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A mean field approximation for hopping transport in disordered materials

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Abstract. By a mean field approximation a macroscopic charge transport equation is derived from a hopping model with long range interaction. The transport coefficients are calculated from microscopic hopping characteristics of the disordered medium.

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1. INTRODUCTION

In this paper transport phenomena are discussed which can be described by a hopping model at microscopic level. Common to all these models is a very large number of particles moving on a discrete set of sites (*lattice*) according to a hopping mechanism. The hopping model of charge carrier motion on a lattice of localized energy states is a typical example. Abrahams, Anderson, Mott *et al.* proposed in the fiftieth the modelling of hopping processes. In numerous papers results both experimental and theoretical ones are published concerning charge carriers transport in solids (insulators, semiconductors, photoconductors, and other amorpheous organic materials)(see [15],[11],[12] and all the references therein). A characterisric feature of these hopping processes is the site-exclusion interaction, that means two carriers can't occupy simultaneously the same state. This exclusion principle arises from the *Pauli principle*. A fundamental theoretical problem is the question, it is possible to derive macroscopic laws of charge transport from the microscopic hopping dynamics. This question is subject of many theoretical investigations. For about twenty years many authors have given contributions about the transition from microscopic model to macroscopic deterministic transport equations by studying more or less general systems. The aim is to calculate the transport coefficients (diffusivity, conductivity, and mobility) in terms of microscopic parameters.

Basic results have been achieved in case of periodic spatial lattice with equal energy. In a rigorous way it could be shown that in absence of an external electric field the diffusivity D coincides with that given from the Green-Kubo formula. For one-dimensional periodic lattice the diffusivity is

$$D = 1/2 \sum_{k=-\infty}^{\infty} k^2 w(0, k). \quad (1.1)$$

The rate of a jump of a carrier from position x to position y is $w(x, y)$ ($= w(y, x) = w(0, y - x)$). The reason why the Green-Kubo formula leads to a closed expression and produces the true macroscopic diffusion coefficient is, roughly speaking, that already on the microscopic level the particles current density has the form of a gradient (*gradient condition*). A review of stochastic dynamics is given by H.Spohn ([22]), and the literature cited therein.

More relevant is a disordered lattice. Disordered means randomly distributed sites in space and energy. In this case we have a system of non gradient type. The situation in this physical relevant case is much more difficult. The key to a succesful treatment of disordered systems seems to be the understanding of microscopic current flow in nonequilibria (in the equilibrium the current vanishes). However, in disordered systems closed formulas for the macroscopic transport coefficients can't be expected.

Special hopping models of random media have been treated by K. W. Kehr and T. Wichmann ([12]), R. C. Brouwer and E. Salomons([19]) and P. Gardner and R. Pitis ([11]).

In this paper we start with a model of the hopping charge carriers transport in the presence of an external electric field. We consider arbitrary spatially homogeneous disordered lattices with arbitrary energy distribution and make a fairly general ansatz for the hopping rate. Due to site-exclusion interaction the transport coefficients are functions of carriers concentration. The main purpose of this paper is to show how one obtains transport

coefficients by a Mean Field Approximation under the condition of long range interaction. The parameters of these functions are the site density, the energy state distribution, and the hopping rate parameters. Finally, the conductivity, diffusivity, and mobility are discussed for special cases (low concentration, Gaussian energy density, 2-band model).

2. MODEL

There are various explanations and models of the microscopic phenomena of charge transport in solids (cf. [6]). We regard the microscopic charge carriers dynamics exclusively as a hopping process ([5], [23], [1]). The charge carriers occupy sites x on a 3-dimensional disordered lattice. Each site x is assigned to a random energy E_x from $(-\infty, \infty)$. The carriers jump on this lattice of *localized energy states* (x_i, E_{x_i}) . Arising from the Pauli principle, multiple occupancies are excluded. Apart from this *site-exclusion principle* no further interactions between the carriers are taken into consideration.

The *lattice* $S = \{(x_i, E_{x_i})\}_{i \in I}$ is an at most countable set of localized energy states. Disorder means both the set of positions $\{x_i\}_{i \in I}$ and the energy states $\{E_{x_i}\}_{i \in I}$ are distributed randomly. We only need the assumption that the probability law \mathcal{P} of S is spatially homogenous. That means \mathcal{P} is invariant under an arbitrary translation of 3-dimensional space. N denotes the *spatial concentration* of lattice sites and $g(E)$ the *energy density*. A simple consequence of homogeneity is that the probability p of finding a state with the energy E at the spatial position x is given by $p = g(E) N dE d^3x$.

N and $g(E)$ do not completely determine the probability law \mathcal{P} . However, for the mean field approximation we do not need further information about the disordered lattice S .

A further microscopic parameter is the hopping rate. It depends on the distance and the energies of sites, and on an electric field. We make the following ansatz for the *hopping rate* $w(x, E_x; y, E_y)$ of a carrier jump from state (x, E_x) to state (y, E_y) .

$$w(x, E_x; y, E_y) = \gamma s(E_x, E_y) \exp(-2|x - y|/\alpha) \exp(\mathbf{F} \cdot (y - x) e/2kT), \quad (2.2)$$

where γ denotes a material constant, e the elementary charge, k the Boltzmann constant, \mathbf{F} the electric field, T the absolute temperature, and \cdot the scalar product. $s(E, Q)$ denotes the energetic component of hopping rate. It is important to point out that the hopping rate is written on the physical macroscopic space scale. As a consequence the hopping parameter α in (1) has the form $\alpha = N^{-1/3} \bar{\alpha}$. $\bar{\alpha}$ is a finite number whereas $N^{-1/3}$ (average lattice distance) is of order of magnitude $10^{-7} \dots 10^{-9} \text{ m}^{-1}$. The material constant γ depends on temperature T .

The exponential ansatz for the spatial part of hopping rate is more or less arbitrary. It is crucial to the modelling that the spatial hopping distance have to be sufficiently small.

From the physical point of view we have to give conditions for the hopping rate $s(E, Q)$. For abbreviation, we set $\pi(E) := \exp(-E/kT)$.

The energy hopping rate $s(E, Q)$ and the energy state density $g(E)$ satisfy the following conditions

- (i) $\pi(E) s(E, Q) = \pi(Q) s(Q, E)$ (*detailed balance relation*)
- (ii) $\int \pi(E) g(E) dE < \infty$
- (iii) $s(E, Q) s(Q, E) \leq s(E, E) s(Q, Q)$.

The detailed balance relation guarantees that the equilibria of the hopping system are Fermi equilibria. From (ii) follows the existence of an equilibrium distribution for a single carrier on lattice with energy state density $g(E)$. Then the density of equilibrium distribution is equal to $\pi(E)g(E)/\int\pi(Q)g(Q)dQ$. A consequence of (iii) is that the degenerated energy band (with only one energy level) has the highest conductivity compared with a spreaded energy band (see Sect.4).

The following three examples of energy hopping rates obey (i) and (iii).

$$(I) \quad s_I(E, Q) = \begin{cases} 1 & Q \leq E, \\ \exp((E - Q)/kT) & Q > E. \end{cases}$$

(cf. [2],[5],[6],[9], [15], [24])

$$(II) \quad s_{II}(E, Q) = \exp((E - Q)/2kT).$$

(cf. [17]).

The energy hopping rates (I) and (II) are of Miller-Abraham type and are mainly used for charge carrier hopping modelling. For the modelling of diffusion of hydrogen in metals or alloys the following Arrhenius law (cf. [12]) is successfully applied.

$$(III) \quad s_{III}(E, Q) = \exp((E - E_0)/kT).$$

Above the random lattice and the hopping rate have been introduced. It remains to describe the dynamics of the hopping model. For the mathematical description of the dynamics of the hopping system with site-exclusion principle the mathematical theory of *exclusion processes* is a appropriate base.

We follow the standard modelling of an exclusion process (cf. [14], [22]). Let $S = \{(x_i, E_{x_i})\}_{i \in I}$ be a realization of random lattice with probability law \mathcal{P} . A state η of the exclusion process, called configuration on the lattice $S = \{(x_i, E_{x_i})\}_{i \in I}$, is a set of occupation numbers $\eta = \{\eta_{(x_i, E_{x_i})}\}_{i \in I}$. Where $\eta_{(x_i, E_{x_i})}$ is either 1, if a particle occupies the localized state (x_i, E_{x_i}) , or 0, if the state is vacant. $(\eta(t))_{t \geq 0}$ denotes the stochastic process of the temporal evolution of the exclusion process. The dynamics of $(\eta(t))_{t \geq 0}$ consists of a sequence of jumps. When $\eta(t)$ is the configuration before the jump of a particles from (x, E_x) to (y, E_y) , then the new configuration $\eta(t + dt)$ occurs with the rate

$$\tilde{w}(x, E_x, y, E_y; \eta(t)) = w(x, E_x; y, E_y) \eta_{(x, E_x)}(t) (1 - \eta_{(y, E_y)}(t)).$$

The dependence of the jump rate \tilde{w} on $\eta(t)$ is the consequence of the site-exclusion interaction. We will here not give an exact mathematical description of an exclusion process characterized as an Markovian jump process but refere the reader to ([14], [22]). We remark that our assumptions concerning the distribution law \mathcal{P} of lattice S and the hopping rate w guarantee that such a construction leads to a physical reasonable process. The description of dynamics of the first moments is uncomplete, but sufficient for our purpose. It is given by

$$\begin{aligned} \frac{d\mathbf{E}(\eta_{(x_i, E_{x_i})}(t))}{dt} = & - \sum_{j \in I \setminus \{i\}} w(x_i, E_{x_i}; x_j, E_{x_j}) \mathbf{E}(\eta_{(x_i, E_{x_i})}(t)(1 - \eta_{(x_j, E_{x_j})}(t))) \\ & + \sum_{j \in I \setminus \{i\}} w(x_j, E_{x_j}; x_i, E_{x_i}) \mathbf{E}(\eta_{(x_j, E_{x_j})}(t)(1 - \eta_{(x_i, E_{x_i})}(t))) \end{aligned} \quad (2.3)$$

for $i \in I$, where $\{(x_i, E_{x_i})\}_{i \in I}$ denotes a fixed realization of lattice and \mathbf{E} the expectation value with respect to the probability law of hopping process $(\eta(t))_{t \geq 0}$. In order to solve this

system of equations one needs the knowledge of the time evolution of the second moments. In the next section we will neglect the correlation and replace the expectation values $\mathbf{E}(\eta_{(x_j, E_{x_j})}(t)(1 - \eta_{(x_i, E_{x_i})}(t)))$ of products by the products $\mathbf{E}\eta_{(x_j, E_{x_j})}(t)\mathbf{E}(1 - \eta_{(x_i, E_{x_i})}(t))$ of expectation values.

3. MEAN FIELD APPROXIMATION

The main purpose of this section is to derive a charge transport equation under the assumption of long range interaction. *Long range interaction* means that the ratio $\bar{\alpha} = \alpha/N^{-\frac{1}{3}}$ is large. As a consequence the sum of jump frequencies $\sum_{j \neq i} e^{-|x_j - x_i|/\alpha}$ at x_i is close to $N \int e^{-|x|/\bar{\alpha}} d^3x$ where N denotes the concentration of the set of positions $\{x_i\}_{i \in I}$. That means the sum is approximately independent of $\{x_i\}_{i \in I}$. In order to derive the mean field approximation we need the following more general

Ergodic proposition: Provided the distribution law \mathcal{P} of $\{(x_j, E_{x_j})\}_{j \in I}$ is homogeneous and ergodic and $v(x, E)$ is continuous in (x, E) and integrable with respect to the measure $g(E) dE d^3x$, then holds for almost all realizations $\{(x_j, E_{x_j})\}_{j \in I}$

$$\frac{1}{\bar{\alpha}^3} \sum_j v\left(\frac{x_j}{\bar{\alpha}}, E_{x_j}\right) \xrightarrow{\bar{\alpha} \rightarrow \infty} \lambda \int_{\mathbf{R}^3} \int v(y, E) g(E) dE d^3y. \quad (3.1)$$

λ is the spatial concentration.

Let $f_\tau(x_i, E_{x_i}) = \mathbf{E}(\eta_{(x_i, E_{x_i})}(\tau))$, $i \in I$ be the average occupancies of states (x_i, E_{x_i}) , $i \in I$ at time τ . We assume $f_\tau(x, E_x)$ is a sufficient smooth function of x and E . The reason for the smoothness of $f_\tau(x, E_x)$ is that due to local character of hopping motion a local equilibria appears in the surroundings of every point x . This is the crucial base for the existence of a macroscopic evolution law. Under neglecting of correlations and using all this physical reasonable assumptions the equation (2.3) can be approximated by following hopping rate equation.

$$\begin{aligned} \frac{\partial f_\tau(x, E)}{\partial \tau} = & -\gamma N f_\tau(x, E) \int_{\mathbf{R}^3} \int (1 - f_\tau(y, Q)) s(E, Q) e^{-2|x-y|/\alpha + \mathbf{F} \cdot (y-x) e/2kT} g(Q) dQ d^3y \\ & + \gamma N (1 - f_\tau(x, E)) \int_{\mathbf{R}^3} \int f_\tau(y, Q) s(Q, E) e^{-2|x-y|/\alpha + \mathbf{F} \cdot (x-y) e/2kT} g(Q) dQ d^3y. \end{aligned} \quad (3.2)$$

We will denote the hopping rate equation (3.2) as Mean Field Approximation (MFA) of the microscopic dynamics (2.3).

The first term describes the average current from state (x, E) to other possible states. Analogously, the second term expresses the average current from outside to the given state.

When the energy variable E is not continuous but discrete then the integrals in this argument should be replaced by sums over possible states in all equations.

Our aim is to solve the hopping rate equation (3.2) under the assumption that the function $f_\tau(x, E)$ is sufficiently smooth. We will see that our mean field approach is well-suited to understand the qualitative different behaviour of the charge carrier ensemble on the microscopic time scale τ and on the macroscopic one t .

When $\epsilon = N^{-1/3}$ denotes the quotient of the microscopic to the macroscopic space scale then ϵ^2 is the usual rescaling factor for the time scales t and τ with $t = \epsilon^2 \tau$.

Now we can make a power series expansion of (3.2) in α ($\alpha \ll 1$). For them, we generate

the Taylor series expansion for the integrand with the exception of $e^{-2|x-y|/\alpha}$ about the point $y_0 = x$ to order y^2 . The interaction range parameter $\bar{\alpha}$ have to be large enough for the mean field approximation and small enough for the Taylor expansion. The calculation of the integrals regarding the variable y leads to

$$\begin{aligned}
\frac{\partial f_\tau(x, E)}{\partial \tau} = & \gamma \bar{\alpha}^3 \pi \left(-f_\tau(x, E) \int (1 - f_\tau(x, Q)) s(E, Q) g(Q) dQ \right. \\
& \left. + (1 - f_\tau(x, E)) \int f_\tau(x, Q) s(Q, E) g(Q) dQ \right) \\
& + \frac{\epsilon^2 \gamma \bar{\alpha}^5 \pi}{2} \left(f_\tau(x, E) \int \Delta f_\tau(x, Q) s(E, Q) g(Q) dQ \right. \\
& \left. + (1 - f_\tau(x, E)) \int \Delta f_\tau(x, Q) s(Q, E) g(Q) dQ \right) \\
& + \frac{\epsilon^2 \gamma \bar{\alpha}^5 \pi e}{2kT} \left(f_\tau(x, E) \int \nabla f_\tau(x, Q) \cdot \mathbf{F} s(E, Q) g(Q) dQ \right. \\
& \left. - (1 - f_\tau(x, E)) \int \nabla f_\tau(x, Q) \cdot \mathbf{F} s(Q, E) g(Q) dQ \right) \quad (3.3)
\end{aligned}$$

with $\epsilon = N^{-\frac{1}{3}}$ and $\bar{\alpha} = \alpha/\epsilon$.

We write the right side in the short symbolic form

$$\frac{\partial f_\tau}{\partial \tau} = \mathcal{A} f_\tau + \epsilon^2 \mathcal{B} f_\tau. \quad (3.4)$$

The Operator \mathcal{B} acts on smooth functions f of x and E whereas \mathcal{A} acts on functions only of E .

If we are interested in the behaviour of the system in microscopic time intervals then the ϵ^2 -term can be neglected. \mathcal{A} only determines the microscopic (mean field) dynamics. The stationary solutions of $\frac{\partial f_\tau}{\partial \tau} = \mathcal{A} f_\tau$ represent the local microscopic equilibria of carriers on energy states for a given local carrier concentration.

In contrast to \mathcal{A} the operator \mathcal{B} produces the spatial carrier current which varies the local concentration. That happens more slowly (of order ϵ^2) than the transition to local equilibrium. Therefore, at the varied time scaling $t \rightarrow \epsilon^{-2}t$ we ever have a local equilibrium at all macroscopic sites x and at all macroscopic times t .

In order to solve equation (3.4) we firstly calculate the stationary solutions of $\frac{\partial f_\tau}{\partial \tau} = \mathcal{A} f_\tau$.

Step 1: We evaluate the solutions from the equation $0 = \mathcal{A} f_\tau$. We write in detail

$$0 = -f(E) \int (1 - f(Q)) s(E, Q) g(Q) dQ + (1 - f(E)) \int f(Q) s(Q, E) g(Q) dQ. \quad (3.5)$$

When the following detailed equilibrium condition

$$f(E) (1 - f(Q) s(E, Q)) = (1 - f(E)) f(Q) s(Q, E) \quad (3.6)$$

is fulfilled then (3.5) holds for every $g(Q)$. Equation (3.6) is equivalent to

$$\frac{f(E)}{1 - f(E)} s(E, Q) = \frac{f(Q)}{1 - f(Q)} s(Q, E). \quad (3.7)$$

Due to the symmetry condition (i) in Sect.2 we get

$$\frac{f(E)}{1-f(E)} = a \exp(-E/kT) \quad (a \geq 0). \quad (3.8)$$

Hence we have finally the solution

$$f(E) = \frac{a \exp(-E/kT)}{1 + a \exp(-E/kT)} \quad (3.9)$$

depending on a parameter $a(a \geq 0)$. Interpreting $\zeta = kT \log a$ as chemical potential f represents the *Fermi probability* of occupation of energy state E in thermal equilibrium

$$f(\zeta, E) = \frac{\exp((\zeta - E)/kT)}{1 + \exp((\zeta - E)/kT)}. \quad (3.10)$$

Let n be the charge carrier concentration. We denote the *relative concentration* n/N by h with $0 \leq h \leq 1$. For a given relative concentration h the chemical potential $\zeta = \zeta(h)$ can be calculated from

$$h = \int f(\zeta, E) g(E) dE. \quad (3.11)$$

Step 2: By multiplying of (3.4) with $g(E)$ and following integration with respect to E we obtain

$$\frac{\partial h_t(x)}{\partial t} = \epsilon^{-2} \int (\mathcal{A} f_t)(x, E) g(E) dE + \int (\mathcal{B} f_t)(x, E) g(E) dE. \quad (3.12)$$

It is easily to see by symmetry arguments that $\int (\mathcal{A} f_t)(x, E) g(E) dE$ vanishes. Before we write the remained equation in detail we introduce a new notation. Because the Fermi probability $f_t(x, E)$ depends implicitly on the concentration $h_t(x)$ we write in (3.3) $f(h_t(x); E)$ instead of $f_t(x, E)$.

$$\begin{aligned} \frac{\partial h_t(x)}{\partial t} = & \frac{\bar{\alpha}^5 \pi}{2} \left(\iint \Delta f(h_t(x); Q) [f(h_t(x); E) s(E, Q) \right. \\ & \left. + (1-f(h_t(x); E) s(Q, E))] g(Q) g(E) dE dQ \right) \\ & + \frac{\bar{\alpha}^5 \pi e}{2kT} \left(\iint \nabla f(h_t(x), Q) \cdot F [f(h_t(x); E) s(E, Q) \right. \\ & \left. - (1-f(h_t(x); E) s(Q, E))] g(Q) g(E) dE dQ \right). \end{aligned} \quad (3.13)$$

For abbreviation we set

$$\hat{D}(h) = \iint \frac{\partial f(h; Q)}{\partial h} ((1-f(h; E)) s(Q, E) + f(h; E) s(E, Q)) g(Q) g(E) dQ dE \quad (3.14)$$

$$\hat{\sigma}(h) = \iint f(h; Q) (1-f(h; E)) s(Q, E) g(Q) g(E) dQ dE \quad (3.15)$$

and obtain via (3.10)

$$\begin{aligned}\hat{D}(h) &= \frac{1}{kT \partial h / \partial \zeta} \iint f(h; Q) (1 - f(h; E)) s(Q, E) g(Q) g(E) dQ dE \\ &= \frac{1}{kT \partial h / \partial \zeta} \hat{\sigma}(h)\end{aligned}\quad (3.16)$$

For a further rewriting of (3.13) we use the identity

$$\begin{aligned}&\iint \frac{\partial f(h_t(x); Q)}{\partial h} [f(h_t(x); E) s(E, Q) + (1 - f(h_t(x); E)) s(Q, E)] g(Q) g(E) dE dQ \\ &= -\frac{\partial}{\partial h} \iint f(h_t(x); Q) (1 - f(h_t(x); E)) s(Q, E) g(Q) g(E) dQ dE.\end{aligned}$$

In this way we obtain finally from (3.13) the temporal evolution equation of the charge density $en_t(x) = eNh_t(x)$

$$\frac{\partial en_t(x)}{\partial t} = -\text{div} \left(\frac{e}{2} N \gamma \bar{\alpha}^5 \pi \left(\hat{D}(h_t(x)) \nabla h_t(x) + \frac{e}{kT} \hat{\sigma}(h_t(x)) \mathbf{F} \right) \right). \quad (3.17)$$

$$(3.18)$$

Thus the diffusivity is

$$D(h) = \frac{e}{2} \gamma \bar{\alpha}^5 \pi \hat{D}(h_t(x)) \quad (3.19)$$

and the conductivity is

$$\sigma(h) = \frac{e}{2} N \gamma \bar{\alpha}^5 \pi \frac{e}{kT} \hat{\sigma}(h_t(x)). \quad (3.20)$$

Specially, in the simplest case of degenerate energy band (only one energy level) one obtains with $\hat{D}(h) \equiv 1$ and $\hat{\sigma}(h) = \text{const. } h(1-h)$ the transport coefficients of the well-know Burgers equation. It is the rigorously derived result for a near neighbourhood hopping model on a regular lattice ([10]). In ([19]) a model is investigated with Arrhenius law hopping rates and finite number of energy states. The result achieved in ([19]) for the diffusion coefficient coincides with $\hat{D}(h)$. We can generalize the MFA result for $D(h)$ and $\sigma(h)$.

Looking at the hopping rate equation (3.2) the MFA works in the same way as in Sect.3 when we replace $\gamma e^{-2x/\alpha}$ by a nonnegative bounded monotone decreasing function $r(x)$ ($x \geq 0$), and the hopping rate ansatz by

$$w(x, E_x; y, E_y) = s(E_x, E_y) r(|x - y|) \exp(\mathbf{F} \cdot (y - x) e/2kT) \quad (3.21)$$

with the conditions (i), (ii), (iii), and set

$$S^2 := \int_{\mathbb{R}^d} |x|^2 r(|x|) d^d x < \infty.. \quad (3.22)$$

It is not difficult to prove that under this conditions the MFA leads via taylor expansion and steps 1 and 2 to the more general formula for the conductivity than (3.20).

$$\begin{aligned}\sigma(h) &= \\ &\frac{(eN)^2}{2dkT} S^2 \iint \frac{s(Q, E) \exp((\zeta(h) - Q)/kT)}{(1 + \exp((\zeta(h) - Q)/kT))(1 + \exp((\zeta(h) - E)/kT))} g(E) g(Q) dE dQ,\end{aligned}\quad (3.23)$$

where $d = 1, 2$ or 3 is the space dimension. Here, $\sigma(h)$ is written on the microscopic time scale in contrast to (3.20). The quantity S^2 can be interpreted as measure of spatial spreading of charge carriers. The term $\hat{\sigma}(h)$ takes into account the energy structure including the Pauli principle (a very simple consequence is $\sigma(1) = 0$).

For the above mentioned example (periodic lattice in one dimension with equal energy and hopping rate $w(x, y)$) we know from (1.1) the exact value of diffusivity is

$$D = 1/2 \sum_{k=-\infty}^{\infty} k^2 w(0, k). \quad (3.24)$$

For $w(x, y) = e^{-2|y-x|/\alpha'}$ the MFA leads to

$$D = 1/2 \int_{-\infty}^{\infty} x^2 e^{-2|x|/\alpha'} dx = (\alpha')^3/4 \quad (3.25)$$

For $\alpha' = 1$ and $\alpha' = 4$ the relative error is 0.0518... and 0.0003..., respectively.

4. CONDUCTIVITY AND DIFFUSIVITY

In this section we discuss more in detail the conductivity $\sigma(h)$ and the diffusivity $D(h)$. We get from (3.23), (3.22), (3.15), (3.16), and (4.6)

$$\sigma(h) = \frac{(eN)^2}{2d kT} S^2 \hat{\sigma}(h), \quad (4.1)$$

$$D(h) = \frac{eN}{2d} S^2 \hat{D}(h), \quad (4.2)$$

and

$$\mu(h) := \frac{\sigma(h)}{en} = \frac{eN}{2d kT} S^2 \hat{\mu}(h) \quad (4.3)$$

with

$$\hat{\sigma}(h) = \iint \frac{s(Q, E) \exp((\zeta(h) - Q)/kT)}{(1 + \exp((\zeta(h) - Q)/kT))(1 + \exp((\zeta(h) - E)/kT))} g(E) g(Q) dE dQ. \quad (4.4)$$

We remark that the integrand is a symmetric function of E and Q because the function $a(E, Q) := \exp(-Q/kT) s(Q, E)$ is symmetric due to the detailed balance relation (i).

For simplicity, we also call $\hat{\sigma}(h)$, $\hat{D}(h)$, and $\hat{\mu}(h) = \hat{\sigma}(h)/h$ the conductivity, diffusivity, and mobility, respectively. From (3.16) we get the formulas for diffusivity

$$\hat{D}(h) = \hat{\sigma}(h) / \int \frac{\exp((\zeta(h) - E)/kT)}{(1 + \exp((\zeta(h) - E)/kT))^2} g(E) dE \quad (4.5)$$

and mobility

$$\hat{\mu}(h) = \hat{\sigma}(h) / \int \frac{\exp((\zeta(h) - E)/kT)}{1 + \exp((\zeta(h) - E)/kT)} g(E) dE. \quad (4.6)$$

The influence of energy state density is not immediately to see because the dependence of the chemical potential ζ on relative concentration h is not explicitly known but only the inverse function

$$h(\zeta) = \int \frac{\exp((\zeta - E)/kT)}{1 + \exp((\zeta - E)/kT)} g(E) dE \quad (4.7)$$

is given. To illustrate the behaviour of conductivity $\hat{\sigma}(h)$ (or mobility $\hat{\mu}(h)$) and diffusivity $\hat{D}(h)$ we investigate several interesting situations.

First, we will give some general relations. When there is only one energy level E_0 then we have a *degenerate energy band* and find from (4.4) the simple formula

$$\hat{\sigma}^{\text{deg}}(h) = s(E_0, E_0) h(1 - h). \quad (4.8)$$

It is easily to see that the hopping rate $s_{II}(E, Q)$ leads to a higher conductivity than $s_I(E, Q)$.

$$\hat{\sigma}_I(h) \leq \hat{\sigma}_{II}(h) \quad (0 \leq h \leq 1) \quad (4.9)$$

holds for an arbitrary energy distribution because of

$$s_I(E, Q) \pi(E) = \min(\pi(E), \pi(Q)) \leq (\pi(E) \pi(Q))^{\frac{1}{2}} = s_{II}(E, Q) \pi(E).$$

The inequation

$$\hat{\sigma}_{II}(h) \leq \hat{\sigma}_{II}^{\text{deg}}(h) = h(1 - h) \quad (0 \leq h \leq 1), \quad (4.10)$$

is as well valid for an arbitrary energy distribution. This is easily seen by using the Schwarz inequation

$$\left(\int f(E)^{\frac{1}{2}} (1 - f(E))^{\frac{1}{2}} g(E) dE \right)^2 \leq \int f(E) g(E) dE \int (1 - f(E)) g(E) dE = h(1 - h).$$

We get analogueous results for the diffusivity $\hat{D}(h)$.

For a degenerate energy band we find

$$\hat{D}^{\text{deg}}(h) \equiv s(E_0, E_0). \quad (4.11)$$

With the same arguments as above it can be shown that

$$\hat{D}_I(h) \leq \hat{D}_{II}(h) \quad (0 \leq h \leq 1) \quad (4.12)$$

holds for an arbitrary energy distribution. Applying the Schwarz inequation in a other way we obtain

$$\hat{D}_{II}(h) \leq \hat{D}_{II}^{\text{deg}}(h) \equiv 1 \quad (0 \leq h \leq 1), \quad (4.13)$$

is as well valid for an arbitrary energy distributions.

Now we consider the class \mathcal{S} of energy hopping rates $s(E, Q)$ with $s(E, E) \equiv s(E_0, E_0)$. Obviously, then all $\hat{\sigma}^{\text{deg}}(h)$ and all $\hat{D}^{\text{deg}}(h)$ have the same value $s(E_0, E_0) h(1 - h)$ and $s(E_0, E_0)$ for $s(E, Q)$ from \mathcal{S} , respectively. If $s(E, Q)$ is from \mathcal{S} then one can prove that

$$\hat{\sigma}(h) \leq \hat{\sigma}^{\text{deg}}(h) = s(E_0, E_0) h(1 - h) \quad (4.14)$$

and

$$\hat{D}(h) \leq \hat{D}^{\text{deg}}(h) = s(E_0, E_0) \quad (4.15)$$

are valid for an arbitrary energy distribution.

Next we note that $D(h)$ and $\mu(h)$ obey a

Generalized Einstein relation: (cf. R. Kubo, M. Toda and N.Hashitsume ([13]) and H. Spohn ([22]))

$$\frac{\mu(h)}{D(h)} = \frac{\partial \ln h}{\partial \zeta}. \quad (4.16)$$

The classical term $1/kT$ is replaced here by $\frac{\partial \ln h}{\partial \zeta}$. For low concentrations h we get from (4.16) the classical Einstein relation

$$\frac{\text{mobility}}{\text{diffusivity}} = \frac{1}{kT} \quad (4.17)$$

using the limit $kT \frac{\partial \ln h}{\partial \zeta} \rightarrow 1$ as $h \rightarrow 0$.

Next, we are interested in explicit results for the diffusivity (mobility) for *low concentrations*. Due to the condition (ii) the limit $\hat{D}(0) = \lim_{h \rightarrow 0} \hat{D}(h)$ exists and $\hat{D}(0)$ is positive. One obtains

$$kT \hat{\mu}(0) = \hat{D}(0) = \frac{\iint s(E, Q) \exp(-E/kT) g(E) g(Q) dE dQ}{\int \exp(-Q/kT) g(Q) dE} \quad (4.18)$$

and for the various energy rates $s(E, Q)$ in I, II and III

$$\hat{D}_I(0) = \frac{\iint \exp(-\max(E, Q)/kT) g(E) g(Q) dE dQ}{\int \exp(-E/kT) g(E) dE}, \quad (4.19)$$

$$\hat{D}_{II}(0) = \frac{(\int \exp(-E/2kT) g(E) dE)^2}{\int \exp(-E/kT) g(E) dE}, \quad \text{and} \quad (4.20)$$

$$\hat{D}_{III}(0) = \frac{\exp(-E_0/kT)}{\int \exp(-E/kT) g(E) dE}. \quad (4.21)$$

Obviously, $\hat{D}_I(0) \leq \hat{D}_{II}(0)$ is true. Let \bar{E} be the mean $\int E g(E) dE$ of the energy state distribution. Then also holds $\hat{D}_{III}(0) \leq \hat{D}_{II}(0)$ for $E_0 \geq \bar{E}$. This is easily to show by using Jensen inequality $e^{-E_0/kT} \leq (e^{-\bar{E}/2kT})^2 \leq (\int e^{-E/2kT} g(E) dE)^2$.

In order to investigate the dependence of diffusivity on the width of the energy density we calculate $\hat{D}(0)$ for a Gaussian density $g(E)$ (E_0 is the mean and σkT is the standard deviation). In this case one obtains from (4.20) and (4.21) elementary expressions for the diffusivities at low charge carrier concentrations

$$\hat{D}_I(0) \leq \hat{D}_{II}(0) = \exp(-\sigma^2/4) \quad (4.22)$$

and

$$\hat{D}_{III}(0) = \exp(-\sigma^2/2). \quad (4.23)$$

Now, we investigate in detail a simple example with a discrete energy distribution.

2-Band model: We approximate a two narrow band system by the two dominant energy levels E_1 and E_2 . For simplicity, we assume that $E_1 = -E_2$ with $E_2 - E_1 = \Delta E \geq 0$. Let E_1 and E_2 occur with the probabilities p and $1 - p$, respectively. Further, we fix $E_0 = E_2$ in $s_{III}(E, Q)$. Then one can prove the following behaviour for large ΔE

of conductivity

$$\hat{\sigma}_I^{\Delta E}(h) \quad \text{and} \quad \hat{\sigma}_{II}^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} h(p-h) & 0 \leq h \leq p \\ (h-p)(1-h) & p \leq h \leq 1, \end{cases} \quad (4.24)$$

$$\hat{\sigma}_{III}^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} 0 & 0 \leq h \leq p \\ (h-p)(1-h) & p \leq h \leq 1, \end{cases} \quad (4.25)$$

of mobility

$$\hat{\mu}_I^{\Delta E}(h) \quad \text{and} \quad \hat{\mu}_{II}^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} p-h & 0 \leq h \leq p \\ (h-p)(1-h)/h & p \leq h \leq 1 \end{cases} \quad (4.26)$$

$$\hat{\mu}_{III}^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} 0 & 0 \leq h \leq p \\ (h-p)(1-h)/h & p \leq h \leq 1, \end{cases} \quad (4.27)$$

and diffusivity

$$\hat{D}_I^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} p & 0 \leq h < p \\ \frac{1}{2} & h = p \\ 1-p & p < h \leq 1 \end{cases} \quad (4.28)$$

$$\hat{D}_{II}^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} p & 0 \leq h < p \\ 1 & h = p \\ 1-p & p < h \leq 1 \end{cases} \quad (4.29)$$

$$\hat{D}_{III}^{\Delta E}(h) \xrightarrow{\Delta E \rightarrow \infty} \begin{cases} 0 & 0 \leq h < p \\ (1-p)/2 & h = p \\ 1-p & p < h \leq 1 \end{cases} \quad (4.30)$$

The conductivities $\hat{\sigma}_I^{\Delta E}(h)$ and $\hat{\sigma}_{II}^{\Delta E}(h)$ show for varying gap widths ΔE a critical Δ^* where the bands E_1 and E_2 are decoupled. Figure 1 illustrates this for $p = \frac{1}{2}$.

For $\Delta E \leq \Delta^*$ the maximum of the conductivity is attained at $\zeta = 0$ ($h = 1/2$), and for $\Delta E > \Delta^*$ there are two relative maxima. For $p = \frac{1}{2}$ we get $\Delta_I^* \approx 2.86 kT$ and $\Delta_{II}^* \approx 3.50 kT$, and the positions of maxima of the conductivities tend to $h = .25$ and $h = .75$ as ΔE tends to ∞ .

It is surprisingly that $\hat{D}^{\Delta E}(h)$ for the hopping rate $s_I(E, Q)$ keeps smoothly whereas

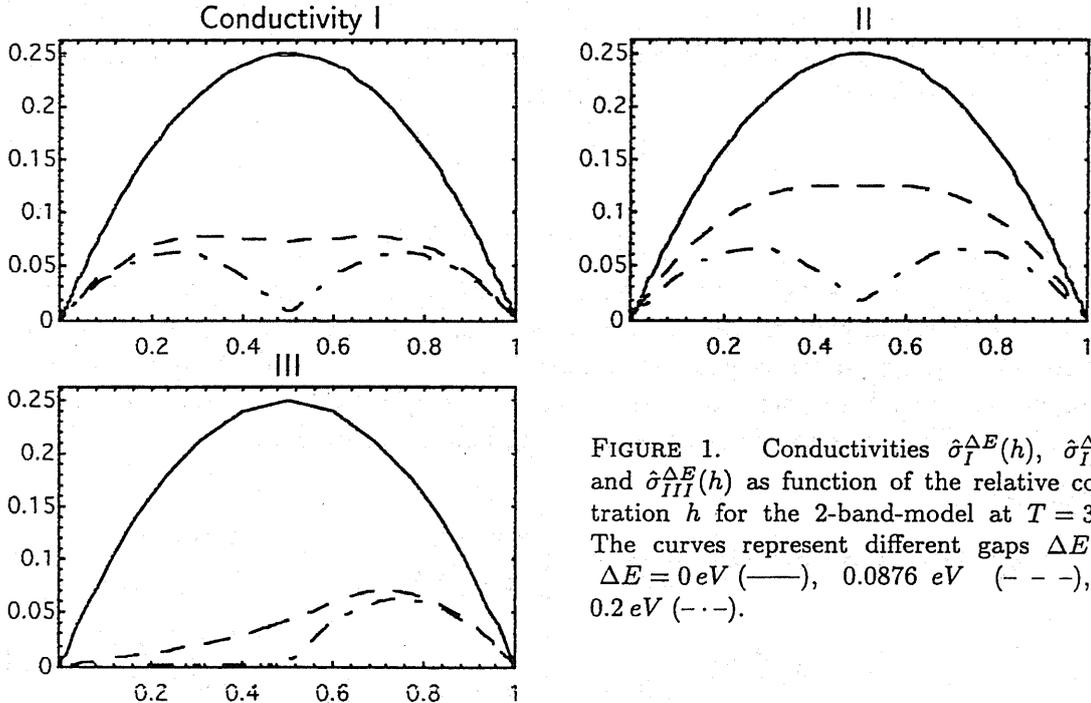


FIGURE 1. Conductivities $\hat{\sigma}_I^{\Delta E}(h)$, $\hat{\sigma}_{II}^{\Delta E}(h)$, and $\hat{\sigma}_{III}^{\Delta E}(h)$ as function of the relative concentration h for the 2-band-model at $T = 300 K$. The curves represent different gaps ΔE with $\Delta E = 0 eV$ (—), $0.0876 eV$ (---), and $0.2 eV$ (-·-).

$\hat{D}_{II}^{\Delta E}(h)$ becomes discontinuous as ΔE tends to ∞ (see Figure 2).

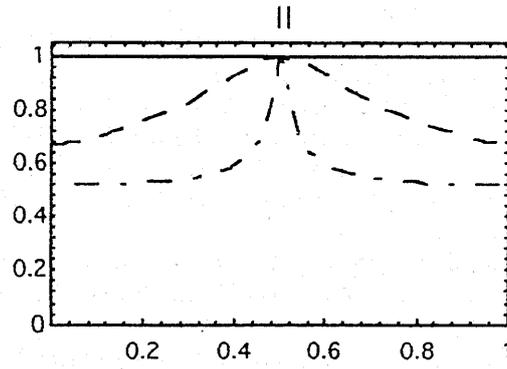
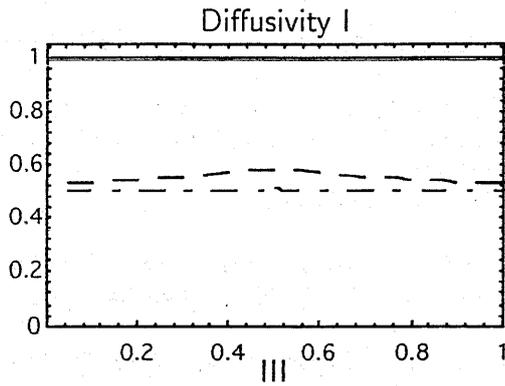


FIGURE 2. Diffusivities $\hat{D}_I^{\Delta E}(h)$, $\hat{D}_{II}(h)$, and $\hat{D}_{III}^{\Delta E}(h)$ as function of the relative concentration h for the 2-band-model at $T = 300$ K. The different curves have the same meaning as in FIGURE 1.

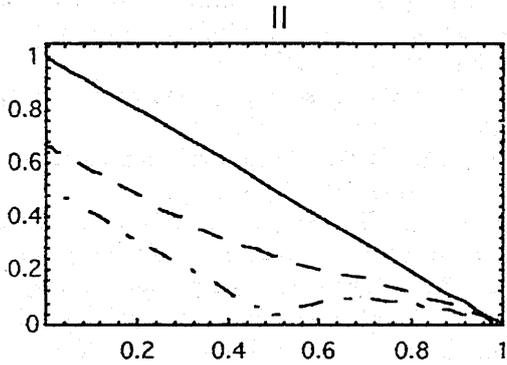
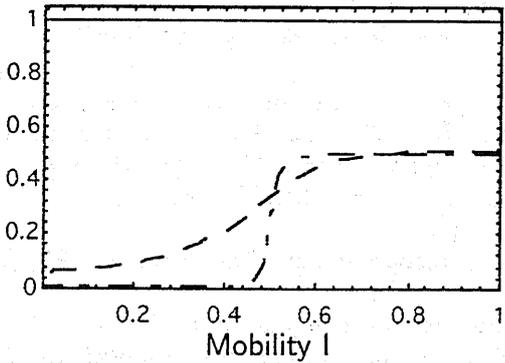
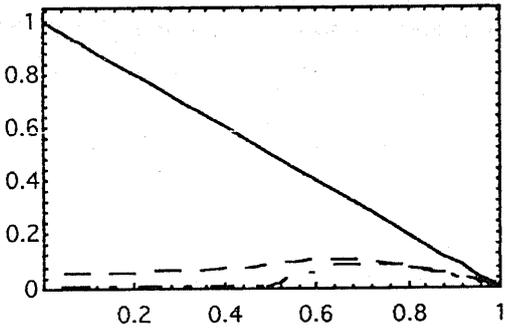
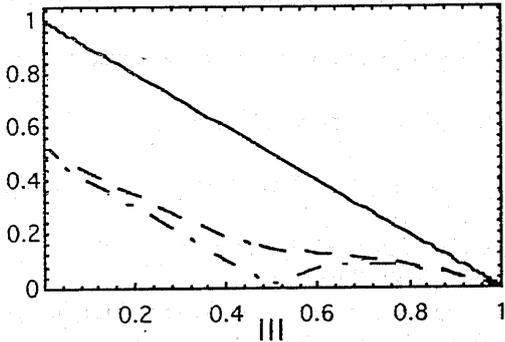


FIGURE 3. Mobilities $\hat{\mu}_I^{\Delta E}(h)$, $\hat{\mu}_{II}^{\Delta E}(h)$, and $\hat{\mu}_{III}^{\Delta E}(h)$ as function of the relative concentration h for the 2-band-model at $T = 300$ K. The different curves have the same meaning as in FIGURE 1.



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