Hopping transport on site-disordered d-dimensional lattices

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We consider here the hopping of an electron among a band of localized electronic states on a d-dimensional lattice. The hopping rates are assumed to be stochastic variables determined by some probability distribution. We restrict our attention to nearest-neighbor transport in the limit in which the fluctuations in the hopping rates are large. In this limit we construct an exact expansion for the frequency-dependent diffusion coefficient $D(\varepsilon)$ that is applicable to a wide range of transport phenomena ($d=1$ conductors, trapping phenomena, molecularly based electronic devices, etc.) in any spatial dimension. For the case of hopping transport with $d=1$, our method confirms earlier results that strong fluctuations in the hopping rates give rise to a non-Markovian $\varepsilon^{1/2}$ correction to normal diffusion. In two dimensions, we establish explicitly the existence of a non-Markovian logarithmic correction $\varepsilon\ln\varepsilon$ to $D(\varepsilon)$. The formalism is then extended to d dimensions and the frequency corrections are discussed. For $d=3$, two frequency corrections must be retained. One is linear in ε and the other proportional to $\varepsilon^{3/2}$. It is shown that only the $\varepsilon^{3/2}$ correction contributes to the long-time tail $t^{-3/2}$ in the time-dependent diffusion coefficient $D(t)$. From these results we show that the long-time tail in the velocity autocorrelation function which is a consequence of the strong fluctuations in the hopping rates is of the form $t^{-(1+d/2)}$. Comparison is made with earlier results.

I. INTRODUCTION

Charge flow in one-dimensional conductors is obtained as a result of electron hopping transport (impurity conduction) among a band of localized electronic states[1] This view of transport in disordered one-dimensional systems is warranted because it is well know that the eigenstates of such systems are localized.[2] Hopping transport among a band of localized states is an inherently incoherent process.[3] Consequently, the dynamics of the transport are governed by a master equation (or continuous-time random-walk equation)

$$\frac{d\mathbf{P}}{dt}=\hat{W}\mathbf{P} \tag{1.1}$$

involving the site-occupation probabilities $P_i(t)$ and the transfer rates ω, the rate of transfer between two sites. The vector $\mathbf{P}(t)=(P_1,P_2,\ldots,P_N)$ and $\hat{W}$ is a random matrix determined by the nature of the transport process.

In a disordered system the transfer rates (or waiting times) vary from site to site and should be treated as independent random (stochastic) variables[1] that are determined by some probability distribution function $\rho(\omega)$. If the fluctuations

$$\Delta_n=\langle(\omega-\langle\omega\rangle)^n\rangle \tag{1.2}$$

in the transfer rates are large, standard weak fluctuation expansions of the transport properties, such as the diffusion coefficient $D(t)$, in terms of Δ_n break down. In (1.2) $\langle\;\rangle$ signifies an average over the distribution of hopping rates. The preferred treatment should the weak fluctuation limit fail is an expansion for $D(t)$ in the inverse moments of the fluctuations

$$z_n=\left\langle\left[\frac{1}{\omega}-\left\langle\frac{1}{\omega}\right\rangle\right]^n\right\rangle . \tag{1.3}$$

For such an expansion to exist, it is necessary and sufficient that $\rho(\omega)$ be nonsingular in the limit that $\omega\to 0$. Should $\rho(\omega)$ be singular in this limit, trapping effects will occur and the mean-square displacement

$$\langle r^2(t)\rangle\sim t^{1/(1+\beta)} \tag{1.4}$$

will be anomalous, that is $\beta>0$. Equivalently, $D(t)$ will vanish at long times. The vanishing of $D(t)$ for certain-hopping models in $d=1$ is well known[4(a)] but only recently established in $d=2$ for random hopping (RH) among impurity sites interacting with an Ohmic dissipative bath.[4(b)]

In this paper we restrict ourselves to random trapping (RT) models for which z_n exists. We focus on the site-disorder problem in which the randomness in the transition rates arises from the distribution of potential wells which can act as trapping sites for the particle. The literature abounds with a plethora of papers which develop expansions for $D(t)$ in terms of z_n in one-dimension.[5–8] The techniques used range from renormalization group calculations[5] on one-dimensional lattices to ε expansions effective medium calculations[8] to arduous exact calculations.[6] Though the techniques used are varied, all of these calculations indicate that fluctuations in the transfer rates give rise to non-Markovian terms in the diffusion coefficient of one-dimensional systems. Hence, only for the ordered system is regular diffusion observed.

We develop in this paper an exact simple expansion for the ac conductivity of one-dimensional conductors in the limit of large fluctuations in the hopping rates. The primary merit of our approach is its simplicity and applicability to a wide range of transport phenomena such as (1) nearest-neighbor hopping on d-dimensional lattices,[1,5–8] (2) charge flow in photosynthetic systems,[9] (3) electron transport in finite-sized systems, for example, proteins[10] and molecularly based electronic devices.[11]

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This paper is organized as follows. In Sec. II we develop the strong fluctuation expansion (SFE) for the transport properties. Our approach is based on the realization that for nearest-neighbor hopping on one-dimensional lattices for a site-disorder problem the generating function

$$F(q,t)=\sum_n e^{iqn}\omega_n P_n(t) \tag{1.5}$$

is directly proportional in the $q\to 0$ limit to $\langle r^2(t)\rangle$. Hence, (1.5) facilitates a direct SFE for $D(t)$. All[1,5–8] previous treatments have used as the generating function for the transport properties

$$\tilde{F}(q,t)=\sum_n e^{iqn}P_n(t)\ . \tag{1.6}$$

The diffusion coefficient is then proportional to the second derivative of $\tilde{F}$ with respect to q. Derivations of the strong fluctuation limit of $D(t)$ from (1.6) encounter singularity problems with the transfer matrix defined in (1.1). As we will see no such problems beset our calculation. In Sec. III we extend our result to $d=2$ and establish the existence of a non-Markovian t^{-1} term in $D(t)$. We close with a discussion of the three-dimensional case and a generalization of the basic approach to d-dimensions.

II. ONE-DIMENSIONAL TRANSPORT

We consider here a $d=1$ lattice of impurity sites and nearest-neighbor hopping between sites. As a further simplification, we assume that for any two sites the transfer rates are symmetric,

$$\omega_{n\to n+1}=\omega_{n\to n-1}\ . \tag{2.1}$$

This is the symmetry condition for a distribution of symmetric wells (traps). The wells, by virtue of the distribution of the hopping rates, have different depths. Hence, the model we consider here corresponds to transport in a site-disordered rather than a bond-disordered system. The master equation for the site-occupation probabilities $P_n(t)$ is

$$P_n(t)=\omega_{n-1}P_{n-1}+\omega_{n+1}P_{n+1}-2\omega_n P_n\ ,\quad -\infty\le n\le\infty \tag{2.2}$$

where ω_n is the rate of transfer from the nth to the $(n+1)$th site. Let us define the Laplace transform of the occupation probabilities as

$$f_n(\varepsilon)=\int_0^\infty e^{-\varepsilon t}P_n(t)dt\ . \tag{2.3}$$

Van Kampen[12] has shown that the mean-square displacement for Eq. (2.2) with symmetric rates

$$\langle n^2(\varepsilon)\rangle=\sum_{n=0}^{\infty}\langle n^2 f_n(\varepsilon)\rangle \tag{2.4}$$

can be written as

$$\varepsilon\langle n^2(\varepsilon)\rangle=2\sum_n\langle\omega_n f_n(\varepsilon)\rangle\ . \tag{2.5}$$

In (2.5) we have initialized $n^2(0)$ to zero. The angle brackets in (2.5) represent an ensemble average over the distribution of hopping rates. The diffusion coefficient is defined as

$$D(\varepsilon)=\frac{l^2\varepsilon^2}{2}\langle n^2(\varepsilon)\rangle=l^2\varepsilon\left\langle\sum_{n=-\infty}^{\infty}\omega_n f_n(\varepsilon)\right\rangle\ . \tag{2.6}$$

Here l is the separation between sites. We now have an exact expression for $D(\varepsilon)$ in terms of the site-occupation probabilities. To derive the strong fluctuation expansion for $D(\varepsilon)$ it is expedient to use the generating function

$$P(q,\varepsilon)=\sum_{n=-\infty}^{\infty}z^n\omega_n f_n(\varepsilon)\ , \tag{2.7}$$

where $z=e^{iq}$. It follows directly from Eqs. (2.3) and (2.7) that

$$f_n(\varepsilon)=\frac{1}{2\pi\omega_n}\int_{-\pi}^{\pi}P(q,\varepsilon)e^{-iqn}dq\ . \tag{2.8}$$

Because none of the ω_n's vanish, $f_n(\varepsilon)$ is well defined. That f_n can be written in general as (some function)$\times\omega_n^{-1}$ should be intuitively clear because in the $\varepsilon=0$ limit for a finite system, f_n is simply $c\omega_n^{-1}$ where c is a normalization factor.[8(c)] On physical grounds this proportionality simply means that the particle spends more time in the deeper wells. We can now use the generating function to obtain the central result for $D(\varepsilon)$,

$$D(\varepsilon)=l^2\varepsilon\langle P(q=0,\varepsilon)\rangle\ . \tag{2.9}$$

The utility of the generating function defined in (2.7) is twofold. First, because the f_n's are now written as (some function)$\times\omega_n^{-1}$, a SFE can be developed straightforwardly by adding and subtracting (some function)$\times\langle\omega_n^{-1}\rangle$. Second, $D(\varepsilon)$ is now related directly to the $q=0$ limit of $\langle P(q,\varepsilon)\rangle$ as opposed to the $q=0$ limit of the second derivative of $P(q,\varepsilon)$. Hence a direct SFE can be developed for $D(\varepsilon)$ once $\langle P(q,\varepsilon)\rangle$ is known. Our approach involves the formulation of an integral equation for $P(q,\varepsilon)$ which is obtained by multiplying both sides of the master equation by e^{iqn} and summing over n. The result is

$$\sum_n e^{iqn}\frac{dP_n}{dt}=-2(1-\cos q)\sum_n\omega_n P_n(t)e^{iqn} \tag{2.10}$$

or

$$-2(1-\cos q)P(q,\varepsilon)=\frac{\varepsilon}{2\pi}\sum_n\frac{e^{iqn}}{\omega_n}\int_{-\pi}^{\pi}P(q',\varepsilon)e^{-iq'n}dq'-F_0(q,0) \tag{2.11a}$$

with

$$F_0(q,0)=\sum_n e^{iqn}P_n(0) \tag{2.11b}$$

and

$$F_0(0,0)=1\ . \tag{2.11c}$$

Equation (2.11a) is a Dyson equation for the generating function $P(q,\varepsilon)$ which we now solve by iteration. We point out that because the left-hand side of (2.11a) is directly proportional to $D(\varepsilon)$, a perturbative expansion of the integral equation leads naturally to an inverse moment expansion for $D(\varepsilon)$. Perturbative expansions[5,6,13] based on standard generating functions invoke *a priori* that $D(\varepsilon=0)\propto\langle 1/W\rangle^{-1}$. On the other hand, as we will see, this new generating function defined here yields this result naturally. For the SFE we will need the quantity

$$D_0^{-1}=\left\langle \frac{1}{N}\sum_n \frac{1}{\omega_n}\right\rangle=\left\langle\frac{1}{\omega}\right\rangle , \tag{2.12}$$

where we have assumed that

$$\left\langle\frac{1}{\omega_m}\right\rangle=\left\langle\frac{1}{\omega_n}\right\rangle \text{ for all } m \text{ and } n . \tag{2.13}$$

We shall further assume[6] that fluctuations

$$\delta\left[\frac{1}{\omega_n}\right]=\frac{1}{\omega_n}-\frac{1}{D_0} \tag{2.14}$$

in the ω_n's are uncorrelated. Hence,

$$\left\langle\delta\left[\frac{1}{\omega_n}\right]\delta\left[\frac{1}{\omega_m}\right]\right\rangle=0 \tag{2.15}$$

for $m\neq n$.

If $\varepsilon D_0^{-1}P(q,\varepsilon)$ is added and subtracted from Eq. (2.11a) we obtain

$$P(q,\varepsilon)=\frac{F_0(q,0)}{s+2(1-\cos q)}-\int_{-\pi}^{\pi}K(q,q',\varepsilon)P(q',\varepsilon)dq' \tag{2.16}$$

with $s=\varepsilon/D_0$. The kernel

$$K(q,q',\varepsilon)=\varepsilon G_0(q,s)\sum_n \delta\left[\frac{1}{\omega_n}\right]e^{i(q-q')n} , \tag{2.17}$$

where

$$G_0(q,s)=\frac{1}{2\pi[s+2(1-\cos q)]} \tag{2.18}$$

contains all information regarding the fluctuations in the hopping rates. It is from this term the non-Markovian behavior arises.

We are interested in the long-time or $\varepsilon\to 0$ limit of $\langle P(q,\varepsilon)\rangle$. Hence, we retain only the first two terms generated by the kernel $K(q,q',\varepsilon)$. Because $\langle K(q,q',\varepsilon)\rangle=0$, the first fluctuation corrections to $\langle P(q,\varepsilon)\rangle$ are

$$\langle K(q,q',\varepsilon)K(q',q'',\varepsilon)\rangle =\left\langle\left[\delta\left[\frac{1}{\omega_n}\right]\right]^2\right\rangle\varepsilon^2 G_0(q,s)\delta(q-q'')G_0(q',s) \tag{2.19}$$

and

$$\langle K(q,q',\varepsilon)K(q',q'',\varepsilon)K(q'',q''',\varepsilon)\rangle =2\pi\varepsilon^3 G_0(q,s)G_0(q',s)G_0(q'',s)\times\left\langle\left[\delta\left[\frac{1}{\omega_n}\right]\right]^3\right\rangle\delta(q-q''') . \tag{2.20}$$

Substituting these expressions into (2.1) and averaging we obtain

$$\langle P(q,\varepsilon)\rangle=2\pi F_0(q,0)G_0(q,s)+(2\pi)^2\left\langle\delta\left[\frac{1}{\omega_n}\right]^2\right\rangle\frac{\varepsilon^2F_0(q,0)G_0^2(q,s)}{2\sinh\eta}+(2\pi)^2\left\langle\left[\delta\left[\frac{1}{\omega_n}\right]\right]^3\right\rangle\varepsilon^3F_0(q,\varepsilon)\times G_0^2(q,s)\frac{1}{4\sinh^2\eta}+\cdots , \tag{2.21}$$

where

$$\cosh\eta=\varepsilon/2D_0+1 . \tag{2.22}$$

Recall that $D(\varepsilon)=l^2\varepsilon\langle P(q=0,\varepsilon)\rangle$. The final result for the frequency-dependent diffusivity is

$$D(\varepsilon)=D_0l^2\left\{1+\left\langle\left[\delta\left[\frac{1}{\omega_n}\right]\right]^2\right\rangle\frac{\varepsilon D_0}{2\sinh\eta}+\left\langle\delta\left[\frac{1}{\omega_n}\right]^3\right\rangle\frac{D_0\varepsilon^2}{4\sinh^2\eta}\right\} . \tag{2.23}$$

In the limit of small ε, $\eta\sim(\varepsilon/D_0)^{1/2}$, we obtain

$$\lim_{\varepsilon\to 0}D(\varepsilon)\sim l^2D_0\left\{1+\left\langle\left[\delta\left[\frac{1}{\omega_n}\right]\right]^2\right\rangle\frac{D_0^{3/2}}{2}\varepsilon^{1/2}+\left\langle\left[\delta\left[\frac{1}{\omega_n}\right]\right]^3\right\rangle\frac{D_{0\varepsilon}^2}{4}\right\} . \tag{2.24}$$

The first term in (2.24), l^2D_0, is the standard zeroth-order strong-fluctuation result for the diffusion coefficient. The next term is the non-Markovian correction derived by Zwanzig[6] and others.[5,7,8(b)] We computed the third-order term explicitly to show that it does not contribute to the $\varepsilon^{1/2}$ correction. The presence of the leading $\varepsilon^{1/2}$ correction dictates the existence of the long-time tail $t^{-3/2}$ in $dD(t)/dt$ (the velocity autocorrelation function) that appears to be an integral part of transport in $d=1$ systems.

III. HOPPING TRANSPORT IN $d=2$

The crucial step in the derivation of (2.24) is the realization that the van Kampen[12] result

$$\varepsilon\langle n^2(\varepsilon)\rangle=2\left\langle\sum_{n=-\infty}^{\infty}\omega_nf_n(\varepsilon)\right\rangle \tag{3.1}$$

for the mean-square displacement leads naturally to a SFE for $D(\varepsilon)$. Extending the analysis of Sec. II to higher dimensions requires generalizing Eq. (3.1). Consider the master equation for nearest-neighbor hopping on the square lattice shown in Fig. 1,

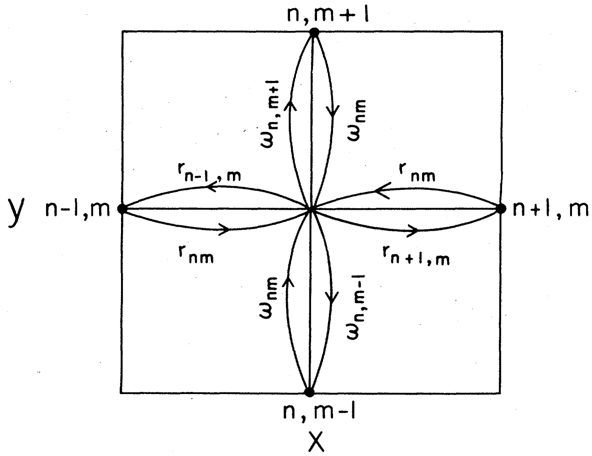

FIG. 1. Nearest-neighbor transport on a square lattice.

$$\frac{dP_{nm}}{dt}=r_{n-1,m}P_{n-1,m}+r_{n+1,m}P_{n+1,m}-2r_{nm}P_{nm}$$
$$+\omega_{n,m-1}P_{n,m-1}+\omega_{n,m+1}P_{n,m+1}-2\omega_{nm}P_{nm} . \tag{3.2}$$

The r_{nm}'s transfer an electron from the nth to the $(n+1)$th site in the x direction while the ω_{nm}'s account for transport in the y direction as specified in Fig. 1. To generalize (3.1) to $d=2$, is it helpful to define the probability density at time t for an arbitrary position r in the lattice as

$$P(r,t)=\sum_{n,m}\delta(x-x_n)\delta(y-y_m)P_{nm}(t) . \tag{3.3}$$

The mean-square displacement is now

$$\langle r^2(t)\rangle=\langle \int d\mathbf{r}\,\mathbf{r}^2P(\mathbf{r},t)\rangle \tag{3.4}$$
$$=l^2\langle \sum_{n,m}(n^2+m^2)P_{nm}(t)\rangle . \tag{3.5}$$

In deriving (3.5) we have used the periodicity of the lattice, that is, $x_n=nl$ and $y_m=ml$. It is straightforward to show from (3.2) that

$$\frac{d}{dt}\langle r^2(t)\rangle=\langle D(t)\rangle=2\left\langle \sum_{n,m}(r_{nm}+\omega_{nm})P_{nm}\right\rangle \tag{3.6}$$

or

$$\frac{\varepsilon^2}{2}\langle n^2(\varepsilon)\rangle=\varepsilon\left\langle \sum_{n,m}(r_{nm}+\omega_{nm})f_{nm}(\varepsilon)\right\rangle , \tag{3.7}$$

where

$$f_{nm}(t)=\int_0^\infty e^{-\varepsilon t}P_{nm}(t)dt . \tag{3.8}$$

Equation (3.7) is the generalization of (2.5) to two dimensions.

We can now proceed with the analysis of the transport. Equation (3.7) suggests that the correct generating function is

$$P(q_1,q_2,\varepsilon)=\sum_{n,m}e^{iq_1n}e^{iq_2m}f_{nm}(\varepsilon)(r_{nm}+\omega_{nm}) \tag{3.9}$$

so that

$$\frac{\varepsilon^2}{2}\langle n^2(\varepsilon)\rangle=\varepsilon\langle P(0,0,\varepsilon)\rangle . \tag{3.10}$$

Hence, as in the 1D case all that is required is the $q_1,q_2=0$ limit of the generating function. For convenience let us define the two vectors $\mathbf{q}=(q_1,q_2)$ and $\mathbf{n}=(n,m)$. The closure relation for the site-occupation probabilities

$$f_{\mathbf{n}}(\varepsilon)=f_{nm}(\varepsilon)=\frac{1}{r_{\mathbf{n}}+\omega_{\mathbf{n}}}\frac{1}{(2\pi)^2}\int_{-\pi}^{\pi}e^{i\mathbf{q}\cdot\mathbf{n}}P(\mathbf{q},\varepsilon)d\mathbf{q} \tag{3.11}$$

reveals that the strong fluctuation expansions will involve averages of the form

$$c^{-1}=\left\langle \frac{1}{N}\sum_{\mathbf{n}}\frac{1}{r_{\mathbf{n}}+\omega_{\mathbf{n}}}\right\rangle=\left\langle \frac{1}{r+\omega}\right\rangle , \tag{3.12a}$$

$$\alpha_1=\left\langle \frac{1}{N}\sum_{\mathbf{n}}\frac{r_{\mathbf{n}}}{r_{\mathbf{n}}+\omega_{\mathbf{n}}}\right\rangle=\left\langle \frac{r}{r+\omega}\right\rangle , \tag{3.12b}$$

and

$$\alpha_2=\left\langle \frac{1}{N}\sum_{\mathbf{n}}\frac{\omega_{\mathbf{n}}}{r_{\mathbf{n}}+\omega_{\mathbf{n}}}\right\rangle=1-\alpha_1 . \tag{3.12c}$$

It should be pointed out that in the limit of symmetric rates in the x and y directions $r_{\mathbf{n}}=\omega_{\mathbf{n}}$, and $\alpha_1=\alpha_2=\frac{1}{2}$. The general result for any dimension for the case of symmetric rates is $\alpha_n=1/d$. In Eqs. (3.12a)–(3.12c) we have assumed that the averages over the distribution of hopping rates are independent of $\mathbf{n}$.[6] The equations of motion for the site-occupation probabilities

$$\sum_{\mathbf{n}}e^{i\mathbf{q}\cdot\mathbf{n}}P_{\mathbf{n}}(t)=-2(1-\cos q_1)\sum_{\mathbf{n}}e^{i\mathbf{q}\cdot\mathbf{n}}r_{\mathbf{n}}P_{\mathbf{n}}(t)$$
$$-2(1-\cos q_2)\sum_{\mathbf{n}}e^{i\mathbf{q}\cdot\mathbf{n}}\omega_{\mathbf{n}}P_{\mathbf{n}}(t) \tag{3.13}$$

are obtained by multiplying the master equation by $e^{i\mathbf{q}\cdot\mathbf{n}}$ and summing over $\mathbf{n}$. To obtain the integral equation for $P(\mathbf{q},\varepsilon)$, we express the Laplace transform of (3.13),

$$\varepsilon\sum_{\mathbf{n}}e^{i\mathbf{q}\cdot\mathbf{n}}f_{\mathbf{n}}(\varepsilon)-F_0(\mathbf{q},0)$$
$$=-2(1-\cos q_1)\sum_{\mathbf{n}}e^{i\mathbf{q}\cdot\mathbf{n}}r_{\mathbf{n}}f_{\mathbf{n}}(\varepsilon)$$
$$-2(1-\cos q_2)\sum_{\mathbf{n}}e^{i\mathbf{q}\cdot\mathbf{n}}\omega_{\mathbf{n}}f_{\mathbf{n}}(\varepsilon) , \tag{3.14}$$

in terms of the averages defined above in (3.12). In (3.14)

$$F_0(\mathbf{q},p)=\sum_{\mathbf{n}}P_{\mathbf{n}}(0)e^{i\mathbf{q}\cdot\mathbf{n}} . \tag{3.15}$$

Let us define, in direct analogy with Eq. (2.18), the zeroth-order Green function in $d=2$ to be

$$G_0(\mathbf{q},s)=\frac{1}{2\pi\{s+2[1-\alpha_1\cos q_1-(1-\alpha_1)\cos q_2]\}} \tag{3.16}$$

with

$$s=\varepsilon/c \;. \tag{3.17}$$

Because $f_{\mathbf{n}}(\varepsilon)\propto(r_{\mathbf{n}}+\omega_{\mathbf{n}})^{-1}$ a strong fluctuation expansion for $P(\mathbf{q},\varepsilon)$ can be generated naturally by adding and subtracting c^{-1} and α_1 from the equations of motion. The integral equation for $P(\mathbf{q},\varepsilon)$ that results is

$$P(q,\varepsilon)=2\pi F_0(\mathbf{q},0)G_0-\int_{-\pi}^{\pi}K(\mathbf{q},\mathbf{q}',\varepsilon)P(\mathbf{q}',\varepsilon)d\mathbf{q}' \;. \tag{3.18}$$

We have defined the kernel $k(\mathbf{q},\mathbf{q}',\varepsilon)$ as

$$K(\mathbf{q},\mathbf{q}',\varepsilon)=\frac{G_0(\mathbf{q},\varepsilon)}{(2\pi)^2}\sum_{\mathbf{n}}e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}}\left[\varepsilon\delta\left[\frac{1}{c_{\mathbf{n}}}\right]-2(\cos q_1-\cos q_2)\delta(\alpha_{\mathbf{n}})\right] \tag{3.19}$$

$$=G_0(\mathbf{q},\varepsilon)K_0(\mathbf{q},\mathbf{q}') \;. \tag{3.20}$$

Two types of fluctuations appear in the definition of $K(\mathbf{q},\mathbf{q}',\varepsilon)$. The first

$$\delta\left[\frac{1}{c_{\mathbf{n}}}\right]=\frac{1}{r_{\mathbf{n}}+\omega_{\mathbf{n}}}-\left\langle\frac{1}{r+\omega}\right\rangle \tag{3.21}$$

accounts for independent (uncorrelated) fluctuations in the $x(r_{\mathbf{n}})$ and $y(\omega_{\mathbf{n}})$ hopping rates. Correlations in the fluctuations in the x and y hopping rates are included in the second term

$$\delta(\alpha_{\mathbf{n}})=\frac{r_{\mathbf{n}}}{r_{\mathbf{n}}+\omega_{\mathbf{n}}}-\left\langle\frac{r}{r+\omega}\right\rangle \;. \tag{3.22}$$

The contribution from this term is only appreciable if some anisotropy exists which makes the $r_{\mathbf{n}}$'s differ from the $\omega_{\mathbf{n}}$'s—that is, the $r_{\mathbf{n}}$'s and $\omega_{\mathbf{n}}$'s are determined by different probability distribution functions. We note that if we assume no such anisotropy exists, then

$$\alpha_1=\left\langle\frac{r}{r+\omega}\right\rangle=\tfrac{1}{2} \tag{3.23}$$

and $\delta(\alpha_{\mathbf{n}})=0$ for all $\mathbf{n}$. We will be interested in this limit later on in our evaluation of the fluctuation corrections to $P(\mathbf{q},\varepsilon)$. The general result for α_1 and c^{-1} for d dimensions if the hopping rates between nearest neighbors in all directions are symmetric is

$$\alpha_1=1/d \tag{3.24}$$

and

$$c^{-1}=\langle 1/r\rangle/d \;. \tag{3.25}$$

A solution to the integral equation for $P(q,\varepsilon)$ is obtained by iterating to low order in K and averaging over the disorder in the rates. To third order in the fluctuations we obtain

$$\begin{aligned}\langle P(q,\varepsilon)\rangle\simeq{}&2\pi F_0(\mathbf{q},0)G_0(\mathbf{q},s)-(2\pi)^2\int_{-\pi}^{\pi}\langle G_0(\mathbf{q},\varepsilon)K_0(\mathbf{q},\mathbf{q}',\varepsilon)\rangle F_0(\mathbf{q}',0)G_0(\mathbf{q}',\varepsilon)d\mathbf{q}'\\&+(2\pi)^3\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\langle K_0(\mathbf{q},\mathbf{q}',\varepsilon)G_0(\mathbf{q},\varepsilon)K_0(\mathbf{q}',\mathbf{q}'',\varepsilon)G_0(\mathbf{q}',\varepsilon)\rangle F_0(\mathbf{q}'',0)G_0(\mathbf{q}'',\varepsilon)d\mathbf{q}'\,d\mathbf{q}''\\&-(2\pi)^4\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\langle K_0(\mathbf{q},\mathbf{q}',\varepsilon)G_0(\mathbf{q},\varepsilon)K_0(\mathbf{q}',\mathbf{q}'',\varepsilon)G_0(\mathbf{q}',\varepsilon)K_0(\mathbf{q}'',\mathbf{q}''',0)G_0(\mathbf{q}'',\varepsilon)\rangle\\&\qquad\times F_0(\mathbf{q}''',0)G_0(\mathbf{q}''',\varepsilon)d\mathbf{q}'\,d\mathbf{q}''d\mathbf{q}''' \;.\end{aligned} \tag{3.26}$$

From the defining equation for K_0, it follows immediately that

$$\langle K_0(\mathbf{q},\mathbf{q}',\varepsilon)\rangle=0$$

and

$$\begin{aligned}\langle K_0(\mathbf{q},\mathbf{q}',\varepsilon)K_0(\mathbf{q}',\mathbf{q}'',\varepsilon)\rangle\\=\left[\frac{1}{2\pi}\right]^2\sum_{n,m}e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}}e^{i(\mathbf{q}'-\mathbf{q}'')\cdot\mathbf{m}}\Bigg[&\left\langle\delta\left[\frac{1}{c_{\mathbf{n}}}\right]\delta\left[\frac{1}{c_{\mathbf{m}}}\right]\right\rangle\varepsilon^2-2(\cos q_1-\cos q_2)\left\langle\delta(\alpha_{\mathbf{n}})\delta\left[\frac{1}{c_{\mathbf{m}}}\right]\right\rangle\varepsilon\\&-2(\cos q_1'-\cos q_2')\left\langle\delta(\alpha_{\mathbf{n}})\delta\left[\frac{1}{c_{\mathbf{m}}}\right]\right\rangle\varepsilon\\&+4(\cos q_1-\cos q_2)(\cos q_1'-\cos q_2')\langle\delta(\alpha_{\mathbf{n}})\delta(\alpha_{\mathbf{m}})\rangle\Bigg] \;.\end{aligned} \tag{3.27}$$

The second and fourth terms in (3.27) vanish in the limit $\mathbf{q}=0$. Because $D(\varepsilon)$ corresponds to $\langle P(\mathbf{q}=0,\varepsilon)\rangle$ terms which vanish when $\mathbf{q}=0$ need not be computed. It is instructive here to point out a general rule for enumerating the nonzero fluctuation corrections to $D(\varepsilon)$. The fluctuation kernal K_0 is of the form

$$K_0(\mathbf{q},\mathbf{q}')=\sum_{\mathbf{n}}\left[A_{\mathbf{n}}(q,q')\delta\left[\frac{1}{c_{\mathbf{n}}}\right]+B_{\mathbf{n}}(\mathbf{q},\mathbf{q}')\delta(\alpha_{\mathbf{n}})\right]. \quad (3.28)$$

From (3.19) we see that $B_{\mathbf{n}}(\mathbf{q}=0,\mathbf{q}')=0$. Hence, in the expansion of $\langle K_0 n\rangle$, all terms in which $B_{\mathbf{n}}(\mathbf{q},\mathbf{q}')$ occurs first do not contribute to $D(\varepsilon)$. That is, terms such as *BAB* and B^n vanish whereas *ABA*, AB^n, etc. do not. This key simplification indicates that the fluctuation contribution from the anisotropy in the hopping rates in the x and y directions is not as important as are the independent fluctuations in the $r_{\mathbf{n}}$'s and $\omega_{\mathbf{n}}$'s. Hence, at this point we will consider only those fluctuations that arise when the anisotropy vanishes. In this limit the hopping rates in x and y are symmetric ($r_{\mathbf{n}}=\omega_{\mathbf{n}}$), $\delta(\alpha_{\mathbf{n}})=0$, and K_0 simplifies to

$$K_0(\mathbf{q},\mathbf{q}')=\frac{1}{2\pi}\sum\nolimits_{\mathbf{n}}e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}}\delta\left[\frac{1}{c_{\mathbf{n}}}\right]\varepsilon , \quad (3.29)$$

where

$$\delta\left[\frac{1}{c_{\mathbf{n}}}\right]=\frac{1}{2r_{\mathbf{n}}}-\frac{1}{2}\left\langle\frac{1}{c_{\mathbf{n}}}\right\rangle .$$

With this simplification in mind we now rewrite $\langle P(\mathbf{q},\varepsilon)\rangle$. As in the $d=1$ case, we assume that

$$\left\langle\delta\left[\frac{1}{c_{\mathbf{n}}}\right]\delta\left[\frac{1}{c_{\mathbf{m}}}\right]\right\rangle=0 \text{ for } \mathbf{n}\neq\mathbf{m} . \quad (3.30)$$

To simplify the notation we will drop the subscripts on $\delta(1/c_{\mathbf{n}})$. Then

$$\langle K_0(\mathbf{q},\mathbf{q}',\varepsilon)K_0(\mathbf{q}',\mathbf{q}'',\varepsilon)\rangle =\frac{\varepsilon^2}{(2\pi)^2}\delta(\mathbf{q}-\mathbf{q}'')\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle , \quad (3.31)$$

$$\langle K_0(\mathbf{q},\mathbf{q}',\varepsilon)K_0(\mathbf{q}',\mathbf{q}'',\varepsilon)K_0(\mathbf{q}'',\mathbf{q}''',\varepsilon)\rangle =\frac{\varepsilon^3}{(2\pi)^3}\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^3\right\rangle\delta(\mathbf{q}-\mathbf{q}''') , \quad (3.32)$$

and

$$\langle P(\mathbf{q},\varepsilon)\rangle=2\pi F_0(\mathbf{q},0)G_0(\mathbf{q},\varepsilon)+(2\pi)^2\varepsilon^2F_0(\mathbf{q},0)G_0^2\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle\int G_0(\mathbf{q}',\varepsilon)d\mathbf{q}'$$
$$-\varepsilon^3(2\pi)^2F_0(q,0)\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^3\right\rangle G_0^2\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}G_0(\mathbf{q}',\varepsilon)G_0(\mathbf{q}'',\varepsilon)dq'\,dq'' . \quad (3.33)$$

Let us define $T(s)$ as the following integral:

$$T(s)=\frac{1}{(2\pi)^2}\int G_0(\mathbf{q},\varepsilon)dq \quad (3.34)$$
$$=\frac{1}{(2\pi)^2}\int_{-\pi}^{\pi}\int_{-\pi}^{\pi}\frac{1}{s+2-\cos q_1-\cos q_2}dq_1\,dq_2 . \quad (3.35)$$

The assumption of symmetric hopping rates requires that $\alpha_1=\alpha_2=\frac{1}{2}$. From (3.35) it follows that

$$\langle P(\mathbf{q},\varepsilon)\rangle=2\pi F_0(q,0)G_0+(2\pi\varepsilon)^2F_0(\mathbf{q},0)\times G_0^2\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle T(s)-(2\pi)^2\varepsilon^3F_0^2(\mathbf{q},0)\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^3\right\rangle G_0^2[T(s)]^2 \quad (3.36)$$

and the diffusion coefficient is given by

$$D(\varepsilon)=\frac{\varepsilon}{2}\langle P(0,\varepsilon)\rangle l^2 =\frac{cl^2}{2}\left\{1+c^2\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle\frac{\varepsilon}{c}T(\varepsilon/c)-c^2\varepsilon\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^3\right\rangle\frac{\varepsilon}{c}\left[T\left[\frac{\varepsilon}{c}\right]\right]^2\right\} . \quad (3.37)$$

It has been shown previously that $T(\varepsilon/c)$ has a logarithmic singularity in the long-time limit.[14] Consequently, the leading non-Markovian corrections to $\lim_{\varepsilon\to 0}D(\varepsilon)$ are

$$\lim_{\varepsilon\to 0}D(\varepsilon)=\frac{cl^2}{2}\left\{1+c^2\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle\times\left[\frac{2}{\pi}\ln 2-\frac{1}{4}-\frac{1}{2}\ln\left[\frac{\varepsilon}{c}\right]\frac{\varepsilon}{c}\right]+O(-\varepsilon^2\ln\varepsilon)\right\} . \quad (3.38)$$

The $\varepsilon\ln\varepsilon$ dependence of $D(\varepsilon)$ signifies a $\ln t$ correction to the long-time limit of $\langle x^2(t)\rangle$ or a t^{-2} long-time tail in $dD(t)/dt$. The appearance of the t^{-2} correction in $dD(t)/dt$ is due entirely to the fluctuation of the hopping rates about the mean (c^{-1}). For small fluctuations in the hopping rates this result has been established previously for hopping transport in two dimensions.[13,15,8(b)] The fact that the number of sites visited during a random walk on a $d=2$ lattice is proportional to $N/\ln N$ (Ref. 13) (N the number of steps) might be related to this result. We point out that fluctuations arising from anisotropic rates ($r_{\mathbf{n}}\neq\omega\mathbf{n}$) do not contribute to the $\varepsilon\ln\varepsilon$ term in (3.38) but rather they modify the zeroth-order result $cl^2/2$. Inclusion of such effects are likley to be essential in describing bond and site percolation problems.

IV. d-DIMENSIONAL TRANSPORT

The formalism presented thus far can be extended immediately to hopping transport on d-dimensional lattices. For nearest-neighbor transport on a d-dimensional lattice, the equation of motion for the site-occupation probabilities is

$$\frac{dP_{\mathbf{n}}}{dt}=\sum_{\alpha=1}^{d}\omega_{\mathbf{n}+1_\alpha}^{(\alpha)}P_{\mathbf{n}+1_\alpha}+\omega_{\mathbf{n}-1_\alpha}^{(\alpha)}P_{\mathbf{n}-1_\alpha}-2\omega_{\mathbf{n}_\alpha}^{(\alpha)}P_{\mathbf{n}}\ , \quad (4.1)$$

where $\mathbf{n}$ is the vector $\mathbf{n}=(n_1n_2\dots n_d)$ and $\mathbf{1}_\alpha$ is a unit vector such that $\mathbf{1}_{(\alpha=1)}=(1,0,\dots,0)$, $\mathbf{1}_{(\alpha=2)}=(0,1,0,\dots,0)$, etc. It is straightforward to show that the correct generalization of Eq. (3.7) for $\langle\mathbf{n}^2(\varepsilon)\rangle$ is

$$\frac{\varepsilon^2}{2}\langle\mathbf{n}^2(\varepsilon)\rangle=\varepsilon\left\langle\sum_{\mathbf{n}}\sum_{\alpha=1}^{d}\omega_{\mathbf{n}}^{(\alpha)}f_{\mathbf{n}}(\varepsilon)\right\rangle . \quad (4.2)$$

In (4.2) $f_{\mathbf{n}}(\varepsilon)$ is the Laplace transform of the site-occupation probability $P_{\mathbf{n}}(t)$. The appropriate generating function

$$P(\mathbf{q},\varepsilon)=\sum_{\mathbf{n}}\sum_{\alpha=1}^{d}e^{i\mathbf{q}\cdot\mathbf{n}}\omega_{\mathbf{n}}^{(\alpha)}f_{\mathbf{n}}(\varepsilon) \quad (4.3)$$

satisfies the following integral equation:

$$\frac{\varepsilon}{(2\pi)^2}\int_{-\pi}^{\pi}d\mathbf{q}'\,P(\mathbf{q}',\varepsilon)\sum_{\mathbf{n}}J_{\mathbf{n}}^{-1}e^{i(\mathbf{q}-\mathbf{q}')\mathbf{n}}-F_0(\mathbf{q},0)$$
$$=2\int_{-\pi}^{\pi}\sum_{\mathbf{n}}\frac{\sum_{\alpha=1}^{d}\omega_{\mathbf{n}}^{(\alpha)}}{J_{\mathbf{n}}}2(1-\cos q_\alpha)P(q',\varepsilon)e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}}\ , \quad (4.4a)$$

where

$$J_n=\sum_{\alpha=1}^{d}\omega_{\mathbf{n}}^{(\alpha)} . \quad (4.4b)$$

Let us define the zeroth-order lattice Green function

$$G_0(\mathbf{q},\varepsilon)=\frac{1}{2\pi\left[s+2\left[1-\sum_{i=1}^{d}\alpha_i\cos q_i\right]\right]}\ , \quad (4.5)$$

where s and $\alpha_{\mathbf{n}}$ are defined in analogy with (3.12a)–(3.12b),

$$s=\varepsilon\Big/\left\langle\frac{1}{N}\sum_{\mathbf{n}}J_{\mathbf{n}}^{-1}\right\rangle=\frac{\varepsilon}{c} \quad (4.6)$$

and

$$\alpha_m=\left\langle\frac{1}{N}\sum\mathbf{n}\,\omega_{\mathbf{n}}^{(m)}J_{\mathbf{n}}^{-1}\right\rangle . \quad (4.7)$$

In the limit of symmetric rates

$$c^{-1}=\frac{1}{d}\left\langle\frac{1}{\omega}\right\rangle ,$$

$$\alpha_i=\frac{1}{d}\ ,$$

and the integral equation reduces to

$$P(\mathbf{q},\varepsilon)=2\pi\mathbf{F}(q,0G_0(\mathbf{q},\varepsilon)-\pi\int_{-\pi}^{\pi}K(\mathbf{q},\mathbf{q}',\varepsilon)P(\mathbf{q}',\varepsilon)d\mathbf{q}' . \quad (4.8)$$

The d-dimensional fluctuation kernel $K(q,q',\varepsilon)$

$$K(q,q',\varepsilon)=G_0(q,\varepsilon)\frac{\varepsilon}{2\pi}\sum_{\mathbf{n}}e^{i(\mathbf{q}-\mathbf{q}')\cdot\mathbf{n}}\delta(1/c_{\mathbf{n}}) \quad (4.9)$$

only involves the symmetric fluctuation

$$\delta(1/c_{\mathbf{n}})=\frac{1}{d}\left[\frac{1}{\omega_{\mathbf{n}}}-\left\langle\frac{1}{\omega}\right\rangle\right] \quad (4.10)$$

because $\omega_{\mathbf{n}}^{(\alpha)}=\omega_{\mathbf{n}}$ for all α.

The integral equation can be solved as before to obtain the transport properties. The only difficult problem involved in such a calculation is the q integration of the Green function,

$$J(s)=\frac{1}{(2\pi)^d}\int_{-\pi}^{\pi}dq_1\cdots\int_{-\pi}^{\pi}dq_d\int_0^{\infty}dt\,e^{-(s+2)t}e^{2t/d(\cos q_1+\dots+\cos q_d)} . \quad (4.11)$$

This integral has been investigated extensively by Montroll[14(a)] and Sahimi *et al.*[14(b)] For small s, the asymptotic behavior is

$$J(s)\simeq\int_0^1e^{-(s+2)t}I_0^d\left[\frac{2t}{d}\right]dt+\int_1^{\infty}\frac{e^{-st}}{t^{d/2}}dt \quad (4.12)$$

$$\simeq\begin{cases}A-\dfrac{(-1)^{d/2}}{(d/2)!}s^{d/2-1}[\gamma-\ln s-e^{-s}s^{-d/2}]\ , & d\text{ even}\\ A-e^{-s}s^{d/2-1}\ , & d\text{ odd}\end{cases} \quad (4.13)$$

where $I_0(t)$ is the zeroth-order modified Bessel function and A the first integral in (4.12). For $d=1$, A vanishes identically as $s\to0$. The exact form for A is given in Eq. (3.38) for $d=2$. In $d=3$ A has been evaluated explicitly by Watson[16] to be $A=0.505$. For higher dimensions A is most likely nonzero; hence we conclude the general asymptotic behavior of $sJ(s)$ is

$$\lim_{s\to0}sJ(s)\sim sA+s^{d/2} \quad (4.14)$$

in odd dimensions and

$$\lim_{s\to 0} sJ(s) \sim sA + s^{d/2}\ln s \tag{4.15}$$

in even dimensions.

From the general expression for $D(t)$ to second order in the fluctuations

$$D(\varepsilon) = \frac{cl^2}{2}\left\{1 + c^2\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle \varepsilon/cJ(\varepsilon/c)\right\}. \tag{4.16}$$

the frequency corrections for the $d=3$ case are easily deduced from Eq. (4.14),

$$D(\varepsilon) = \frac{cl^2}{2}\left\{1 + c^2\left\langle\left[\delta\left[\frac{1}{c}\right]\right]^2\right\rangle \times[0.505\varepsilon/c - (\varepsilon/c)^{3/2}]\right\} \tag{4.17}$$

$$= D_0 + D_1\varepsilon + D_2\varepsilon^{3/2}\,, \tag{4.18}$$

where D_0, D_1, and D_2 follow immediately from (4.17). The linear frequency correction arises from the constant term in $J(s)$. Indeed, this term is somewhat unanticipated. However, it is straightforward to show that this term has no bearing on the long-time behavior of $D(t)$. To proceed we first calculate $\langle x^2(\varepsilon)\rangle$,

$$\langle x^2(\varepsilon)\rangle = 6\left[\frac{D_0}{\varepsilon^2} + \frac{D_1}{\varepsilon} + \frac{D_2}{\varepsilon^{1/2}}\right], \tag{4.19}$$

using Eq. (2.6) generalized to d dimensions. The inverse Laplace transform of $\langle x^2(\varepsilon)\rangle$ is

$$\langle x^2(t)\rangle = 6(D_0 t + D_1 + D_2 t^{-1/2})\,. \tag{4.20}$$

Consequently, the time-dependent diffusion coefficient

$$D(t) = \frac{d}{dt}\langle x^2(t)\rangle = 6(D_0 - \tfrac{1}{2}D_2 t^{-3/2}) \tag{4.21}$$

is independent of D_1 and the $\varepsilon^{3/2}$ frequency term gives rise to a $t^{-5/2}$ long-time tail in the velocity autocorrelation function, $dD(t)/dt$. A similar result has been established by Machta *et al.*[13] for random-hopping models with small fluctuations in the hopping rates. Our results are valid in the limit of large fluctuations of the transfer rates and hence are valid for transport in any site-disordered material. Frequency-dependent measurements of the conductivity in disordered systems are needed to confirm the predictions made here. It is our hope that this work will provide the impetus for such measurements. Alternatively, molecular dynamics simulations of hopping transport in d dimensions can be performed to verify the existence of the long-time tail $t^{-(1+d/2)}$ in $dD(t)/dt$ (the velocity autocorrelation function) found here.

V. SUMMARY OF REASONING

We have presented in this paper a powerful formalism for treating hopping transport among a band of localized states in d dimensions. The primary motivation for this approach is the realization that the van Kampen[12] formula for $\langle r^2(t)\rangle$ for 1D hopping among a distribution of symmetric wells (1) can be generalized to any dimension and (2) leads naturally to a strong fluctuation expansion of $D(t)$. This approach will undoubtedly be applicable to numerous trapping and hopping-transport problems in disordered materials. In forthcoming publications we apply the theory developed here to investigate the feasibility of molecularly based electronic devices[11(b)] and to study percolation in the random-hopping model.[17]

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