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Diffusion in a Lattice of Randomly Placed Sites and Application to ac Conductivity

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The transition probability for a carrier hopping between randomly placed sites is determined for a system in thermodynamic equilibrium. The effect of the first waiting time is included and the result is shown to be consistent with the theory of statistical thermodynamics. Furthermore, a comparison is made with the master equation approach, which is shown to be exact when the waiting times are exponentially distributed. The application to ac conductivity is discussed.

KEY WORDS: Random walk; diffusion; master equation.

1. INTRODUCTION

Similar expressions for the ac conductivity for classical hopping conduction have been obtained by Scher and Lax[1] and by Butcher.[2] In both cases a Green's function is required. Attempts to find this have been made by these authors, the first through probabilistic methods using the Montroll–Weiss[3] continuous-time random walk formalism as an approximation to a hopping over a random collection of sites, and the second through the establishment of rate equations. In the present study a rather general probabilistic approach will be undertaken to find a Green's function for a simple mechanism of transport: This will then be compared with the master equation (rate equation) approach.

The model is one in which the carriers move independently, performing jumps (which are virtually instantaneous) between highly localized sites corresponding to potential wells. The positions and the depths of the wells can in principle be described by a joint probability density. It is assumed that

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a carrier is trapped at a site before hopping by virtue of the thermal agitation of the lattice and that the waiting intervals between hops in a particular lattice are statistically independent random variables. Furthermore, the individual jump vectors are independent of the associated waiting times but consecutive vectors may be dependent.

In applications to ac conductivity the Green's function is inserted into the appropriate equation for the conductivity and an average performed over the ensemble of all possible site locations and energies. This turns out to be rather difficult in practice. The problem is circumvented by Scher and Lax by using an approximation. Unfortunately, it is not clear that the particular approximation employed is justified since an apparent improvement in the formalism reduces their result to a triviality.[4] This occurs when account is taken of the "first waiting time density."

Although the concept of a Green's function appears straightforward, there are a number of possible probabilistic interpretations. Thus we may have, for example,

$$G_{ij}(t) = P\{\text{carrier is observed at site } j \text{ at time } t \text{ given it was at site } i \text{ at } t = 0\} \tag{1}$$

$$G_{ij}(t) = P\{\text{carrier is observed at site } j \text{ at time } t \text{ given it hopped into site } i \text{ at } t = 0\} \tag{2}$$

$$G_{ij}(t) = P\{\text{carrier is observed at site } j \text{ at time } t \textit{ and} \text{ at site } i \text{ at } t = 0\} \tag{3}$$

where definition (3) is actually a joint probability. In applications to ac conductivity of a lattice with carriers in thermodynamic equilibrium the time $t = 0$ is presumably arbitrary. Nevertheless, Scher and Lax employ the definition (2), which particularizes the starting times to those at which a hop occurs. Although it would intuitively be expected that this should not lead to significant error in the Green's function at sufficiently long times and therefore to the ac conductivity at low frequency, this is not necessarily true.[4] It has been shown that the use of definitions (1) or (3) can lead to quite different behavior: the Montroll–Weiss formalism has recently been modified to include the effect which is represented by the inclusion of the first waiting time probability density.[5]

A rate equation approach ostensibly avoids both difficulties since the probability distributions for any hopping time interval do not appear explicitly. The method is equivalent to the use of a master equation in stochastic theory. However, the master equation can only be valid under certain circumstances and it will be shown that it holds when the waiting

times are exponentially distributed. Fortunately, this is the most likely assumption.[2]

2. DEFINITIONS AND FIRST WAITING TIME DISTRIBUTION

We consider a fixed number of sites N and assume that the probability density for a single hop in a particular site configuration can be determined and cast into the form of a matrix $\lambda_{ij}(t)$. The quantity $\lambda_{ij}(t)\,dt$ is then the conditional probability that in a single hop the carrier jumps onto site j in the time interval $(t, t + dt)$ given that at $t = 0$ it jumped onto site i. If sooner or later the carrier must jump from any site,

$$\sum_j \Lambda_{ij}(\infty) = 1, \qquad \text{all } i \tag{4}$$

where $\Lambda_{ij}(t)$ is the probability distribution corresponding to $\lambda_{ij}(t)$: Λ_{ij} is a stochastic matrix by virtue of Eq. (4). At this stage $\Lambda_{ij}(t)$ is quite general apart from condition (4) and cannot be diagonalized.

From earlier considerations $\lambda_{ij}(t)$ can be decomposed into a product:

$$\lambda_{ij}(t) = \psi_i(t)\lambda_{ij} \tag{5}$$

where $\psi_i(t)$ is the probability density for the first hop occurring out of site i in time interval $(t, t + dt)$, given that the carrier hopped into site i at time $t = 0$. The λ_{ij} are the probabilities that, given a hop from site i, the carrier goes directly to site j. The matrix elements λ_{ij} form a stochastic matrix and since the hops are instantaneous, it is useful to put $\lambda_{ii} = 0$. The energy depth E_i of a well can be related to $\psi_i(t)$ using simple models: If μ_i is the mean time between hops into and out of well i, we may expect (to be verified later)

$$\mu_i = \nu^{-1} \exp(E_i/kT) \tag{6}$$

where ν is of the order of the Einstein frequency of the lattice, k is Boltzmann's constant, and T is the temperature. A model involving a large number of Bernoulli trials leads to an exponential density (see footnote 2)

$$\psi_i(t) = \mu_i^{-1} \exp(-t/\mu_i) \tag{7}$$

It will be convenient to work with the Laplace transform of $\psi_i(t)$ (not necessarily exponential), namely $\bar{\psi}_i(s)$ (it can be shown that this is completely monotone), which can be expanded for a small s and if μ_i is finite:

$$\psi_i(s) = 1 - s\mu_i + \cdots \tag{8}$$

We begin by finding the probability of $u_{kn}(t)\,dt$ that the carrier makes a hop to site n in interval $(t, t + dt)$, given that it jumped into site k at $t = 0$.

[2] An exponential density results for simple models of radioactive decay. A particle oscillates in a potential well and each time it reaches the wall it has a very small probability of escape p. As $p \to 0$ and the rate of "trials" increases, the probability that the particle does not escape $(1 - p)^n$ approaches $e^{-\alpha t}$.

This event could be the result of a single hop or many hops over different paths. Summing the probabilities for all these mutually exclusive outcomes yields

$$u_{kn}(t) = \delta_{kn}\delta(t) = \lambda_{kn}(t) + \sum_i \lambda_{ki}(t) * \lambda_{in}(t) + \cdots \tag{9}$$

where δ_{kn} represents the Kronecker δ, $\delta(t)$ is the Dirac δ-function, and the symbol $*$ represents a convolution in time. Taking the Laplace transform with respect to time and expressing the result in matrix form, we obtain

$$\bar{\hat{u}}(s) = \hat{1} + \bar{\hat{\psi}}\hat{\lambda} + (\bar{\hat{\psi}}\hat{\lambda})^2 + \cdots \tag{10}$$

where

$$\bar{\hat{\psi}}(s) = \bar{\psi}_i(s)\delta_{ij} \tag{11}$$

Provided $(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})$ is not singular, we may write

$$\bar{\hat{u}}(s) = (\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1} \tag{12}$$

We shall require $\lim_{t\to\infty} \hat{u}(t)$ and can obtain this by employing a limit theorem:

$$\lim_{t\to\infty} \hat{u}(t) = \lim_{s\to 0} s(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1} \tag{13}$$

because $\bar{\hat{\psi}}(0) = \hat{1}$ and $\hat{\lambda}$ is a stochastic matrix obeying a condition like (4), the sums of the individual rows of $(\hat{1} - \bar{\hat{\psi}}(0)\hat{\lambda})$ are zero, so that its determinant is zero. This leads to some complications in the evaluation of $\hat{u}(\infty)$. In principle the pole that will arise at $s = 0$ need not be simple. However, the λ_{ij} are actually random variables, so that we shall assume that the probability of a multiple-order pole occurring in a lattice in which sooner or later all sites will be occupied is zero. The latter restriction is necessary because if we have, for example, two quite separate lattices, the probability matrix $\hat{\lambda}$ can be partitioned into two matrices along the diagonal and clearly when $s = 0$ the determinant of $\hat{1} - \bar{\hat{\psi}}\hat{\lambda}$ will possess a second-order zero.

Concentrating on lattices that may not be subdivided in this way, let

$$(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1} = \bar{\hat{\Gamma}}(s)/\Delta(s) \tag{14}$$

where $\hat{\Gamma}^T$ (the transpose of $\hat{\Gamma}$) are the cofactors of $(\hat{1} - \hat{\psi}\hat{\lambda})$ and $\Delta(s)$ is the determinant. Evidently

$$\hat{u}(\infty) = \hat{\Gamma}(0)/\Delta'(0) \tag{15}$$

The derivation of cofactors $\hat{\Gamma}^T$ is found in the appendix, where it is shown that condition (4) leads to the surprising result

$$\Gamma_{ij}(0) = \begin{bmatrix} \alpha_1 & \alpha_2 & \alpha_3 & \cdots \\ \alpha_1 & \alpha_2 & \alpha_3 & \cdots \\ \alpha_1 & \alpha_2 & \alpha_3 & \cdots \end{bmatrix} \tag{16}$$

The elements α_i depend only on $\hat{\lambda}$.

The differentiation of the determinant can be performed by rows to yield a sum of determinants:

$$\Delta'(0) = \begin{vmatrix} 0 & \mu_1\lambda_{12} & \mu_1\lambda_{13} & \cdots \\ -\lambda_{21} & 1 & -\lambda_{23} & \cdots \end{vmatrix} + \cdots \tag{17}$$

$$= \mu_1\Gamma_{11}(0) + \mu_2\Gamma_{22}(0) + \mu_3\Gamma_{33}(0) + \cdots \tag{18}$$

From Eqs. (15), (16), and (18) we have

$$u_{kn}(\infty) = \alpha_n\left(\sum_i \alpha_i\mu_i\right)^{-1} = u_n \quad \text{(say)} \tag{19}$$

As expected, after a long time the probability of observing the carrier jumping into site n in a time interval dt is independent of its initial position.

We do not wish to particularize the starting time for the Green's function and so use definition (3), which is actually a joint distribution (intersection): That of definition (1) will be obtained from it later. For this it is necessary to introduce $H_{mn}(\tau, \zeta)$, which is defined to be the probability that the carrier jumps in a single hop to site n in a time less than ζ *and* it was on site m at time τ, where $\zeta = 0$, given that the carrier was put into the lattice at $\tau = 0$. This quantity takes care of the difference in definitions and is the first waiting time distribution. To represent a system in thermodynamic equilibrium we are going to let $\tau \to \infty$. If the carrier hops into site m at some time x, measured from $\tau = 0$, the probability that we observe a single hop from site m to site n in the time interval $(\tau + \zeta - x, \tau - x)$ is just equal to

$$\Lambda_{mn}(\tau + \zeta - x) - \Lambda_{mn}(\tau - x) \tag{20}$$

Thus, using Eq. (19),

$$H_{mn} = \int_0^\tau u_m(x)\,dx\,[\Lambda_{mn}(\tau + \zeta - x) - \Lambda_{mn}(\tau - x)] \tag{21}$$

As $\tau \to \infty$, we can treat $u_m(x)$ as a constant given by Eq. (19) and, by changing the variables, show that in the limit (see Feller[6]).[3]

$$\hat{H}(\zeta) = \hat{\alpha}\left(\sum_i \alpha_i\mu_i\right)^{-1} \int_0^\zeta [\hat{\Lambda}(\infty) - \hat{\Lambda}(\zeta)]\,d\zeta \tag{22}$$

where $\alpha_{ij} = \alpha_i\delta_{ij}$. Taking Laplace transforms gives for the corresponding density

$$\bar{\hat{h}}(s) = \left(s\sum_i \alpha_i\mu_i\right)^{-1}\hat{\alpha}(\hat{\lambda} - \bar{\hat{\psi}}\hat{\lambda}) \tag{23}$$

[3] Care must be exercised to ensure convergence of the integrals that appear in the transformation of variables.

We shall also need the probability that, if the particle is located at site n at $\zeta = 0$, it does not hop in a time less than ζ. This is given by

$$P_i\{T > \zeta\} = \int_0^\tau u_n(x)\,dx \left[1 - \sum_j \Lambda_{nj}(\tau - x + \zeta)\right] \tag{24}$$

Letting $y = \tau + \zeta - x$, we have

$$P_i\{T > \zeta\} = \int_\zeta^{\tau+\zeta} u_n(\tau + \zeta - y)\left[1 - \sum_j \Lambda_{nj}(y)\right] dy \tag{25}$$

and taking the limit $\tau \to \infty$ as before

$$P\{T > \zeta\} = \hat{\alpha}\left(\sum_i \alpha_i\mu_i\right)^{-1} \int_\zeta^\infty \sum_j [\Lambda_{nj}(\infty) - \Lambda_{nj}(y)]\,dy \tag{26}$$

An integration by parts shows that

$$\int_0^\infty [\Lambda_{nj}(\infty) - \Lambda_{nj}(y)]\,dy = \int_0^\infty y\lambda_{nj}(y)\,dy = \mu_n\lambda_{nj} \tag{27}$$

so that Eq. (26) can be expressed as

$$P\{T > \zeta\} = \left(\sum_i \alpha_i\mu_i\right)^{-1}\alpha_n\left\{\mu_n - \int_0^\zeta \sum_j [\Lambda_{nj}(\infty) - \Lambda_{nj}(y)]\,dy\right\} \tag{28}$$

and taking the Laplace transform, we have

$$\bar{P}_n(s) = \left(s^2 \sum_i \alpha_i\mu_i\right)^{-1}\alpha_n[s\mu_n - 1 + \bar{\psi}_n(s)] \tag{29}$$

or in matrix form (it is diagonal)

$$\bar{\hat{P}} = \left(s^2 \sum_i \alpha_i\mu_i\right)^{-1}\hat{\alpha}(s\hat{\mu} - \hat{1} + \bar{\hat{\psi}}) \tag{30}$$

where $\hat{\mu} = \mu_i\delta_{ij}$.

3. OCCUPATION PROBABILITY IN THERMODYNAMIC EQUILIBRIUM

The first waiting time probability distribution is defined essentially by Eq. (22): It is interpreted as the probability that a particle jumps from site m to site n in a single hop for the first time in interval $[0, \zeta]$ *and* that it was located at site m at $t = 0$. The time $t = 0$ is now arbitrary and should correspond to the time we first observe the particles in a system in thermodynamic equilibrium. Since $H_{mn}(\zeta)$ is a joint distribution, we can easily find the occupation probability Q_m, which is just a marginal distribution, i.e.,

$$Q_m = \sum_n H_{mn}(\infty) \tag{31}$$

where $H_{mn}(\infty)$ is the probability that the particle leaves site m to go to site n in a single hop. Thus since $\hat{H}(\infty) = \lim_{s\to 0} \hat{h}(s)$, we have from Eqs. (23) and (8)

$$Q_m = \sum_n \left[\left(\sum_i \alpha_i \mu_i \right)^{-1} \alpha_m \mu_m \lambda_{mn} \right] \tag{32}$$

This is simplified by noting that $\hat{\lambda}$ is a stochastic matrix, so that

$$Q_m = \left(\sum_i \alpha_i \mu_i \right)^{-1} \alpha_m \mu_m \tag{33}$$

From the theory of statistical thermodynamics we expect that Q_m should only be a function of the site energy E_m (i.e., μ_m), whereas α_m contains information about all other sites. The choice of $\hat{\lambda}$ is rather general and can include the application of fields in a physical system. If we reject this possibility, it seems reasonable that the α_j should all be equal, so that the standard result is obtained. This would imply that $\bar{\Gamma}(0)$ is symmetric, so that $\hat{\lambda}$ is also symmetric, i.e., doubly stochastic. The actual value of α is immaterial since it cancels out in Eq. (33), for example, though some tedious calculations involving $\hat{\lambda}$ show that it is unity. With $\alpha_m = 1$ and Eq. (6) we now have

$$Q_m = [\exp(E_m/kT)] \Big/ \sum_i \exp(E_i/kT) \tag{34}$$

which is the usual result from statistical thermodynamics.

It is important to note that, conversely, the above considerations, together with the standard result, lead directly to a relation between μ_i and E_i of the form of Eq. (6), and that this conclusion does not depend on a choice of probability density $\psi_i(t)$.

If we do not insist on the independence of the time to make a hop and the outcome of the hop, and instead of Eqs. (5) and (8) write

$$\lambda_{ij}(s) = \lambda_{ij}(1 - \eta_{ij} s + \cdots) \tag{35}$$

then an identical series of steps yields

$$Q_m = \left(\sum_{ij} \alpha_i \eta_{ij} \lambda_{ij} \right)^{-1} \alpha_m \sum_n \eta_{mn} \lambda_{mn} \tag{36}$$

Thus with α_i again constant and λ_{mn} symmetric the equivalent to Eq. (6) is

$$\sum_n \eta_{mn} \lambda_{mn} \propto \exp(E_m/kT) \tag{37}$$

The lhs is just the mean time for a hop (randomized over all outcomes from site m).

4. TRANSITION PROBABILITY

The joint transition probability can now be determined by adding the probabilities associated with the mutually exclusive outcomes in which the carrier arrives at site n in a time less than t and does not jump out of this site in the remaining interval *and* was on site m at $t = 0$: For $m \neq n$

$$G_{mn}(t) = H_{mn}(t) + \sum_j H_{mj}(t) * \Lambda_{jn}(t) + \sum_{jk} H_{mj}(t) * \Lambda_{jk}(t) * \Lambda_{kn}(t) + \cdots$$

$$- \left[H_{mn}(t) + \sum_j H_{mj}(t) * \Lambda_{jn}(t) + \cdots \right] * \sum_r \Lambda_{nr}(t) \tag{38}$$

where the symbol $*$ now indicates a convolution of distributions in the sense of Feller.[6] Taking the Laplace transform yields

$$\bar{\hat{G}}(s) = \bar{\hat{h}}(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1}(\hat{1} - \bar{\hat{\psi}})/s, \qquad m \neq n \tag{39}$$

Equations (38) and (39) take care of jumps from site n back to itself but we must include the event that a jump from site n does not occur at all. Therefore we must add on the rhs of Eq. (30). Inserting the expression for $\bar{\hat{h}}$ from Eq. (23) gives

$$\bar{\hat{G}}(s) = \left(s^2 \sum_i \mu_i \right)^{-1} [(\hat{1} - \bar{\hat{\psi}}\hat{\lambda}(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1}(\hat{1} - \bar{\hat{\psi}}) + s\hat{\mu} - \hat{1} + \bar{\hat{\psi}}] \tag{40}$$

which may be simplified:

$$\bar{\hat{G}}(s) = \left(s^2 \sum_i \mu_i \right)^{-1} [s\hat{\mu} - (\hat{1} - \hat{\lambda})(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1}(\hat{1} - \bar{\hat{\psi}})] \tag{41}$$

At this point we can determine the Green's function of definition (1). This is a conditioned probability distribution and is equal to that in Eq. (41) divided by Q, i.e.,

$$G^{(c)}_{mn} = G_{mn}/Q_m$$

Thus

$$\bar{G}^{(c)}_{mn} = (s^2\hat{\mu})^{-1}[s\hat{\mu} - (\hat{1} - \hat{\lambda})(\hat{1} - \bar{\hat{\psi}}\hat{\lambda})^{-1}(\hat{1} - \bar{\hat{\psi}})] \tag{42}$$

It can be verified that the Green's function in Eq. (41) is symmetric (expand the reciprocal matrix in a power series), while that of Eq. (42) is not.

5. COMPARISON WITH MASTER EQUATION

The master equation (or Kolmogorov's forward equation) for the process can be written in the form

$$\partial G^{(m)}_{ik}/\partial t = \sum_j G^{(m)}_{ij} R_{jk} - \sum_l G^{(m)}_{ik} R_{kl} + \delta_{ik}\delta(t) \tag{43}$$

where $G_{ik}^{(m)}$ is a Green's function according to definition (1) and the R_{jk} are the rates of hopping from site j to site k. The first term on the rhs represents the rate of hopping into site k from all other sites and the second term is the net rate of hopping from site k.

Comparison of the master equation approach with the probabilistic method has been made for simple random walks by Bedeaux *et al.*[7] In their case the two methods are equivalent if the waiting time distributions are all exponentially distributed with identical means. Here the discussion will be generalized.

We assume now that the $\psi_i(t)$ correspond to exponential distributions so that

$$\bar{\psi}_i(s) = (1 + s\mu_i)^{-1} \tag{44}$$

If this is inserted into Eq. (42), it is readily shown that

$$\bar{G}_{mn}^{(c)} = [s\hat{1} - \hat{\mu}^{-1}(\hat{\lambda} - \hat{1})]^{-1} \tag{45}$$

On the other hand, we may take the Laplace transform of Eq. (43) and the result is

$$\bar{\hat{G}}^{(m)} = (s\hat{1} - \hat{R} + \hat{T})^{-1} \tag{46}$$

where

$$T_{ij} = \delta_{ij} \sum_1 R_{j1}$$

Consequently, provided we identify the rates

$$\hat{R} = \hat{\mu}^{-1}\hat{\lambda} \tag{47}$$

the two treatments give the same result. When $\hat{\mu}$ is a scalar, the result is identical to that of Bedeaux *et al.* It is important to note that $\hat{R}$ is not symmetric except when all the μ_i are equal. Thus the identification satisfies the principle of detailed balance, since we have

$$R_{mn}/R_{nm} = \exp[-(E_m - E_n)]/kT \tag{48}$$

and supports the conclusion that λ_{ij} should be symmetric for a system in thermodynamic equilibrium.

The Green's function of Eq. (41) becomes now

$$\bar{\hat{G}}(s) = \hat{\mu}(s\hat{\mu} - \hat{\lambda} + \hat{1})^{-1}\hat{\mu} \Big/ \sum_i \mu_i \tag{49}$$

(This is obviously symmetric.) It is worthwhile remarking that one of the reasons for the simplicity of Eq. (49) is that the first waiting time density given by Eq. (23) with $\hat{\alpha} = \hat{1}$ is now given by

$$\bar{h}(s) = \left(\hat{\mu} \Big/ \sum \mu_i\right)\bar{\hat{\psi}}\hat{\lambda} = \hat{Q}\bar{\hat{\psi}}\hat{\lambda} \tag{50}$$

In effect the conditional density corresponding to a hop for the first time to site j in time interval $[t + dt]$ *given* that the particle was on site i at $t = 0$ is the same as single hop transition probability $\hat{\bar{\psi}}\hat{\lambda}$, which particularizes the starting time of the waiting period. The exponential densities given by Eq. (44) are unique in this respect.

6. ac CONDUCTIVITY

To establish the conductivity, the Scher and Lax formula can be employed using the Green's function of definition (3):

$$\sigma(\omega) = (-\omega^2 ne^2/2kT) \sum_{mn} (x_m - x_n)^2 \bar{G}_{mn}(i\omega) \tag{51}$$

where n is the carrier density, e is the carrier charge, and x_i is the coordinate of the ith site for a direction parallel to the electric field which is applied to make a measurement. If the interhop intervals are exponentially distributed, the rate equation is valid and the expression of Eq. (49) can be employed. This is essentially the route taken by Butcher. It is evident that the ensemble averaging over the μ_i and the x_i is not at all trivial and even the low-frequency behavior is difficult to ascertain. An additional complication, which does not appear in other work, involves the fact that the rates are not statistically independent because of condition (4) and the symmetry of $\hat{\lambda}$. In principle this will have an effect even if the energy depths of the wells are independent random variables: Hopping only to nearest neighbors will be the most seriously affected situation.

Scher and Lax use a technique in which they effectively replace the Green's function in Eq. (41) by one appropriate to a Montroll–Weiss continuous-time random walk, i.e.,

$$\bar{G}_{mn}(i\omega) \rightarrow Q_m \bar{G}'_{mn}(i\omega)$$

where $\bar{G}'_{mn}(i\omega)$ is the Green's function according to definition (2), which particularizes the starting time. As long as the hopping time densities are exponential, given by Eq. (44), this is unimportant. However in the MW walk all individual hopping times are independent and are identically distributed and they now insert into $\bar{G}'_{mn}(i\omega)$ a randomized density which is not exponential. Of course it can be argued that definition (1) should really be involved in the replacement of $\bar{G}_{mn}(i\omega)$, but if this is done and the randomized density inserted, the result is trivial and gives a conductivity which is constant. Another argument involves the use of the master equation. Again the argument finally must involve the approximation that all the $\psi_i(t)$ may be replaced by nonexponential $\psi(t)$ and that the hopping times are independent. Naturally the effect of the generalized first waiting time is not included in the formulation of the master equation since the basic probability distributions are exponential. Therefore the validity of this type of approach is uncertain.

APPENDIX

The cofactors of the matrix $(\hat{1} - \hat{\lambda})$ can be found by picking an element of the matrix: Let the cofactor be Γ_{ji}. The jth row and ith column are now deleted and it is necessary to evaluate the determinant that remains. This can be considered as a row of column vectors a_i, where the subscript refers to the column, i.e.,

$$\Gamma_{ji} = (-1)^{i+j} \det(\mathbf{a}_1; \cdots; \mathbf{a}_{i-1}; \mathbf{a}_{i+1}; \cdots)$$

Comparing this with $\Gamma_{j,i+1}$, we obtain

$$\Gamma_{j,i+1} = (-1)^{i+j+1} \det(\mathbf{a}_1; \cdots; \mathbf{a}_{i-1}; \mathbf{a}_i; \mathbf{a}_{i+2}; \cdots)$$

However, because the row sums of $\hat{1} - \hat{\lambda}$ are zero according to Eq. (4), we have

$$\sum_k \mathbf{a}_k = 0$$

so that substituting for $\mathbf{a}_i$ in $\Gamma_{j,i+1}$ yields

$$\Gamma_{j,i+1} = (-1)^{i+j+1} \det(\mathbf{a}_i; \cdots; \mathbf{a}_{i-1}; -\mathbf{a}_1 - \mathbf{a}_2 \cdots - \mathbf{a}_{i-1} - \mathbf{a}_{i+1}; \cdots; \mathbf{a}_{i+2}; \cdots)$$

Thus $\Gamma_{j,i+1}$ is a sum of determinants but all except one of them have two similar columns and are equal to zero. We have

$$\Gamma_{j,i+1} = (-1)^{i+j+1} \det(\mathbf{a}_i; \cdots; -\mathbf{a}_{i+1}; \mathbf{a}_{i+2}; \cdots) = \Gamma_{ji}$$

Therefore the elements of each row of the cofactor matrix are the same and it can be expressed as

$$\Gamma_{ji} = \begin{bmatrix} \alpha_1 & \alpha_1 & \alpha_1 & \cdots \\ \alpha_2 & \alpha_2 & \alpha_2 & \cdots \\ \alpha_3 & \alpha_3 & \alpha_3 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{bmatrix}$$

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