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Theory of Hopping and Multiple-Trapping Transport in Disordered Systems

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We present a general theory to describe equilibrium as well as nonequilibrium transport properties of systems in which the carriers perform an incoherent motion that can be described by means of a set of master equations. This includes hopping as well as trapping in the localized energy region of amorphous or perturbed crystalline semiconductors. Employing the mathematical analogy between the master equations and the tight binding problem we develop approximation schemes using methods of many-particle physics to derive expressions for the averaged propagator of the carriers and the conductivity tensor. The calculated conductivity and Hall conductivity of hopping systems compare extremely well to computer simulations over the whole range of frequency, density, and temperature. We are able to derive expressions for dispersive transport in hopping as well as trapping systems that contain the results of earlier theories of Scher, Montroll and Noolandi, Schmidlin as special cases and establish criteria for the occurrence of dispersive transport in such systems. We find that in principle hopping can lead to dispersive transport if the times and densities are very low, but actual experimental data are more easily explained in terms of multiple trapping.

KEY WORDS: Hopping transport; trapping; master equation; hopping Hall effect; dispersive transport.

1. INTRODUCTION

In the last decade the problem of incoherent transport of particles between spatially and energetically disordered localized states which can be described by a set of Markovian master equations (ME) has evolved into a subject of considerable interest with a wide range of applications.[1-3] This

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includes hopping and trapping of electrons in the localized region of amorphous or perturbed crystalling semiconductors.

The existing approaches for solving linearized versions of the ME may be roughly divided into three groups: (a) the equivalent random network method, combined with percolation techniques,[4] the continuous-time random walk method,[5] and the Green's function method,[6,7] which is the basis of the present treatment. Since the averaged Green's function that solves the ME can be interpreted as the probability to find a particle in a state when it started in another, the Green's function method allows for a random walk interpretation.[8] So our Green's function approach is effectively a microscopically based random walk theory.

The present authors have shown in a series of papers[9–11] that, if one employs the mathematical analogy between the ME and the tight-binding problem and uses methods of many-particle physics, one can derive approximation schemes that have proved to be very successful in describing equilibrium[11,12] and nonequilibrium[13,14] hopping and trapping transport across the whole density, temperature, and frequency range. This holds both for comparison with computer simulations as well as with experimental data.

The present formalism also has the advantage that its results include those of the other existing approaches as special cases. This makes it possible to discuss the merits and shortcomings of the latter and to discuss different proposed transport mechanisms on a common footing. In particular we are able to treat hopping, trapping, and combinations of both in the same framework and discuss the conditions under which these mechanisms lead to experimentally observable anomalies like an ω^s-law in the ac conductivity or non-Gaussian transients in time-of-flight experiments.

The present contribution, which comprises a survey of this theory and some new results is organized as follows: In Section 2 we briefly show how the linearized master equations are solved approximately for the averaged propagator. Results for the conductivity tensor in the presence of weak applied magnetic fields are presented in Section 3. In Section 4 we demonstrate how dispersive transport due to hopping and trapping may be described in terms of microscopic parameters.

2. GENERAL FORMALISM

2.1. The Linearized Master Equation

We start with the linearized ME which quite generally can be put into the form[15]

$$\frac{d}{dt} n_i = -\sum_j K_{ij} n_i + \sum_j K_{ji} n_j - \delta_i n_i \tag{2.1}$$

Here i denotes the position $\mathbf{r}_i$ and the local chemical potential E_i of the state i, and n_i is the (linearized) occupation probability. The effective transition rates K_{ij} are related to the transition rates W_{ij} that appear in the nonlinear ME by $K_{ij} = \tau_{ij}/F_i$[16] $\tau_{ij} = f(E_i)[1 - f(E_j)]W_{ij}$ and $F_i = f(E_i)[1 - f(E_i)]$, where $f(E)$ is the Fermi function. (For symmetric transition rates the ME itself is linear, and we have $K_{ij} = W_{ij} = W_{ji}$.) The $\delta_i n_i$ are additional loss terms to be specified below.

We have assumed that a localized level can be either empty or singly occupied. To put a second electron into a singly occupied state costs an extra Coulomb energy U (Hubbard energy). In this paper we shall only consider the $U \to \infty$ limit. The more realistic finite U transport problem has been recently solved.[17]

The formal solution of (2.1) is given by the resolvent matrix (Green's function)

$$G_{ij}(\omega) = \left[i\omega - \hat{K} \right]^{-1}_{ij} \tag{2.2}$$

where the matrix $\hat{K}$ has diagonal elements $-\delta_i - \sum_j K_{ij}$ and off-diagonal elements K_{ij}.

Note that $G_{ij}(\omega)$ can be interpreted as the Laplace transform of the probability $G_{ij}(t)$ of finding the particle at site j at time t when it was started at time $t = 0$ at site i. This naturally leads to an analogy to the random walk description of hopping transport of Scher and Lax.[5] On the other hand it is observed that $G_{ij}(\omega)$ is mathematically equivalent to the Green's function of a tight binding Hamiltonian.

The quantity of interest is the configurationally averaged Green's function $\langle G_{ij} \rangle_{ij}$ with the sites i and j held fixed (not averaged over). Because of this, the analogy with the tight binding problem is a very useful one, and in particular we can take over all the renormalization techniques and approximation schemes which have been developed to calculate the electronic properties of liquid metals and alloys, e.g., the CPA and cluster CPA for diagonal and off-diagonal disorder.[18] The usefulness of these schemes when applied to the master equation depends on the problem under consideration. The CPA is very powerful when dealing with purely diagonal disorder (except in one dimension[15,19]). In other words, one considers the δ_i term in Eq. (2.1) as a diagonal disturbance of the diffusion process.[15,20] This includes for example trapping (and release, see Refs. 13, 14 and Chap. 4), recombination or relaxation of charge carriers and excitations at particular centers.[3,15] For off-diagonal disorder the situation is less clear.[21–24] Here it seems to us that there is only a limited number of physical situations for which the CPA is of value: diffusion in weakly disordered systems with nearest-neighbor jump rates. In the more general problem of interest which involves transport in low-density systems, non-

nearest-neighbor transfer becomes important and it is better to use a direct approach.

2.2. Green's Function Expansions and the Effective Medium Approximation

The linearized master equation can be formally solved using standard Green's function techniques. The two major difficulties one then encounters are (a) to find reasonable approximations to the path summation problem and (b) the problem of carrying out the configurational averages for the quantities of interest.

First let us consider point (a). The probability or Green's function G_{ij} can be directly expanded using perturbation theory either as

$$\hat{G} = \frac{\hat{1}}{i\omega} + \frac{\hat{1}}{i\omega}\hat{K}\frac{\hat{1}}{i\omega} + \frac{\hat{1}}{i\omega}\hat{K}\frac{\hat{1}}{i\omega}\hat{K}\frac{\hat{1}}{i\omega} + \cdots \tag{2.3}$$

or alternatively as

$$G_{ij} = \frac{\delta_{ij}}{i\omega + \sum_\mu K_{i\mu}} + \frac{1}{i\omega + \sum_\mu K_{i\mu}} K_{ij} \frac{1}{i\omega + \sum_\mu K_{j\mu}} + \cdots \tag{2.4}$$

Gochanour *et al.*[7] derived a diagrammatic theory for the case of purely positional disorder using the form (2.3). The Scher–Lax approximation,[5] on the other hand, is easily derived using the form (2.4).[6] We have found it more useful and more transparent to work with the renormalized expansion (RPE) given by[11]

$$G_{ij} = G_{ii}\delta_{ij} + G_{ii}K_{ij}G_{jj}^{(i)} + \sum_{l\neq i\neq j} G_{ii}K_{il}G_{ll}^{(i)}K_{lj}G_{jj}^{(i,l)} + \cdots \tag{2.5}$$

where $G_{hk}^{(n,i,\ldots,s)}$, for example, represents the exact local Green's function with transfer forbidden to the sites $(n, i, \ldots, s)$. We also have for example

$$G_{kk}^{(n)} = \left[i\omega + \sum_s K_{ks} - \Delta_k^{(n)} \right]^{-1} \tag{2.6}$$

where the self-energies $\Delta_k^{(n)}$ are given by

$$\Delta_k^{(n)} = \sum_{l\neq n} K_{kl}G_{ll}^{(n,k)}K_{lk} + \sum_{l\neq s\neq n} K_{kl}G_{ll}^{(n,k)}K_{ls}G_{ss}^{(n,k,l)}K_{sk} + \cdots \tag{2.7}$$

Since all repeated indices have been eliminated by partial summations, the RPE represents an exact self-avoiding walk expansion. We note that diagonal and off-diagonal terms are correlated in (2.4) and it is convenient to rewrite (2.5) in the form

$$G_{ij} = G_{ii}\delta_{ij} + G_{ii}g_{ij}G_{jj}(ij) + \sum_{l\neq i\neq j} G_{ii}g_{il}G_{ll}(il)g_{lj}^{(i)}G_{jj}(il;lj) + \cdots \tag{2.8}$$

where

$$g_{il} = \frac{K_{il}}{K_{li}} \left[G_{ll}(il) + K_{li}^{-1} \right]^{-1} \tag{2.9a}$$

$$g_{lj}^{(i)} = \frac{K_{lj}}{K_{jl}} \left[G_{jj}(il; lj) + K_{jl}^{-1} \right]^{-1} \tag{2.9b}$$

and so on.

The quantity $G_{jj}(il; lj)$, for example, now refers to the exact local Green's function of site j with transfer excluded to the sites i and l, and, additionally, with the bonds $(i - l)$ and $(l - j)$ entirely removed from the system.

Equation (2.8) is still exact; the advantage of this form is that approximations can now be formulated in terms of memories of previous sites visited.

The simplest approximation is to keep the exact memory of the previous "site" (however many times the particle may have jumped backwards and forwards) and forget the other sites visited. This is equivalent to replacing

$$G_{nn}(il; lk, \ldots, sn) \rightarrow G_{nn}(sn) \tag{2.10}$$

everywhere in (2.8) and (2.9). We now obtain

$$G_{ij} = G_{ii}\delta_{ij} + G_{ii}g_{ij}G_{jj}(ij) + \sum_{l \neq i \neq j} G_{ii}g_{il}G_{ll}(il)g_{lj}G_{jj}(lj) + \cdots \tag{2.11}$$

where

$$\begin{aligned} g_{il} &= \frac{K_{il}}{K_{li}} \left[G_{ll}(il) + K_{li}^{-1} \right]^{-1} \\ &= F_i^{-1} \left[F_l G_{ll}(il) + \tau_{il}^{-1} \right]^{-1} \end{aligned} \tag{2.12}$$

and

$$G_{ll}(il) = \left[i\omega + \sum_{\mu \neq i} g_{l\mu} \right]^{-1} \tag{2.13}$$

It is interesting to note that this approximation is exact on a Cayley tree. An improved theory is obtained by noting that in the first place the effect of loops is to reduce the total number of self-avoiding paths from i to j and thus leads to an effective reduction of the site density. Formally this can be derived by noting the exact relation ($\omega = 0$):

$$\sum_{\mu} K_{i\mu} - \Delta_i(\omega = 0) = \sum_{l} g_{il}^{R}(\omega = 0) \tag{2.14}$$

where

$$g_{il}^{R} = \sum_{\substack{i\neq l\neq s \\ \cdots \neq \mu \neq n}} \left[\frac{K_{il}}{K_{li} + G_{ll}^{-1}(il)} \right] \times \left[\frac{K_{ls}}{K_{sl} + G_{ss}^{-1}(il;ls)} \right] \cdots \left[\frac{K_{m\mu} \cdots K_{\mu n}}{K_{\mu m} + G_{\mu\mu}^{-1}(\cdots)} \right] \tag{2.15}$$

The effect of closed loops in the self-energy has been to remove all repeated indices in the iteration of (2.12). Within the approximation scheme this leads to a scaling down of the site density n from n to $a_p n$ where $a_p = \exp(-1)$.

For configurational averaging we now apply the effective medium approximation (EMA) to equation (2.12). This together with the above considerations leads to the following nonlinear integral equation for the quantity $m(E_i, \omega) = \langle \sum_l F_i g_{il} \rangle_i$

$$m(E,\omega) = na_p \int d\mathbf{R} \int dE' \frac{\rho(E')\tau(E,E',\mathbf{R})}{1 + \tau(E,E',\mathbf{R})/\left[i\omega F(E') + m(E',\omega) \right]} \tag{2.16}$$

where $\rho(E)$ is the normalized energy distribution function and we have assumed that the sites are randomly distributed.

One can also develop a self-consistent three-site approximation along the same lines. The details are given in Refs. 11 and 12. The idea is to keep the memory of the *two* previous sites visited by the particle and re-randomize over the rest. The proper treatment of three-site loops, which is thus guaranteed, is essential for the Hall conductivity in low-density systems (see Chapter 3). The longitudinal conductivity, however, is well approximated by the two-site theory.

In the case of symmetric rates we need not keep the energy dependence in $m(\omega)$ and obtain a simpler EMA equation for $m(\omega) = \langle (1/N) \sum_{ij} g_{ij} \rangle$, where $N = nV$ is the number of sites (V is the volume):

$$m(\omega) = na_p \int d\mathbf{R} \int d\Delta E \frac{\rho(\Delta E)\, W(\Delta E, \mathbf{R})}{1 + W(\Delta E, \mathbf{R})/\left[i\omega + m(\omega) \right]} \tag{2.17}$$

where $\rho(\Delta E)$ is the distribution of energy differences $\Delta E = |E_i - E_j|$. For this case we can give a closed expression for the averaged propagator. Defining

$$m(\mathbf{k},\omega) = \left\langle \frac{1}{N} \sum_{ij} g_{ij} \exp\{ i\mathbf{k} \cdot \mathbf{r}_{ij} \} \right\rangle \quad \text{and} \quad G(\mathbf{k},\omega) = \left\langle \frac{1}{N} \sum_{ij} G_{ij} \exp\{ i\mathbf{k} \cdot \mathbf{r}_{ij} \} \right\rangle$$

we have from (2.11) and the EMA:

$$G(\mathbf{k},\omega) = \left[i\omega - m(\mathbf{k},\omega) + m(\mathbf{o},\omega) \right]^{-1} \tag{2.18}$$

This obviously is the solution of a generalized master equation for $G(\mathbf{r},t)$ with the rates K_{ij} replaced by memory kernels $m(\mathbf{r}-\mathbf{r}', t-t')$.[13,43]

Expanding $m(\mathbf{k},\omega)$ to lowest order in $\mathbf{k}$ leads to $G(\mathbf{k},\omega) = [i\omega + D(\omega) k^2]^{-1}$ where

$$D(\omega) = -\frac{1}{2}\left(\frac{\partial}{\partial k_x}\right)^2 m(\mathbf{k},\omega)\bigg|_{\mathbf{k}=\mathbf{o}} = \frac{n}{6}\int d^3R \frac{R^2 \rho(\Delta E) W(\Delta E, \mathbf{R})}{1 + W(\Delta E, \mathbf{R})/\left[i\omega + m(\omega) \right]} \tag{2.19}$$

is the frequency-dependent diffusion coefficient connected with the conductivity by the Einstein relation

$$G_{xx}(\omega) = (nn_c e^2/k_B T) D(\omega) \tag{2.20}$$

Here e is the electronic charge and n_c is the number of carriers per site. In the case of asymmetric, energy-dependent rates the current–current correlation function must be evaluated directly for the conductivity tensor. The corresponding expressions will be given below.

2.3. Comparison with Other Theories

We can recover the two-body self-consistent diagrammatic theory of Gochanour *et al.*[7] (GAF) by rewriting the renormalized expansion[7] in the form

$$G_{ij} = \frac{\delta_{ij}}{i\omega + \sum_\mu g_{i\mu}} + \frac{}{i\omega + \sum_{\mu\neq j} g_{i\mu}} \tilde{g}_{ij} \frac{}{i\omega + \sum_{l\neq i} g_{jl}} + \cdots \tag{2.21}$$

where

$$\tilde{g}_{ij} = \left[g_{ij}^{-1} + \left(i\omega + \sum_{\mu\neq j} g_{i\mu}\right)^{-1} \right]^{-1} \tag{2.22}$$

If we now replace the $\sum_{\nu\neq s} g_{\mu\nu}$ everywhere in (2.21) and (2.22) with $\sum_{\nu\neq s} \tilde{g}_{\mu\nu}$ and carry out the EMA we recover precisely the two-body approximation of GAF. In fact it is equivalent to replacing the bare propagator g_{ij} with the effective pair propagator $\tilde{g}_{ij}$ determined self-consistently within an effective medium. Another way of interpreting this result is to note that in comparison to (2.15) the GAF theory is approximating the loop processes in a different manner from our theory. Indeed the results of the GAF theory are equivalent to ours if the inverse "percolation" number a_p is replaced by $1/2$ and the hop rates are effectively changed by a factor of 2. Yet another approximation which we shall call the symmetrized EMA is obtained by

replacing $g_{\mu\nu}$ with $\tilde{g}_{\mu\nu}$ in Eq. (2.21) only. This is then equivalent to the result of the conductance network approximation derived recently by Summerfield and Butcher[25] (SB). In the case of R-hopping, the SB results can hardly be distinguished from ours. These authors take a_p^{-1} from the start to be a percolation number. Within this approximation, however, some new features arise: (a) the pair result is recovered exactly in the limit $n \to 0$; (b) average currents and the average diffusion coefficient are related in the small field limit by the Einstein relation as they should.

Nevertheless all of these theories fail in describing the right high field limit. We therefore conclude—besides the considerable success of the present theory in the Ohmic regime—that a unified treatment of the complete electric field regime within the Green's function formalism is still missing.

3. THE CONDUCTIVITY AND HALL MOBILITY IN POSITIONALLY AND ENERGETICALLY DISORDERED SYSTEMS

3.1. The Conductivity Tensor

The general expressions for the frequency-dependent longitudinal and transverse (Hall-) conductivity are given by[12,16]

$$\sigma_{xx}(\omega) = \frac{e^2(i\omega)^2}{k_B T V} \left\langle \sum_{ij} x_{ij}^2 F_i G_{ij}(\omega) \right\rangle \tag{3.1}$$

$$\sigma_{xy}(\omega) = \frac{e^2(i\omega)^2}{k_B T V} \left\langle \sum_{ij} x_j y_i F_i \Delta G_{ij}^H(\omega) \right\rangle \tag{3.2}$$

where $x_i(y_i)$ are the components of $\mathbf{r}_i$ and $x_{ij} = x_i - x_j$. $G_{ij}^H = G_{ij} + \Delta G_{ij}^H$ is the solution of a generalization of (2.1) for hopping in the presence of a weak magnetic field of strength H, and ΔG_{ij}^H is the linear term in the field. The transition rates have been decomposed in the same fashion: $W_{ij}^H = W_{ij} + \Delta W_{ij}^H$ where W_{ij} are the field-free rates, so that we have

$$\tau_{ij}^H = \tau_{ij} + \sum_p \Delta\tau_{ipj}^H \tag{3.3}$$

with

$$\Delta\tau_{ipj}^H = f(E_i)\left[1 - f(E_p)\right]\left[1 - f(E_j)\right]\Delta W_{ipj}^e(H) + \left[1 - f(E_i)\right] f(E_p) f(E_j) \Delta W_{ipj}^h(H) \tag{3.4}$$

The first-order modification of $\tau_{ij}^{(H)}$ is induced by the magnetic field due to an interference process over a third site p. $W_{ipj}^{e}(H)$ is the transition probability for an electron from site i to j if the intermediate site p is empty and $W_{jpi}^{(h)}(H)$ represents the interference process for a hole from site j to i (an electron from site i to j) if the intermediate site p is occupied.[26] As noted before a three-site EMA which treats the $i-p-j$ interference processes exactly is necessary for evaluating σ_{xy}.

The final results for the conductivities are

$$\sigma_{xx}(\omega) = \frac{e^2}{k_B T}\frac{n^2}{6}\int d\mathbf{R}_{ij}\int dE_i \int dE_j \frac{\rho(E_i)\rho(E_j)\tau_{ij}}{1+\tau_{ij}/\tilde{m}(E_j,\omega)} \tag{3.5}$$

$$\sigma_{xy}(\omega) = \frac{e^2}{k_B T}\frac{n^3}{2}\int d\mathbf{R}_i \int d\mathbf{R}_j \int dE_i \int dE_p \int dE_j$$

$$\times \frac{(\mathbf{R}_i \times \mathbf{R}_j)_z \rho(E_i)\rho(E_p)\rho(E_j)\Delta\tau_{ipj}^{H}}{\left[1+\dfrac{\tau_{ij}+\tau_{jp}}{\tilde{m}(E_j,\omega)}\right]\left[1+\dfrac{\tau_{pj}+\tau_{pi}}{\tilde{m}(E_p,\omega)}\right] - \dfrac{\tau_{jp}\tau_{pj}}{\tilde{m}(E_j,\omega)\tilde{m}(E_p,\omega)}} \tag{3.6}$$

where $\tilde{m}(E,\omega) = [m(E,\omega) + i\omega F(E)]$, and $m(E,\omega)$ is given by (2.16). The Hall mobility is then given by

$$\mu_H(\omega) = \sigma_{xy}(\omega)/\mathrm{Re}\{\sigma_{xx}(\omega)\}H \tag{3.7}$$

It is obvious that whenever the factor $\tilde{m}^{-1} = [m(E,\omega) + F(E)i\omega]^{-1}$ which appears in the denominators of Eqs. (2.16), (3.5), and (3.6) becomes very small, i.e., at high densities, temperatures, and frequencies, the expressions in curly brackets may be put $= 1$. This approximation, which corresponds to the quasicrystalline approximation (QCA) in the tight-binding problem, could be called "diffusion equation approximation" since in this limit $D(\omega)$ does not depend on frequency. A similar argument applies to Eqs. (2.17) and (2.19).

3.2. Analytical and Numerical Results

An advantage of our EMA scheme is that in special cases one can obtain analytic results in a simple manner. In the case of symmetric rates Eqs. (2.17) and (2.19) are evaluated easily for the ac and dc conductivity. For asymmetric energy-dependent rates one has to solve the integral equation (2.16) numerically. However, as shown in Ref. 11 in the case of phonon-assisted hopping with a constant density of states it is

a good approximation to use symmetric "barrier" jump rates $W_{ij} = \nu_0 \exp\{-2\alpha|\mathbf{R}_{ij}| - \Delta E/k_B T\}$ with a constant $\rho(\Delta E) = \rho_0$. From (2.17) we immediately obtain for $m(\omega = 0)$

$$1 = (4T/T_0)\int_0^\infty dx\, x^3 \left[1 + \frac{m(0)}{\nu_0}\exp(x)\right]^{-1} \tag{3.8}$$

which for $T \ll T_0$ gives us

$$m(0) = \nu_0 \exp\left[-(T_0/T)^{1/4}\right]$$

with

$$T_0 = \frac{24\alpha^3}{a_p \pi n \rho_0 k_B} = \frac{T_0^{\text{Mott}}}{a_p}$$

Mott's optimization procedure[28] is therefore equivalent to neglecting closed loops. In the low-temperature regime the ac conductivity can be well approximated by[13]

$$\sigma_{xx}(\omega) = \left(\frac{nn_c e^2}{k_B T 60 \alpha^2 a_p}\right)\left(\frac{T_0}{T}\right)^{1/2} m(0)\left\{1 + \left[\frac{i\omega}{m(0)}\right]^{1-\beta}\right\} \tag{3.9}$$

with $\beta = 6(T/T_0)^{1/4}$. [At high frequencies $\sigma_{xx}(\omega)$ saturates at the QCA value.] For pure spacial hopping ("R-hopping") with $W_{ij} = \nu_0 \exp\{-2\alpha|\mathbf{R}_{ij}|\}$ we obtain in the low-density and -frequency limit ($n\alpha^{-3} \ll 1$, $\omega \ll \nu_0$)

$$m(0) = \nu_0 \exp\{-q\alpha n^{-1/3}\} \tag{3.10}$$

$$\sigma_{xx}(\omega) = \left(nn_c e^2/k_B T 40 a_p\right) n^{1/3} q^2 m(0)\left\{1 + \left[\frac{i\omega}{m(0)}\right]^{1-\beta}\right\} \tag{3.11}$$

where $q = (6/a_p\pi)^{1/3} = 1.73$ and $\beta = 5n^{1/3}/q\alpha$. σ_{xy} is easily evaluated from a formula which follows from (3.6) by letting $F(E) \to n_c$, $\tau_{ij} \to n_c W_{ij}$, etc., $\rho(E) = \delta(E)$ and $m(E, \omega) \to n_c m(\omega)$ (see Ref. 12).

The low-density result for the dc Hall mobility is

$$\mu_H \propto n^{1/3} \exp\left(-\tfrac{1}{2} q\alpha n^{-1/3}\right) \tag{3.12}$$

Note that Eqs. (3.10) and (3.12) are essentially the "percolation results."[27,29,30]

The analytic results for $\sigma_{xx}(0)$ and μ_H as well as for $\sigma_{xx}(\omega)$ are in good agreement with the full numerical evaluation of Eqs. (2.19) and (2.17) for densities $\alpha n^{-1/3} \geqslant 8$. As an example we show results of a numerical

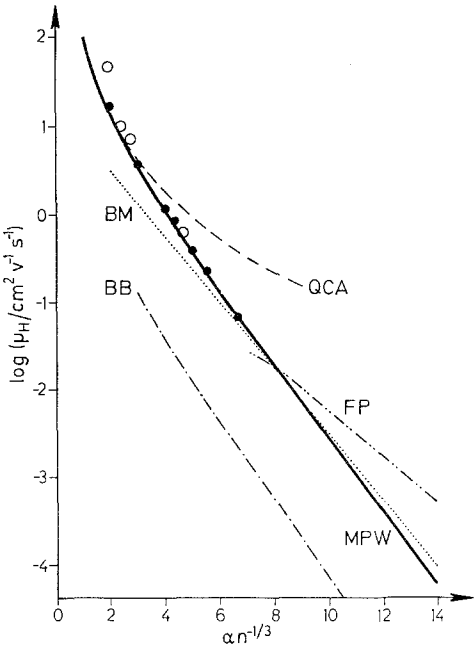

Fig. 1. dc-Hall mobility μ_H plotted against $\alpha n^{-1/3}$ for R-hopping. The solid line represents our theory. Full points are numerical simulations due to McInnes and Butcher (Ref. 32), dotted line is their theory. Open circles are experimental results by Biskupski on InP (Ref. 31). The curves marked FP and BB refer to the work of Refs. 30 and 27, QCA is the "quasi-crystalline" or diffusion equation approximation.

calculation of the Hall mobility vs. $\alpha n^{-1/3}$ in Fig. 1 and compare it with both experimental and simulation data. Open circles are experimental results of Biskupski[31] on InP samples for different doping ratios, the full points are the numerical values of McInnes and Butcher.[32] The random walk theory is in excellent agreement over the whole density range, comparing well to the experimental and simulation data.

We now apply our theory to phonon-assisted hopping at the Fermi level which is governed by the AHL jump rates[4]

$$\tau_{ij} = \nu_0 \exp\left[-2\alpha|R_{ij}| - (|E_i - E_j| + |E_i| + |E_j|)/2k_BT\right] \qquad (3.13)$$

As the rates are asymmetric, we need the full energy-dependent solution of Eqs. (2.16) and (3.5). Figure 2 shows some new results for a box-shaped density of states in comparison with computer simulations for the same set of parameters. Again we find excellent agreement between theory and computer experiment. The deviations at high densities are explained by

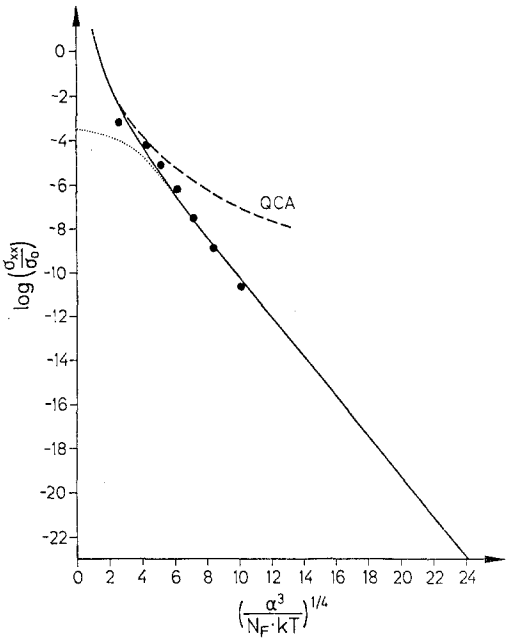

Fig. 2. The dc-conductivity $\sigma_{xx}(0)$ for the full energy-dependent model, corresponding to Eq. (3.5) is plotted against $(\alpha^3/N_F kT)^{1/2}$ (where $N_F = n\rho_0$). Points are the numerical simulations due to Summerfield and Butcher (Ref. 25) for $\alpha n^{-1/3} = 3.4$ and band width $B = 10$ meV for the energy distribution ρ_0. The solid line is the present theory with infinite band width. Making the band width finite leads to the dotted line at high T. The curve marked QCA is the "quasicrystalline" or diffusion equation approximation.

Summerfield and Butcher[25] as systematic errors of the computational procedure used by McInnes.

For the same model the temperature-dependent Hall mobility was evaluated too. As there are until now neither simulation nor experimental results available, comparison is made with other theories (Fig. 3). The percolation theoretic results of Friedman and Pollak[33] and Grünewald *et al.*[34,35] show for low densities and low temperatures the same behavior, nearly a $T^{-1/4}$ law as the random walk result, but are lower in their absolute magnitude. At high densities and high temperatures the present theory reaches the diffusion equation limit, whereas percolation theory breaks down. Note that the absolute value of the Hall mobility, marked by an arrow in Fig. 3 for a set of characteristic parameters, is very small and perhaps beyond the experimental range.

There are more theoretical and experimental results which are well

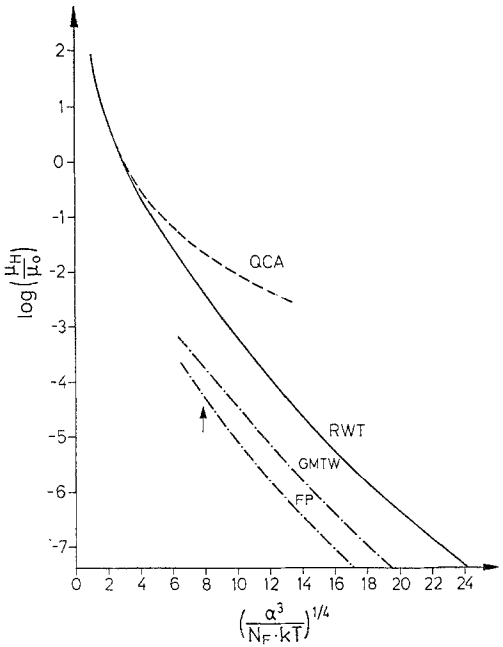

Fig. 3. The normalized Hall mobility $\log(\mu_H/\mu_0)$ plotted against $(\alpha^3/N_F kT)^{1/4}$. The full curve is the result of the present theory. The dashed line is the high-density and high-temperature QCA result. The lower broken curves have been calculated using percolation theory in Refs. 34, 35, and 33, respectively. The arrow indicates the magnitude of μ_H/μ_0 for $T = 300$ K, $N_F = 10^{19}/\text{cm}^3$ eV and $\alpha^{-1} = 10\text{Å}$ (Ref. 34).

described by the present theory: e.g., the ac Hall effect measurements of Amitay and Pollak.[36,37]

4. DISPERSIVE TRANSPORT: HOPPING VS. MULTIPLE TRAPPING

We have considered the equilibrium transport properties of phase incoherent motion in disordered systems. Let us now turn to nonequilibrium dynamic transport properties. Dispersive transport, i.e., non-Gaussian transient current traces of the form

$$i(t) \propto \begin{cases} t^{-(1-\beta)}, & t < t_T \\ t^{-(1+\beta)}, & t > t_T \end{cases} \tag{4.1}$$

(where t_T is the transient time of the fastest carriers and $0 < \beta < 1$) are a common feature of time-of-flight measurements in disordered organic and inorganic semiconductors.[38]

In their pioneering work[5,39] Montroll, Scher, and Lax explained these features in terms of incoherent hopping motion in the framework of a continuous-time random walk formalism. Later, some alternative models involving multiple trapping have been proposed.[40,41] There has been some controversy as to the mechanism which actually leads to a behavior of the form (4.1). Schirmacher[13] has shown that in principle both hopping and trapping can account for the effect. In practice it is, however, much easier to explain experimental data by including the multiple-trapping mechanism than by pure hopping as shown by Godzik and Schirmacher.[14] This will also be demonstrated below.

Considering a planar sheet of carriers created by a light flash on the surface ($x = 0$) of an infinitely extended sample of thickness L at $t = 0$, the transient current in the presence of an applied electric field of strength E can be written as[39,44]

$$i(t) = \frac{d}{dt}\overline{x - L} = \frac{d}{dt}\int_0^L dx \frac{x - L}{L} n(x,t) \tag{4.2}$$

where $n(x,t)$ is the x-dependent carrier density ("pulse shape") given by

$$n(x,t) = n_0 \int dy \int dz\, G(\mathbf{r},t) \tag{4.3}$$

and $G(\mathbf{r},t)$ is the averaged propagator (Green's function) in the continuum representation. If boundary effects are neglected $G(\mathbf{r},t)$ is just the inverse Fourier and Laplace transform of $G(\mathbf{k},\omega)$ introduced in Section 2. To include multiple trapping effects we now follow Schmidlin[42] in distinguishing between states of approximately equal energy among which hopping is allowed (transport states, occupation probability n_i) and states of much lower energy (traps, occupation probability p_i) which are only accessible via the transport states. In the absence of infinitely deep traps ($\delta_i = 0$) Eqs. (2.1) take the form

$$\begin{aligned} \frac{d}{dt} n_i &= -\sum_j K_{ij} n_i + \sum_j K_{ji} n_j - w_i n_i + r_i \sum_j n_j \\ \frac{d}{dt} p_i &= -r_i p_i + w_i n_i \end{aligned} \tag{4.4}$$

w_i and r_i are the trapping and releast rates, respectively. By Laplace transforming and assuming $p_i(t = 0) = 0$ we obtain an effective (non-Markovian) rate equation for the transport states:

$$i\omega n_i(\omega) - n_i(t = 0) = -\left[\delta_i(\omega) + \sum_j K_{ij}\right] n_i + \sum_j K_{ji} n_j \tag{4.5}$$

where $\delta_i(\omega)$ is given by $\delta_i(\omega) = i\omega w_i/(i\omega + r_i)$.

For simplicity we assume the transport rates in the absence of the field to be symmetric $K_{ij}(E=0) = W_{ij} = W_{ji}$ so that we have to first order in the field E: $K_{ij}(E) = (1 - \eta x_{ij}) W_{ij}$, where $\eta = eE/2k_BT > 0$.

As a consequence of particle conservation the propagator G can always be written as a solution of a generalized master equation[43]

$$G(\mathbf{k},\omega) = \left[i\omega - m(\mathbf{k},\omega) + m(0,\omega) \right]^{-1} \tag{4.6}$$

where the generalized transfer rates $m(\mathbf{k},\omega)$ (memory kernels) depend on the approximation scheme employed to solve the microscopic master equations (2.1). In the absence of trapping ($r_i = w_i = 0$) we obtain from (2.18) and the symmetrized version of the EMA the following self-consistent equation:

$$m(\mathbf{k},\omega) = \left\langle \frac{1}{N} \sum_{ij} \exp\{i\mathbf{k}\mathbf{R}_{ij}\} \left\{ (1 - \eta x_{ij}) \left[W_{ij}^{-1} + \left(i\omega + m(\omega) \right)^{-1} \right]^{-1} \right\} \right\rangle \tag{4.7}$$

with $m(\omega) = a_p m$ $(\mathbf{k} = 0, \omega)$. In the presence of multiple trapping, using the CPA to deal with the diagonal perturbation $\delta_i(\omega)$, $m(k,\omega)$ has to be replaced by

$$m_{\text{eff}}(\mathbf{k},\omega) = \left\{ i\omega \Big/ \left[\sum(\omega) + i\omega \right] \right\} m\left(\mathbf{k}, \sum(\omega) + i\omega\right) \tag{4.8}$$

where the self-energy $\sum(\omega)$ is determined from the CPA condition

$$\left\langle \frac{\sum(\omega) - \delta_i(\omega)}{1 - G_0\left(\sum(\omega) + i\omega\right)\left[\sum(\omega) - \delta_i(\omega)\right]} \right\rangle = 0 \tag{4.9}$$

and $G_0(i\omega) = [i\omega + m(\mathbf{0},\omega)]^{-1}$. Since δ_i is small for small ω one can use the simple equation $\sum = \langle \delta_i \rangle$ as a good approximation.

A small $\mathbf{k}$ expansion of $m(\mathbf{k},\omega)$ yields to lowest order in E

$$G(\mathbf{k},\omega) = \left[i\omega - D(\omega)\left(2\eta i k_x - k^2\right) \right]^{-1} \tag{4.10}$$

In the pure hopping case ($w_i = r_i = 0$) $D(\omega)$ is the diffusion coefficient in the absence of the field as given by Eqs. (2.19) and (2.17). In the case of additional multiple trapping we obtain from (4.8)

$$D_{\text{eff}}(\omega) = \left\{ i\omega \Big/ \left[\sum(\omega) + i\omega \right] \right\} D\left(\sum(\omega) + i\omega\right) \tag{4.11}$$

where $D(\omega)$ is the diffusion coefficient without traps.

In the form (4.1) $G(\mathbf{k},\omega)$ is the solution of a generalized Einstein–Smoluchowski equation studied by Leal Ferreira[44] and Butcher and Clark.[45] They have shown that the transient current has the form (4.1) if

$D(\omega)$ is given by

$$D(\omega) \propto (i\omega)^{1-\beta} \tag{4.12}$$

and the term $D(\omega)k^2$ in (4.1) is ignored. In fact it is quite easy to demonstrate[45] that in this case the ratio of the spread and the mean of the pulse does not depend on time, which is one of the striking features of dispersive transport.[20] As shown in Ref. 13 the $D(\omega)k^2$ term can be ignored if the experimental time scale is larger than $t_R = 1/\omega_R$, where ω_R is defined by

$$\omega_R / \mathrm{Re}\big[D(\omega_R)\big]\eta^2 = 1 \tag{4.13}$$

In all cases of practical interest this condition is fulfilled.[14,46] Evaluating the EMA and CPA, respectively, for $D(\omega)$, according to Eqs. (4.3) and (4.4), one quite generally obtains the following features: Up to the value $m_0 = m_0(\omega = 0) = 1/t_0$ $D(\omega)$ will be constant. For $\omega > \omega_0$ $\mathrm{Re}[D(\omega)]$ will rise monotonically and finally saturate if $\omega > \omega_\infty$ (ω_∞ is of the order of the microscopic time scale.)

This holds both for hopping in the absence of traps as well as for multiple trapping with constant hop rates. (The latter mechanism has been shown[13] to be identical to the model considered by Noolandi[40] and Schmidlin.[41]) In the more complicated case of trap-controlled hopping, where both W_{ij} and the trap rates r_i fluctuate, multiple trapping leads to an increase of the dispersive range of $D(\omega)$ if the hopping and trapping time scales are not well separated. If they are well separated the frequency dependence of $\mathrm{Re}[D(\omega)]$ will have a steplike structure. If now in the regime $\omega_0 < \omega < \omega_\infty$ $D(\omega)$ varies as $i\omega^{(1-\beta)}$ it follows that dispersive transport in the sense of Scher and Montroll[39] will be observable if the experimental time scale lies in the range $t_R < t < t_0$. Neglecting boundary effects the transit current within this time window is given by[44,45]

$$i(t) = \mathscr{L}^{-1}\left\{ n_0 \left[\frac{2D(\omega)\eta}{i\omega L} \right] \left[1 - \exp\left(- \frac{i\omega L}{2D(\omega)\eta} \right) \right] \right\} \tag{4.14}$$

where $\mathscr{L}^{-1}$ denotes an inverse Laplace transform. If $D(\omega)$ is parametrized as $D(\omega) = \frac{1}{6} R^2 m_0 (\omega/m_0)^{(1-\beta)}$ this will lead to a behavior of the form (4.1) with the transit time

$$t_T = t_0 (3L/\eta R^2)^{1/\beta} \tag{4.15}$$

In terms of t_T the time t_R is simply given by $t_R = t_T (2/\eta L)^{1/\beta}$. For $t > t_R$ and $\beta = 1/2$ (4.14) can be inverted analytically:[44]

$$i(t) = n_0 (t_T/\pi t)^{1/2} \big[1 - \exp(-t_T/4t) \big] \tag{4.16}$$

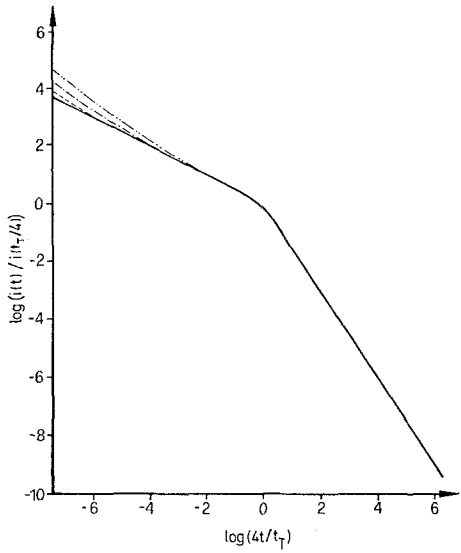

Fig. 4. log–log plot of the current $i(t)$ vs. time for $D(\omega) \propto (i\omega)^{1/2}$. The full curve is the analytic formula (4.16) (Ref. 44). The other curves are the evaluation of $i(t)$ using correct boundary conditions and the full propagator for $\eta L = 20$ (- · · · · · -), 200 (- · · · -), and 2000 (- - - -). These curves coincide completely with the full curve for $t/t_T > (\eta L)^{-2}$.

To test the quality of the approximations that led to (4.15) $i(t)$ has been evaluated[46] imposing a reflecting boundary at $x = 0$ and an absorbing boundary at $x = L$ and using the full $G(\mathbf{k}, \omega)$ including the $D(\omega)k^2$ term. In Fig. 4 the results for $i(t)$ with different values of ηL are compared with the analytic expression (4.16). Since the curves merge completely beyond the corresponding values of t_R we conclude that boundary and free diffusion effects may be neglected in the time regime $t > t_R$. In cases of experimental interest $\eta L \gg 1$ so that t_R is very small compared with the experimental time scale.

The crucial condition for the occurrence of dispersive transport now becomes

$$t_T \ll t_0 \tag{4.17}$$

or, in terms of the parameters η, L, and R: $R^2 \gg L/\eta$.

With the help of our EMA and CPA equations it is straightforward to perform reliable $i(t)$ calculations based on microscopic transport models.[46] The advantage of our method is that the main results can already be obtained from looking at the structure of $D(\omega)$. Therefore one can show[13] that both energy-dependent hopping in an exponential band tail as well as

multiple trapping with an exponential trap depth distribution lead to dispersive transport with a dispersion parameter $\beta = T/T_0$, where $k_B T_0$ is the width of the band tail.

However, if one looks at the microscopic parameters it becomes difficult to explain the experimental data by pure hopping as shown by Godzik and Schirmacher.[14]

We demonstrate this by considering the example of pure spatial hopping with a random distribution of sites (R-hopping). This case is also interesting since there have been controversal arguments as to whether such a model can lead to dispersive transport.[5,9,39–42,47,49] If $\alpha n^{-1/3}$ is smaller than 1 we are in the QCA or diffusion equation limit, i.e., D does not depend on ω, which corresponds to Gaussian transport. In the limit $\alpha n^{-1/3} \gg 1$, on the other hand, $D(\omega)$ will behave as $(i\omega)^{1-\beta}$ in the frequency range $m_0 = \nu_0 \exp\{-1.73\alpha n^{-1/3}\} = t_0^{-1} < \omega < \nu_0$ with $\beta \cong 3\alpha^{-1} n^{1/3}$. This means that systems in which the overlap of the wave functions is finite but very small ($\alpha^{-3} \ll n^{-1}$) are *in principle* capable of showing dispersive transport whereas systems with large overlap ($\alpha^{-3} \gtrsim n^{-1}$) are not. For observing the anomalous dispersion in the small-overlap (or low-density) systems the experimental time scale including t_T must lie in the interval $\nu_0^{-1} < t < t_0$. Since ν_0 is of the order of or larger than a phonon frequency (10^{12} Hz), t_0 will reach the μs region for $\alpha n^{-1/3} = 8$ and the ms region for $\alpha n^{-1/3} = 12$.

Marshall[48] made a computer simulation of a spatial hopping system identical with the above model. Although he took values of $\alpha n^{-1/3}$ up to 10, his choice of parameters corresponded in all cases to the situation $t_0 \ll t_T$, in which, according to condition (4.17) the dc current dominates the transport. This is exactly what he found and interpreted as evidence against possible dispersive transport in R-hopping systems. Which are now the parameters that lead to observable dispersive transport according to (4.17)? For R-hopping the parameter R in the prefactor of the diffusion coefficient is given by $R = 1.05 n^{-1/3}$, so that (4.17) together with (4.15) takes the form $n \ll (\eta/L)^{3/2}$ (note that α does not appear in this condition!) Marshall took $n = 1$, $\eta = 1/2$, and $L = 50$ (and varied α) which yields $(\eta/L) = 0.01$. Experimental values of η/L in the Ohmic region are[38] 10^{-10} $(\text{cm})^{-2}$ or smaller so that we must have $n \ll 10^{15}$ cm^{-3} for the observation of dispersive transport. This condition will only be fulfilled for hopping between impurities but not for bulk systems.

We conclude that the experimentally observed non-Gaussian currents in organic and anorganic amorphous semiconductors are probably always a result of multiple trapping. This confirms earlier conjectures[40,41,47] based on qualitative arguments.

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