},\vec{m}}'P_{\vec{m}}=\sum_{\text{all }\vec{m}}W_{\vec{n},\vec{m}}\xi_{\vec{m}}\xi_{\vec{n}}P_{\vec{m}}, \tag{3}$$

where $\xi_{\vec{m}}$ is a variable which equals 1 if $\vec{m}$ is occupied by a guest molecule and 0 if $\vec{m}$ is occupied by a host molecule. The last sum in Eq. (3) is now over *all* lattice sites because of the introduction of the $\xi_{\vec{m}}$. We solve Eq. (3) formally, assuming that at $t=0$ the electron is at $\vec{n}=\vec{0}$ so that

$$\boldsymbol{P}_{\vec{n}}(t)=[\exp(\underline{V}t)]_{\vec{n},\vec{0}}, \tag{4}$$

where

$$V_{\vec{n},\vec{m}}=W_{\vec{n},\vec{m}}'\xi_{\vec{n}}\xi_{\vec{m}}. \tag{5}$$

We now average over all possible configurations to find

$$\langle P_{\vec{n}}(t)\rangle=\langle\exp(\underline{V}t)\rangle_{\vec{n},\vec{0}} \tag{6}$$

and, by Laplace transform,

$$\langle\tilde{P}_{\vec{n}}(z)\rangle=\langle(z\underline{1}-\underline{V})^{-1}\rangle_{\vec{n},\vec{0}}. \tag{7}$$

An exact form for this can be derived with use of the Zwanzig projection operator method.[18] Defining a projection operator D as the configuration-averaging operator

$$DA\equiv\langle A\rangle, \tag{8}$$

then

$$\frac{d}{dt}[D\exp(\underline{V}t)]=D\underline{V}\exp(\underline{V}t)=D\underline{V}D\exp(\underline{V}t)+D\underline{V}(1-D)\exp(\underline{V}t),$$

$$\frac{d}{dt}[(1-D)\exp(\underline{V}t)]=(1-D)\underline{V}D\exp(\underline{V}t)+(1-D)\underline{V}(1-D)\exp(\underline{V}t), \tag{9}$$

so that

$$(1-D)\exp(\underline{V}t)=\int_0^t d\tau\exp[(1-D)\underline{V}(t-\tau)](1-D)\underline{V}D\exp(\underline{V}\tau) \tag{10}$$

and

$$\frac{d}{dt}[D\exp(\underline{V}t)]=D\underline{V}D\exp(\underline{V}t)+\int_0^t d\tau\, D\underline{V}(1-D)\exp[(1-D)\underline{V}(t-\tau)](1-D)\underline{V}D\exp(\underline{V}\tau). \tag{11}$$

Then, by Laplace transform,

$$\langle(z\underline{1}-\underline{V})^{-1}\rangle=[z\underline{1}-\langle\underline{V}\rangle-\langle\delta\underline{V}[z\underline{1}-(1-D)\underline{V}\rangle]^{-1}\equiv[z\underline{1}-\underline{M}(z)]^{-1}, \tag{12}$$

where $\delta\underline{V}=\underline{V}-\langle\underline{V}\rangle$ and $\underline{M}(z)$ is the self-energy matrix. Since

$$[z\underline{1}-\underline{M}(z)]^{-1}=\{z^{-1}\underline{1}+z^{-1}\underline{M}(z)[z\underline{1}-\underline{M}(z)]^{-1}\}, \tag{13}$$

we find, using Eq. (7), that $\langle\tilde{P}_{\vec{n}}(z)\rangle$ obeys a GME:

$$z\langle\tilde{P}_{\vec{n}}(z)\rangle = \delta_{\vec{n},\vec{0}} + \sum_{\vec{m}} \tilde{M}_{\vec{n},\vec{m}}(z)\langle\tilde{P}_{\vec{m}}(z)\rangle. \tag{14}$$

By conservation of probability $\sum_{\vec{n}} \tilde{M}_{\vec{m},\vec{n}}(z) = 0$, therefore

$$\tilde{M}_{\vec{n},\vec{n}}(z) = -\sum_{\vec{m}\neq\vec{n}} \tilde{M}_{\vec{m},\vec{n}}(z) \tag{15}$$

and

$$z\langle\tilde{P}_{\vec{n}}(z)\rangle = \delta_{\vec{n},\vec{0}} + \sum_{\vec{m}\neq\vec{n}} \{\tilde{M}_{\vec{n},\vec{m}}(z)\langle\tilde{P}_{\vec{m}}(z)\rangle - \tilde{M}_{\vec{m}\vec{n}}(z)\langle\tilde{P}_{\vec{n}}(z)\rangle\}, \tag{16}$$

which may be rewritten as

$$\langle\dot{P}_{\vec{n}}(t)\rangle = \sum_{\vec{m}\neq\vec{n}} \int_0^t d\tau \{M_{\vec{n},\vec{m}}(t-\tau)\langle P_{\vec{m}}(\tau)\rangle - M_{\vec{m},\vec{n}}(t-\tau)\langle P_{\vec{n}}(\tau)\rangle\}. \tag{17}$$

Thus, the basic equation for transport in a disordered system is a GME, Eq. (17), in contradiction to some arguments of Pollak[7] concerning a conceptual problem of the applicability of a homogeneous non-Markovian equation in the case of disordered systems.[19] We should emphasize that the GME, Eq. (17), is exact only for the averaged probability $\langle P_{\vec{n}}(t)\rangle$. *An equation for the variance of the* $P_{\vec{n}}(t)$*'s would almost assuredly involve more than* $\psi_{\vec{n}-\vec{m}}(t)$.

Upon averaging, each site is identical, so that the system is translationally invariant, and thus

$$\tilde{M}_{\vec{n},\vec{m}}(z) = \tilde{M}_{\vec{n}-\vec{m}}(z). \tag{18}$$

We now define

$$\tilde{M}_{\vec{n}-\vec{m}}(z) = \tilde{\psi}_{\vec{n}-\vec{m}}(z)\{z/[1-\tilde{\chi}(z)]\}, \tag{19}$$

where

$$\tilde{\chi}(z) = \sum_{\vec{n}\neq\vec{m}} \tilde{\psi}_{\vec{n}-\vec{m}}(z) = z^{-1}[1-\tilde{\chi}(z)] \sum_{\vec{n}\neq\vec{m}} \tilde{M}_{\vec{n}-\vec{m}}(z), \tag{20}$$

or

$$\tilde{\chi}(z) = \sum_{\vec{n}\neq\vec{m}} \tilde{M}_{\vec{n}-\vec{m}}(z)[z + \sum_{\vec{m}\neq\vec{n}} \tilde{M}_{\vec{n}-\vec{m}}(z)]^{-1}. \tag{21}$$

Substituting Eq. (19) into the GME, Eq. (16), we find

$$\left(z + \tilde{\chi}(z)\frac{z}{1-\tilde{\chi}(z)}\right)\langle\tilde{P}_{\vec{n}}(z)\rangle = \delta_{\vec{n},\vec{0}} + \sum_{\vec{m}\neq\vec{n}} \frac{z}{1-\tilde{\chi}(z)}\tilde{\psi}_{\vec{n}-\vec{m}}(z)\langle\tilde{P}_{\vec{m}}(z)\rangle, \tag{22}$$

which is rewritten as

$$\langle\tilde{P}_{\vec{n}}(z)\rangle = \delta_{\vec{n},\vec{0}}\, z^{-1}[1-\tilde{\chi}(z)] + \sum_{m\neq n} \tilde{\psi}_{\vec{n}-\vec{m}}(z)\langle\tilde{P}_{\vec{m}}(z)\rangle. \tag{23}$$

Inverting the Laplace transform

$$\langle P_{\vec{n}}(t)\rangle = \delta_{\vec{n},\vec{0}}\,\Phi(t) + \sum_{\vec{m}\neq\vec{n}} \int_0^t d\tau\, \psi_{\vec{n}-\vec{m}}(\tau)\langle P_{\vec{m}}(t-\tau)\rangle, \tag{24}$$

where $\Phi(t)$ is the inverse Laplace transform of $[1-\chi(z)]/z$:

$$\Phi(t) = 1 - \int_0^t \chi(\tau)\, d\tau = 1 - \int_0^t d\tau \sum_{\vec{m}\neq\vec{n}} \psi_{\vec{m}-\vec{n}}(\tau). \tag{25}$$

These equations, (24) and (25), can be identified as the generalized CTRW of Scher and Lax,[4] where $\psi_{\vec{n}-\vec{m}}(\tau)$ is the probability of the particle jumping from a distance $R_{\vec{n}} - R_{\vec{m}}$ after a waiting time τ. $\Phi(t)$ is therefore the probability of remaining on the initial site for time t. Note that, by configuration averaging, the translational invariance of the lattice has been reintroduced into the exact equations of motion in spite of the fact that, for any configuration, there is no translational invariance.

We have derived the CTRW equation from the exact transport equation, Eq. (16), and so shown that it is also exact. However, in order to proceed, the *exact* form for $\psi_{\vec{n}-\vec{m}}(\tau)$ has to be formed, which contains all the microscopic details of the system. Alternatively, an exact form for $\tilde{M}_{\vec{n}-\vec{m}}(z)$ must be found. Note that these are related by the *exact* relation, Eq. (19), namely,

$$\tilde{\psi}_{\vec{n}-\vec{m}}(z) = \tilde{M}_{\vec{n}-\vec{m}}(z)\tilde{\Phi}(z) \tag{26}$$

or

$$\psi_{\vec{n}-\vec{m}}(t) = \int_0^t d\tau\, M_{\vec{n}-\vec{m}}(t-\tau)\Phi(\tau). \tag{27}$$

These exact relations provide an extension of conclusions by existing theories[3b,11] that the CTRW is equivalent to modified pair approximations in solving the ME, Eq. (1). Making use of the translational symmetry of the configurational-

ly averaged system, Eq. (18), we are now able to directly relate the CTRW to a $\vec{k}$ representation of SE in the GME. Define

$$\tilde{M}(\vec{k},z) = \sum_{\vec{m}\neq\vec{n}} \exp[i\vec{k}\cdot(\vec{m}-\vec{n})]\tilde{M}_{\vec{m}-\vec{n}}(z), \quad (28a)$$

$$\tilde{M}(\vec{k}=0,z) = \sum_{\vec{m}\neq\vec{n}} \tilde{M}_{\vec{n}-\vec{m}}(z) = -M_{\vec{n},\vec{n}}(z). \quad (28b)$$

The GME, Eq. (16), can be rewritten as

$$\langle\tilde{P}_{\vec{k}}(z) = [z+\tilde{M}(\vec{k}=0,z)-\tilde{M}(\vec{k},z)]^{-1} \quad (29)$$

which is similar to the form derived in Ref. 2. Note, however, that any function of z [say, $H(z)$] can be added to $\tilde{M}(\vec{k},z)$, for *all* $\vec{k}$, and the form of Eq. (29) remains invariant. In our case, we have the added condition that $\sum_{\vec{k}}\tilde{M}(\vec{k},z)=0$, from Eq. (28a); this must be satisfied in order to make the connection to the CTRW. A variety of forms for $\Sigma(\vec{k},z)\equiv\tilde{M}(\vec{k},z)+H(z)$ can be derived, depending on the method of summing the diagrammatic series. Care must be taken in identifying the correct form to insert in the CTRW.

The above arguments establish for the first time the correctness of the CTRW and provide a deeper insight into the nature of the hopping-time distribution function $\psi_{\vec{m}-\vec{n}}(t)$ via its exact relations with the self-energy, $\tilde{M}_{\vec{n}-\vec{m}}(z)$. In forthcoming publications, we will derive the hopping-time distribution function from an *exact* one-dimensional self-energy,[20] and adopt a modified undecoupled pair approximation[2] to study the short- and long-time behavior of the mean square displacement of an excitation in an impure crystal.[21]

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