Spacetime dependence of the anomalous exponent of electric transport in the disorder model

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Abstract

Spacetime dependence of the anomalous exponent of electric transport in the disorder model is investigated. We show that the anomalous exponent evolves with time, according to the time evolution of the number of the effective neighbouring sites. Transition from subdiffusive to normal transport is recovered at macroscopic timescales. Plateaus appear in the history of the anomalous exponent due to the discreteness of the hopping sites, which is compatible with the conventional treatment to regard the anomalous exponent as a constant. We also show that, among various microscopic spatial structures, the number of the effective neighbouring sites is the only element which determines the anomalous exponent. This is compatible with the mesoscopic model of Scher–Montroll. These findings are verified by means of Monte Carlo simulation. The well-known expression of the anomalous exponent in the conventional multiple trapping model is derived by deducing it as a special case of the disorder model.

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1. Introduction

Noncrystalline materials, representative examples of which are organic electro-luminescence, organic photoconductors and amorphous Si photoconductors, are readily seen around us. For instance, photoconductors are used in photocopiers, laser beam printers and solar cells. Since to control the electric conductivity in the above-mentioned devices is crucial for their development and design, it is necessary to investigate the mechanisms of their carrier transport.

Electric conductivity in noncrystalline materials is known to be dominated by the so-called hopping conductance. It is widely recognized that hopping conductance results in anomalous diffusion (subdiffusion) at a certain mesoscopic scale [1]. Experimentally, the anomaly manifests itself in the long tail of the time-of-flight (TOF) signal [1–3].
Anomalous diffusion has been thoroughly studied in the context of continuous-time random walk (CTRW) [4]. Anomalous diffusion is characterized by an exponent \( \alpha \) of the power-law behaviour of the mean-squared displacement with respect to time \( t \). This exponent is referred to as the anomalous exponent, and subdiffusion corresponds to the case \( 0 < \alpha < 1 \). In this case, the anomalous exponent is essentially coincident with the exponent of the power law of the waiting time of the walker \( w(t) \) at its tail, i.e. \( w(t) \sim t^{-(1+\alpha)} \) in the long-time limit. It is known that the continuum limit of CTRW with the above waiting time is described by the fractional diffusion advection equation of order \( \alpha \) [4]. It is notable that, in CTRW, the above-mentioned anomaly can be expressed by a single parameter \( \alpha \). In fact, by varying \( \alpha \), the long tail of the TOF signals can be fitted, as shown in [1]. However, since \( \alpha \) is treated as a parameter in the CTRW, it is significant to study the relation of \( \alpha \) and physical quantities of interest, such as the density of state (DOS) of the trap levels, or the spatial structure of the hopping sites, for physical understanding of the hopping conductance.

Such relations were partially given by the ‘multiple trapping model (MTM)’ [5, 6] and the ‘Scher–Montroll model (SMM)’ [1, 3, 7, 8]. In the MTM, \( \alpha \) is related to the DOS of the trap levels and the temperature \( T \) as \( \alpha = T/T_c \), where \( T_c \) is the typical width of the DOS. The DOS is assumed to be of the exponential type, \( p(E) = e^{E/(k_BT_c)}/(k_BT_c) \) \( (E \leq 0) \), where the origin of the energy is set to the edge of the conduction band. This type of DOS is typical for disordered inorganic semiconductors [9]. However, in the MTM, the relation of the anomalous exponent and the spatial structure of hopping sites is unclear. On the other hand, in the SMM, which is an effective media model in the mesoscopic scale, spatial structures of hopping sites, such as the number density and the lattice spacing, are taken into account. Here, the number density is assumed to be constant and the lattice spacing be continuous [7, 8]. The exact form of the waiting time in the SMM is determined, although complicated, by using the mathematical technique given in [10]. However, in the SMM, the relation of the anomalous exponent and (i) the DOS and (ii) the microscopic spatial structure of hopping sites, such as the connectivity and the discreteness, is unclear.

On the other hand, hopping conductance has been studied mainly by two microscopic models, which take into account both the microscopic spatial structure of the hopping sites and the DOS. One is the ‘disorder model’ [11], which is studied in this paper, and the other is the ‘polaron model’ [12–14]. The former is suitable for a system where the anomalous charge transport is dominantly activated by the static energy disorder of the hopping sites, and where the effect of the weak electron–phonon coupling is relatively negligible. In contrast, the latter is suitable for a system with strong electron–phonon couplings, and with relatively negligible effects of the energy disorder [15].

In the disorder model, the hopping rate between two sites is described by the conventional model of [16], which is based on [17]. As we will review briefly, this model incorporates the information of the microscopic spatial structure of the hopping sites, which both the MTM and the SMM neglect. To solve the model of [16], Monte Carlo (MC) simulation has been performed [11], and the anomalous exponent has been extracted numerically. However, the relation of the anomalous exponent and physical quantities, such as the microscopic spatial structure of the hopping sites and the DOS, has not been established theoretically until present. In other words, the theoretical understanding of the ‘disorder model’ seems to be left in a premature state. The aim of this paper is to promote this issue.

In this paper, we first review the disorder model and its related issues. Secondly, we calculate the anomalous exponent theoretically and derive its asymptotic form. Then, the theoretical result is verified by MC simulation. The methodology of the simulation is briefly

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1 In [24, 25], a weak breakdown of ergodicity is reported in subdiffusive processes of CTRW type.

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explained and the consistency of the theory and the simulation is shown. The relation of the
derived form of the anomalous exponent and the conventional one in the MTM, $\alpha = T/T_c$, is
an interesting issue. In fact, the relation between the disorder model and the MTM has been
studied numerically [18]. Hence, we discuss the relation of our result and that of the MTM
before conclusion. Finally, we summarize our study.

2. Theory

In this study, we consider the disorder model. We adopt as the DOS the exponential type
mentioned above, in order for the correspondence to the MTM. For other types of DOS, e.g.
Gaussian DOS, which is typical for organic semiconductors, similar techniques would be
applicable.

Before we proceed to the derivation of the anomalous exponent, we briefly review the
waiting time $w(t)$ of the CTRW and the hopping probability of the model of [16]. In CTRW,
the probability distribution that the carrier is at position $x$ at time $t$ is given as
\[
\rho(x,t) = \sum_{x' \neq x} \int_0^t d\tau \rho(x',\tau)\psi(x,x',t-\tau) + \Phi(x,t)\delta_{0t},
\]
if the carrier is situated at $x = 0$ at $t = 0$. Here, $\Phi(x,t) \equiv 1 - \int_0^t d\tau w(x,\tau)$, and $\psi(x',x,t)$
denotes the probability density that the carrier hops from $x$ to $x'$ after waiting time $t$. The
waiting-time probability distribution $w(x,t)$ is given in terms of $\psi(x',x,t)$ as
\[
w(x,t) = \sum_{x' \neq x} \psi(x',x,t).
\]
In the disorder model, $\psi(x',x,t)$ is expressed in the splitted form, $\psi(x',x,t) = w(t)\phi(x',x)$, where $\phi(x',x)$ is the spatial part of the probability distribution, which is normalized as $\sum_x \phi(x',x) = 1$. The time-dependent part $w(t)$ is of our interest.

The hopping probability, i.e. the probability per unit time of the carrier to hop from site $i$
to site $j$, which is denoted $v_{ij}$, is given as [16]
\[
v_{ij}(R_{ij},E_j - E_i) = v_0 e^{-2R_{ij}/\xi(E_j - E_i)/\Theta(E_j - E_i)/k_B T}.
\]
(1)
Here, $E_j$ is the energy of site $i$, $R_{ij}$ is the distance of sites $i$ and $j$, $\xi$ is the localization length
of the localized state, $v_0$ is a coefficient which represents the magnitude of the hopping rate
(typically of the order of $10^{12}$ (s$^{-1}$)), $\Theta(x)$ is Heaviside’s step function and $T$ is the temperature.
Dependence on microscopic physics, such as the carrier–phonon interaction and the phonon
DOS, is assumed to be incorporated in $v_0$. The waiting time of the carrier on site $i$, which we
denote as $w_i(t)$, is expressed in terms of $v_{ij}$ as
\[
w_i(t) = \Lambda_i e^{-\Lambda_i t},
\]
(2)
where $\Lambda_i \equiv \sum_{j \in \mathcal{N}} v_{ij}$. Here, $\mathcal{N}$ represents the set of all the sites in the system. Equation (2)
indicates that the hopping process is modelled as a homogeneous Poisson process with decay
rate $\Lambda_i$. The physical origin of the disorder of energy is that of the spatial distribution of the
hopping sites. In the disorder model, the spatial disorder is assumed to be moderate enough
that the positions of the sites fluctuate around the structured lattice points, according to some
distribution (e.g. Gaussian distribution). However, for the sake of simplicity, we incorporate
the effect of the spatial disorder to that of the disorder of the site energy, and assume that
the sites compose a structured lattice with lattice spacing $a$.

Now we calculate the anomalous exponent. We consider a system with arbitrary spatial
dimensions, where the carrier at each site is allowed to hop to all the sites in the system.
The crucial observation is that the waiting-time distribution equation (2) is merely valid for a certain energy of the site. If the energy is distributed according to some probability distribution, then the ensemble average with respect to the energy distribution, which we denote as $\langle w(t) \rangle$, should be regarded as the effective waiting time of the system [19]. The explicit expression of $\langle w(t) \rangle$ is

$$\langle w(t) \rangle = \left( \prod_{j \in N} \int_{-\infty}^{\infty} \text{d}e_{ij}p_{L}(e_{ij}) \right) w_{ij}(t)$$

$$= \left( \prod_{j \in N} \int_{-\infty}^{\infty} \text{d}e_{ij} e^{-|e_{ij}|/k_{B}T_{c}} \right) \left( \sum_{i \in N} K_{ii} e^{-\mu_{i}/k_{B}T_{c}} e^{-\sum_{e \in N, e \neq i} K_{ij} e^{-\mu_{j}/k_{B}T_{c}}} \right),$$

where

$$K_{ii} \equiv v_{0} e^{-2R_{ij}/T_{c}},$$

and $\epsilon_{ji} \equiv E_{j} - E_{i}$ is the difference of the energy of sites $i$ and $j$. It is clear from equation (4) that $K_{ii}$ can be regarded as an ‘effective hopping rate’ between sites $i$ and $j$. Note that translational invariance is assumed, as a result of the spatial coarse graining due to the integration with respect to site energies, and the subscript $i$ is omitted in the expression $w(t)$. In equation (3), we have utilized the fact that the energy difference $\epsilon_{ji}$, which is the difference of two identical probabilistic variables, obeys the Laplace distribution $p_{L}(\epsilon_{ji}) \equiv e^{-|\epsilon_{ji}|/k_{B}T_{c}}/(2k_{B}T_{c})$. We can calculate the integrals in equation (3) by two successive transformations of the integration variables, i.e. $A_{ji} = e^{-\epsilon_{ji}/k_{B}T_{c}}$ for the first step, and $C_{ji} = K_{ji}A_{ji}t$ for the second [20]. By the first transformation $A_{ji} = e^{-\epsilon_{ji}/k_{B}T_{c}}$, and using $dA_{ji}/d\epsilon_{ji} = -A_{ji}/k_{B}T_{c}$, we obtain

$$\int_{0}^{\infty} \text{d}e_{ji} e^{-K_{ii} e^{-\epsilon_{ji}/k_{B}T_{c}}} e^{-|\epsilon_{ji}|/k_{B}T_{c}} \frac{1}{2k_{B}T_{c}} = \frac{1}{2} \frac{T}{T_{c}} \int_{0}^{1} dA_{ji} A_{ji}^{-1+\frac{T}{T_{c}}} e^{-K_{ji}A_{ji}T_{c}}.$$

Then, by the second transformation $C_{ji} = K_{ji}A_{ji}t$, we obtain

$$\frac{1}{2} \frac{T}{T_{c}} \int_{0}^{1} dA_{ji} A_{ji}^{-1+\frac{T}{T_{c}}} e^{-K_{ji}A_{ji}t} = \frac{1}{2} \frac{T}{T_{c}} (K_{ji}t)^{-\frac{T}{T_{c}}} \int_{0}^{K_{ji}t} dC_{ji} C_{ji}^{-1+\frac{T}{T_{c}}} e^{-C_{ji}}$$

$$= \frac{1}{2} \frac{T}{T_{c}} (K_{ji}t)^{-\frac{T}{T_{c}}} \gamma \left( \frac{T}{T_{c}}, K_{ji}t \right).$$

Here,

$$\gamma(T/T_{c}, K_{ji}t) \equiv \int_{0}^{K_{ji}t} d\tau \tau^{-1+T/T_{c}} e^{-\tau}$$

is the lower incomplete gamma function. Similarly, we obtain

$$\int_{0}^{\infty} \text{d}e_{ji} e^{-\epsilon_{ji}/k_{B}T_{c}} e^{-K_{ii} e^{-\epsilon_{ji}/k_{B}T_{c}}} e^{-|\epsilon_{ji}|/k_{B}T_{c}} \frac{1}{2k_{B}T_{c}} = \frac{1}{2} \frac{T}{T_{c}} (K_{ji}t)^{-1-\frac{T}{T_{c}}} \gamma \left( \frac{T}{T_{c}} + 1, K_{ji}t \right).$$

Substituting equations (6) and (8) into equation (3), we have

$$\langle w(t) \rangle = \sum_{k \in N} \left[ K_{kk} \left[ \frac{T}{T_{c}} \gamma \left( \frac{T}{T_{c}} + 1, K_{kk}t \right) + e^{-K_{kk}t} \right] \prod_{j \in N, j \neq k} \frac{1}{2} \left[ \frac{T}{T_{c}} \gamma \left( \frac{T}{T_{c}}, K_{jt} \right) + e^{-K_{jt}} \right] \right].$$

This is the exact form of the effective waiting time of the disorder model. Note that equation (9) includes transitions at a single hop of a carrier to all the sites in the system.

Although equation (9) is exact, its physical meaning and its dependence on the model parameters are not clear. To elucidate these issues, we derive approximate expressions in 4
the following by extracting the dominant contribution from the neighbouring sites and by simplifying its analytic structure. We concentrate on the mesoscopic timescale, which is at most 1 (s).

It is important to note that, for the sites which satisfy the condition $K_{ij}t \ll 1$, the following relations hold:

\[
\frac{1}{2} \left[ \frac{T}{T_c} \gamma \left( \frac{T}{T_c}, K_{ij}t \right) - e^{-K_{ij}t} \left( K_{ij}t \right) + e^{-K_{ij}t} \right] \simeq 1,
\]

\[
\frac{1}{2} \left[ \frac{T}{T_c} \gamma \left( \frac{T}{T_c} + 1, K_{ij}t \right) - e^{-K_{ij}t} \left( K_{ij}t \right) + e^{-K_{ij}t} \right] \simeq 1.
\]

Furthermore, the following relation also holds for these sites:

\[
\frac{K_{ij}t}{2} \left[ \frac{T}{T_c} \gamma \left( \frac{T}{T_c} + 1, K_{ij}t \right) - e^{-K_{ij}t} \left( K_{ij}t \right) + e^{-K_{ij}t} \right] \ll 1,
\]

in combination with equation (11). Therefore, the contribution of the sites which satisfy $K_{ij}t \ll 1$ to the effective waiting time is negligible. To extract the dominant contribution, we introduce the notion of ‘effective neighbours’. We define the ‘effective neighbours’ as neighbours to which a carrier can move at a single hop. Then, by denoting the ‘effective neighbours’ at time $t$ as $\mathcal{N}_R(t)$, equation (9) can be approximated as

\[
\langle w(t) \rangle \simeq \sum_{k \in \mathcal{N}_R(t)} \left\{ \frac{K_{ik}t}{2} \left[ \frac{T}{T_c} \gamma \left( \frac{T}{T_c}, K_{ik}t \right) - e^{-K_{ik}t} \left( K_{ik}t \right) + e^{-K_{ik}t} \right] \prod_{j \in \mathcal{N}_R(t), j \neq k} \frac{1}{2} \left[ \frac{T}{T_c} \gamma \left( \frac{T}{T_c}, K_{ij}t \right) - e^{-K_{ij}t} \left( K_{ij}t \right) + e^{-K_{ij}t} \right] \right\}.
\]

Here, $\mathcal{N}_R(t)$ is identified as a set of neighbours where sites which satisfy $K_{ij}t \ll 1$ are removed from $\mathcal{N}$. For typical mesoscopic systems, it is sufficient to consider as effective neighbours the sites inside the region of radius $3a$, as will be discussed later.

Next, to simplify the analytic structure of equation (13), we attempt to approximate the lower incomplete gamma function by the gamma function. From equation (7), it is obvious that

\[
\gamma \left( \frac{T}{T_c}, K_{ij}t \right) \simeq \Gamma \left( \frac{T}{T_c} \right)
\]

holds for $K_{ij}t \gg 1$. To keep the approximation under control, we introduce a criterion which defines the precision of the approximation equation (14). We introduce a constant $C_\gamma$, where the following replacement is performed for the case $K_{ij}t > C_\gamma$:

\[
\gamma \left( \frac{T}{T_c}, K_{ij}t \right) \rightarrow \Gamma \left( \frac{T}{T_c} \right) \quad (K_{ij}t > C_\gamma, 0 < T/T_c \leq 2).
\]

Then, we can define the ‘critical radius’ $R(t)$ at time $t$,

\[
\ln \frac{C_\gamma}{2/\xi} \equiv -\frac{\ln R(t)}{V_0t},
\]

where the approximation equation (14) is applied into equation (13) for sites with $R_{ij} < R(t)$.

We further approximate equation (13) by restricting the ‘effective neighbours’ to the sites which satisfy $K_{ij}t > C_\gamma$, or, equivalently, $R_{ij} < R(t)$. As discussed below, the contribution of
the neglected sites with $1 < K_{ij}t < C_γ$ is subdominant compared to the sites in consideration. Then, equation (13) is approximated as

$$\langle w(t) \rangle \approx \sum_{k \in N_n(t)} \left\{ \frac{K_k}{2} \left[ \left( \frac{T}{T_c} \right)^2 \left( \frac{\Gamma(\frac{T}{T_c})}{(K_{ik})^{1+\frac{T}{T_c}}} + e^{-K_{ik}t} \right) \right] \prod_{j \in N_{n}(t), j \neq k} \left[ \frac{1}{2} \left( \frac{T}{T_c} \right)^2 \left( (K_{ij})^{1+\frac{T}{T_c}} + e^{-K_{ij}t} \right) \right] \right\},$$

(16)

where $N_n^c(t)$ is the ‘effective neighbours’ with $R_{ij} < R(t)$. Let us denote the set of the $n$th-nearest neighbouring sites in $N_n^c(t)$ as $N_n$. From the definition of $K_{ij}$, equation (4), it is obvious that

$$K_{ik}t = e^{-2(R_k-R_{ij})/\xi} K_{ij} t$$

(17)

($k \in N_{n-m}, j \in N_n, m \in N$) holds for the $n$th-nearest and the $(n-m)$th-nearest neighbours. For a system with typical parameters (e.g. the case shown in the numerical simulation later), $e^{-2(R_k-R_{ij})/\xi} \gg 1$ holds for the effective neighbours at the mesoscopic timescale.

Hence, for time $t$ where the $n$th-nearest neighbours are excluded in equation (13), i.e. $K_{ij}t < C_γ \ (j \in N_n)$, there exists $m \in N$ such that $K_{ij}t > C_γ \ (j \in N_{n-m})$, i.e. $(n-m)$th-nearest neighbours are included in $N_n^c(t)$. For the case $m = 1$, $(n-1)$th-nearest neighbours are included in $N_n^c(t)$, and hence $N_n^c(t)$ in equation (13) and $N_n(t)$ in equation (16) coincide. In general, the $(n-m)$th-nearest neighbours with $1 < K_{ij}t < C_γ$ are omitted in equation (16), but as far as the mesoscopic timescale is concerned, their effect on the effective waiting time is subdominant compared to that of the sites with $K_{ij}t > C_γ$, i.e. $R_{ij} < R(t)$.

We can introduce a characteristic time $τ_{ij}$, at which the site $j \in N_n$ contributes to the effective waiting time, as

$$τ_{ij} \equiv \frac{C_γ}{τ_k e^{-2K_{ij}/\xi}}.$$

(18)

As mentioned above, since $e^{-2(R_k-R_{ij})/\xi} \gg 1$ holds for the effective neighbours at the mesoscopic timescale, $τ_{ij} \gg τ_k (j \in N_n)$ also holds. This indicates that the $n$th-nearest neighbours are negligible around or below the typical timescale where $(n-1)$th neighbours are dominant. Thus, we can define a time interval $I_γ$ where the number of the ‘effective neighbours’ equals $N$. Then, it can be stated that equation (16) is valid for $t \in I_γ(t)$, where $N(t)$ is the number of sites in $N_n^c(t)$. From equation (15), the critical radius $R(t)$ increases monotonically with time. As a result, $N(t)$ increases monotonically as $\lim_{t \to \infty} N(t) = N_{tot}$, where $N_{tot}$ is the total number of sites in the system.

From equation (16), we can derive simple results for the following two limiting cases: $N(t)T \ll T_c$ and $N(t)T \gg T_c$. For the case $N(t)T \gg T_c$, taking the limit $T \to \infty$ with $T_c$ fixed in equation (16) leads to

$$\langle w(t) \rangle \approx \frac{1}{2N_e} \sum_{k \in N_n^c(t)} K_k e^{-\sum_{n \neq n_0} K_{ik}t}.$$

(19)

This is the usual Poisson distribution, and hence $α = 1$, i.e. the diffusion is normal. This is consistent with our understanding that the band conduction dominates at high temperatures.

For the case $N(t)T \ll T_c$, one can see that the first terms are dominant, respectively, in the two squared brackets in equation (16):

$$\langle w(t) \rangle \propto T^{-1-N_{n_0}(t)/2}.$$

(20)
The asymptotic form \( \langle w(t) \rangle \propto t^{-(1+N_R(t)/T_c)} \) \( t \in I_{N_R(t)} \) indicates that the coarse-grained hopping conductance possesses the feature of subdiffusion with a time-dependent anomalous exponent \( \alpha(t) = N_R(t)T/T_c \).

To summarize, we derived the asymptotic form of the anomalous exponent,

\[
\alpha(t) = \begin{cases} 
N_R(t) \frac{T}{T_c} & (N_R(t)T \ll T_c), \\
1 & (N_R(t)T \gg T_c),
\end{cases} \tag{21}
\]

which is valid for time \( t \in I_{N_R(t)} \). Equation (21) indicates that, although the microscopic spatial structure of the hopping sites\(^2\) is considered in the disorder model, the anomalous exponent is determined solely by the number of the ‘effective neighbouring sites’. (Note that the microscopic structure is reflected in the ‘effective hopping rate’ \( K_{ji} \).) This is compatible with SMM, where the anomalous exponent is determined by the number density (assumed to be constant) of the hopping sites. Our result justifies the mesoscopic treatment of the SMM. It is also clear from equation (21) that the anomalous exponent depends on time [21]. Since \( N_R(t) \) increases with time, \( \alpha(t) \) eventually becomes 1 at some time in the future, i.e. subdiffusive transport necessarily becomes normal. This is consistent with the common knowledge of nonequilibrium statistical mechanics that the Markovian property is recovered by a proper coarse graining [22]. An interesting observation of this result is that, since \( N_R(t) \) increases with time, a discrepancy with the MTM, which corresponds to the case of \( N_R(t) = 1 \), shows up. This issue will be discussed later.

3. Simulation

The asymptotic form of the anomalous exponent equation (21) is examined by the MC simulation of the hopping conductance. We mainly focus on the following three theoretical predictions: (i) the transition from subdiffusive to normal transport, (ii) the transient behaviour of the anomalous exponent and (iii) the effect of the microscopic structure of the hopping sites.

The existence of the anomalous exponent leads to the time dependence of the transport coefficients. This fact suggests that one cannot adopt the naive definition of the transport coefficients, e.g.,

\[
D = \left[ \langle x^2(t_{\text{tot}}) \rangle - \langle x(t_{\text{tot}}) \rangle^2 \right]/t_{\text{tot}}
\]

for the diffusion coefficient [11], where \( t_{\text{tot}} \) is the total duration time of the hopping process. Rather, one should estimate the corresponding moments at intermediate times, e.g.,

\[
D(t) = \left[ \langle x^2(t) \rangle - \langle x(t) \rangle^2 \right]/t \quad (0 \leq t \leq t_{\text{tot}}).
\tag{22}
\]

Estimate such as equation (22) cannot be performed in the conventional MC methods [11], which is difficult to synchronize the hopping procedure of the independent walkers. An algorithm is developed to synchronize the hopping of the walkers, whose details will be published elsewhere [23]. We adopted this algorithm to calculate the time dependence of the transport coefficients, or, equivalently, the anomalous exponent. To be more precise, in order to estimate \( \alpha \) from the MC simulation results, we used the following relation which holds for subdiffusion:

\[
\langle x^2(t) \rangle - \langle x(t) \rangle^2 \propto t^\alpha \quad (0 \leq t \leq t_{\text{tot}}).
\tag{23}
\]

From equation (23), we can estimate \( \alpha \) by fitting the simulation result at time \( t \) to the function \( f(t) = Ft^\alpha \), where \( F \) is a constant.

\(^2\) In [26], a model of random distance matrices which exhibits anomalous diffusion was studied. Dependence of the anomalous exponent on the spatial structure is shown, while the effect of energy disorder is not considered.
Before proceeding to the discussion of the simulation results, we estimate the value of $C_T$ in equation (15). Since the incomplete gamma function $\gamma(T/T_c, C_T)$ coincides with the gamma function $\Gamma(T/T_c)\) at $C_T = 100$ in at least 6 to 7 digit accuracy, we chose $C_T = 100$ for the case $0.05 \leq T/T_c \leq 1$. Substituting the following typical values, $t = 10^{-2} (s)$, $2a/\xi = 10$, $a = 10^{-9} (m)$ and $v_0 = 10^{12} (s^{-1})$ into equation (15), we obtain the critical radius $R = 1.8 \times 10^{-8} (m)$ for $C_T = 100$. This indicates that it is enough to consider at most the neighbours inside the radius $R < 3a$ for typical systems. Therefore, in realistic mesoscopic timescales, the number of the ‘effective neighbours’ is typically at most of the order of 10. This is consistent with the choice of the number of the neighbouring sites to which hopping is allowed in the disorder model of the hopping MC [11].

Now, we examine the validation of equation (21) by the MC simulation. First, in order to illuminate the transition from subdiffusive to normal transport, we study a one-dimensional system with carriers allowed to hop up to the second-nearest neighbouring sites. For a one-dimensional system, we can simplify the characteristic time defined in equation (18) as

\[
\tau_n \equiv \frac{C_T}{\gamma e^{-2an/\xi}},
\]

(24)

at which the $n$th-nearest neighbours contribute to the effective waiting time. In addition, using the above parameter values, we obtain a recurrence relation of characteristic times,

\[
\tau_{n+1} = e^{2a/\xi} \tau_n \simeq 2.2 \times 10^4 \tau_n.
\]

As mentioned in the previous section, this confirms that $(n + 1)$-th-nearest neighbours are negligible for timescales around or below $\tau_n$. The condition of the simulation is as follows: the number of carriers is $N_p = 1000000$, the parameters are $2a/\xi = 10$, $v_0 = 10^{12} (s^{-1})$ and $T/T_c = 0.375$. These values correspond to the characteristic times $\tau_1 = 2.2 \times 10^{-6} (s)$, $\tau_2 = 4.9 \times 10^{-2} (s)$, etc. Initially, all the carriers are rested at the origin. For the case where the correlation between the carriers can be neglected, this initial configuration is sensible, since in the algorithm [23] neighbours are generated independently for each carrier, where each neighbour spans a probabilistically independent sample space.

We can theoretically estimate characteristic values of $\alpha(t)$ at characteristic times. Since $T/T_c = 0.375$ and there are two sites in the first- and second-nearest neighbouring sites in the system, respectively, $\alpha(t)$ becomes

\[
\alpha(t) \simeq \begin{cases} 
0.75 & (t = \tau_1), \\
1.0 & (t \geq \tau_2).
\end{cases}
\]

(25)

Equation (25) indicates that $\alpha(t)$ approaches 1.0 eventually, taking the value 0.75 at $t = \tau_1$.

The result of the MC simulation is shown in figure 1. One can see that the result is compatible with the theoretical estimate, equation (25). Thus, transition from subdiffusive to normal transport is verified. Moreover, it can be seen that the transport is normal in the early stage of the diffusion. In this stage, since only carriers with short waiting times can hop to the neighbouring sites, the hopping is approximately unimodal. Therefore, the transport is almost normal.

Next, in order to illuminate the transient behaviour of the anomalous exponent, we chose a one-dimensional system with carriers allowed to hop up to the third-nearest neighbouring sites. The condition of the simulation is as follows: the number of carriers is $N_p = 1000000$, the parameters are $2a/\xi = 10$ and $T/T_c = 0.1$. These values correspond to the characteristic times $\tau_1 = 2.2 \times 10^{-6} (s)$, $\tau_2 = 4.9 \times 10^{-2} (s)$, $\tau_3 = 1.1 \times 10^{3} (s)$, etc.

Characteristic values of $\alpha(t)$ at characteristic times are estimated as follows. Since $T/T_c = 0.1$ and there are two sites in the first-, second- and third-nearest neighbours in the system, respectively, $\alpha(t)$ is

\[
\alpha(t) \simeq \begin{cases} 
0.2 & (t = \tau_1), \\
0.4 & (t = \tau_2), \\
0.6 & (t \geq \tau_3).
\end{cases}
\]

(26)
The result of the MC simulation is shown in figure 2. One can see that the result is compatible with the theoretical estimate, equation (26). In addition, plateaus are found around each characteristic time $\tau_n$ ($n = 1, 2, 3$). This indicates that $\alpha(t)$ can be regarded as constant at a certain time interval. This is compatible with the common treatment that $\alpha(t)$ can be regarded as constant [1]. The appearance of the plateaus originates in the discreteness of the hopping sites. Since the characteristic times of the $n$th and $(n - 1)$th neighbours, $\tau_n$ and $\tau_{n-1}$ defined in equation (24), differ by four orders of magnitude, the separation of the timescale occurs. As a result, the history of the anomalous exponent becomes stepwise.

Finally, in order to illuminate the effect of the microscopic structure of the hopping sites, two cases are chosen for illustration. One is a one-dimensional system with carriers...
allowed to hop up to the second-nearest neighbours (four sites in total; see the upper figure in figure 3). Another is a two-dimensional system with carriers allowed to hop only to the nearest neighbours (four sites in total; see the lower figure in figure 3). The condition of the simulation is as follows: the number of carriers is $N_P = 1000000$, the parameters are $2\alpha/\xi = 1$, $v_0 = 10^{12} \text{ (s}^{-1})$ and $T/T_c$ is varied in the range 0.025–1.0. The duration of the
simulation is chosen to be larger than $\tau_2$. From equation (21), it is expected theoretically that the results for the two cases are identical.

The result of the MC simulation is shown in figure 3. One can see that the results for the two cases are identical. For both cases, the simulation result coincides with the theoretically derived line $\alpha = 2T/T_c$ for $T/T_c < 2$, and it reaches $\alpha = 1$ for $T/T_c > 0.6$. The number of the neighboring sites of the two systems is identical, while microscopic structures such as the distance and the orientation between the sites differ. This result indicates that the anomalous exponent is determined solely by the number of the neighboring sites, which might be classified as a mesoscopic quantity.

The origin of this dependence to the number of the neighboring sites resides in the feature of the model that the probability distribution of the waiting time is described by a Poisson distribution equation (2) for a given site energy. Due to this feature, the dependence of the time-dependent part of $\langle w(t) \rangle$ on the distance of the sites appears (through $K_{ij} t$) in the upper limit of the integral of the incomplete gamma function, which is wiped out to infinity in the long-time limit, leaving the power-law dependence of $K_{ij} t$. The emergence of the Poisson distribution is attributed to the independence of each hopping procedure, which is valid in the weak-coupling limit of the carriers. For the strong-coupling case, intricate distribution will possibly emerge, and it is beyond the scope of this paper.

4. Relation to MTM

One of the consequences of this paper is that the anomalous exponent in the disorder model [16] is in general larger than that in the MTM [6]. To the extent of our knowledge, an exact correspondence between the disorder model and the MTM has not been stated clearly so far. In the remainder we will clarify their correspondence.

In the MTM, the carriers reside in the infinite tower of almost-continuous energy levels ('trapped levels'), as well as in the conduction band. The carriers in the conduction band ('conduction carriers') and those in the trapped level ('trapped carriers') are treated separately. The 'conduction carriers' are allowed to move to the neighbouring sites according to normal diffusion, while there is no diffusion for the 'trapped carriers'.

On the other hand, there is no distinction between the 'conduction carriers' and the 'trapped carriers' in the disorder model. In particular, the 'trapped carriers' are allowed to hop to the neighbouring sites as well. These two models apparently seem to be independent, but by imposing a constraint on the disorder model that hopping to the neighbouring sites is allowed only when the energy level of the sites coincides with $E_c$ (the energy of the lower edge of the conduction band), the anomalous exponent of the MTM can be obtained. To illuminate this correspondence, we choose a one-dimensional system with a carrier allowed to hop only to the nearest neighbouring sites. Imposing the above constraint to equation (1), the hopping rate from site $i$ to site $i \pm 1$ becomes

\[
\nu'_{i, i \pm 1} = \begin{cases} 
\nu_1 e^{-(E_i - E_{i+1})/k_B T} & (E_{i\pm 1} = E_c), \\
0 & (E_{i\pm 1} < E_c),
\end{cases}
\]

where $\nu_1 \equiv \nu_0 e^{-2a/\xi}$. Using equation (27) and choosing $E_c = 0$ for simplicity, we obtain the waiting time for this case (which we denote as $w'$) as follows:

\[
w'(E_{i-1}, E_i, E_{i+1}) = \begin{cases} 
2\nu_1 e^{E_i/k_B T} e^{-2\nu_1 e^{E_i/k_B T}} & (E_{i+1} = 0, \ E_{i-1} = 0) \\
\nu_1 e^{E_i/k_B T} e^{-\nu_1 e^{E_i/k_B T}} & (E_{i+1} = 0, \ E_{i-1} < 0) \\
\nu_1 e^{E_i/k_B T} e^{-\nu_1 e^{E_i/k_B T}} & (E_{i+1} < 0, \ E_{i-1} = 0) \\
0 & (E_{i+1} < 0, \ E_{i-1} < 0)
\end{cases}
\]
By averaging over the site energy, we obtain the effective waiting time as

\[
\langle w' (E_{i-1}, E_i, E_{i+1}) \rangle = \int_{-\infty}^{0} \frac{E_{i+1}}{k_BT_c} \int_{-\infty}^{0} \frac{E_i}{k_BT_c} \int_{-\infty}^{0} \frac{E_{i-1}}{k_BT_c} \times \langle w' (E_{i-1}, E_i, E_{i+1}) \rangle e^{E_{i+1}/k_BT_c} \epsilon^{E_i/k_BT_c} e^{-E_{i-1}/k_BT_c} \epsilon^{E_i/k_BT_c} = \int_{-\infty}^{0} \frac{E_i}{k_BT_c} 2v_1 \epsilon^{E_i/k_BT_c} e^{-2v_1 E_i/k_BT_c} \epsilon^{E_i/k_BT_c} + \int_{-\infty}^{0} \frac{E_i}{k_BT_c} v_1 \epsilon^{E_i/k_BT_c} e^{-v_1 E_i/k_BT_c} \epsilon^{E_i/k_BT_c} \int_{-\infty}^{0} \frac{E_{i-1}}{k_BT_c} \epsilon^{E_{i-1}/k_BT_c} + + \int_{-\infty}^{0} \frac{E_{i+1}}{k_BT_c} v_1 \epsilon^{E_{i+1}/k_BT_c} e^{-v_1 E_{i+1}/k_BT_c} \epsilon^{E_{i+1}/k_BT_c} \int_{-\infty}^{0} \frac{E_{i+1}}{k_BT_c} \epsilon^{E_{i+1}/k_BT_c},
\]

(29)

where \(0_- = 0 - \lim_{\delta \to +0} \delta\). Note that, due to the introduction of a specific energy \(E_i(= 0)\), the integral in equation (3) should be performed independently for the three sites \(i, \pm 1\), in the region \(E_{i\pm 1} \in (-\infty, E_i)\), respectively. Now, taking the limit \(t \gg \tau_1\), and using equation (8), we have

\[
\langle w' (E_{i-1}, E_i, E_{i+1}) \rangle \simeq v_1 \frac{T}{T_c} (2v_1 T)^{-1-\frac{T}{T_c}} \Gamma \left( \frac{T}{T_c} + 1 \right) + 2v_1 \frac{T}{T_c} (v_1 T)^{-1-\frac{T}{T_c}} \Gamma \left( \frac{T}{T_c} + 1 \right) \lim_{\delta \to +0} \epsilon^\delta
\]

\[
\propto t^{-1 - \frac{T}{T_c}}.
\]

(30)

From equation (30), we have \(\alpha = T/T_c\). This is exactly the result of the MTM [5, 6]. The generalization of the above result to the system with arbitrary numbers of neighbouring sites is tedious but straightforward, and the same result can be obtained. Thus, the MTM can be regarded as a special case of the disorder model. From the viewpoint of the disorder model, the spatial factor \(N_R(t)\) in the anomalous exponent is exactly cancelled by the constraints imposed above, leaving \(\alpha\) to be superficially insensitive to the spatial structure.

5. Summary

In this study, we have theoretically calculated the anomalous exponent in the disorder model. First of all, we have shown that the anomalous exponent is time dependent. In particular, since the characteristic timescales where the \(n\)th-nearest and the \((n + 1)\)th-nearest neighbours contribute to the effective waiting time are well separated, i.e. \(\tau_{ij} \gg \tau_{ik} (j \in N_{n+1}, k \in N_n)\), the \((n + 1)\)th-nearest neighbours can be ignored for timescales around or below \(\tau_{ik}\). This indicates that the number of the effective neighbouring sites \(N_R(t)\) is at most of the order of 10 in realistic/experimental timescales for typical systems. On the other hand, since \(N_R(t)\) increases monotonically with time, \(\alpha(t)\) eventually becomes 1 at some time in the future, i.e. subdiffusive transport eventually becomes normal. This is consistent with the common knowledge of nonequilibrium statistical mechanics.

Secondly, we have shown that, although the microscopic spatial structure is considered in the disorder model, the anomalous exponent is determined solely by the number of the ‘effective neighbouring sites’ at time \(t, N_R(t)\). This can be seen in the asymptotic form of the anomalous exponent, \(\alpha(t) = N_R(t)T/T_c\). This feature is compatible with the SMM, where the anomalous exponent is determined by the number density of the hopping sites, and justifies their mesoscopic treatment.

We have verified the above theoretical results by means of MC simulation of the hopping conductance. First, we chose a one-dimensional system with carriers allowed to hop up to the second-nearest neighbouring sites to verify the transition from subdiffusive to normal
transport. The result actually showed the transition, and the anomalous exponent was identical to the theoretical values. Next, we chose a one-dimensional system with carriers allowed to hop up to the third-nearest neighbouring sites to verify that \((n + 1)\)th-nearest neighbours can be ignored for timescales around or below \(\tau_n\). The result was consistent with the theoretical prediction. Moreover, because of the discreteness of the hopping sites, plateaus were found around each \(\tau_n\). This indicates that the anomalous exponent can be regarded as constant for certain time intervals. This is compatible with the common treatment where the anomalous exponent is assumed to be constant. Finally, a one-dimensional and a two-dimensional system, with identical numbers of effective neighbouring sites, were compared. The results were identical for the two cases, in agreement with the asymptotic form of the anomalous exponent, equation (21). It was verified that microscopic spatial structures, such as the distance and the orientation between the sites, are insensitive to the anomalous exponent.

Several comments are provided for the comparison of the disorder model and the SMM. As stated above, the mesoscopic treatment of the SMM is compatible with the disorder model. However, there are differences as well. In the SMM, the distance of the hopping sites is assumed to be continuous. As a result, the history of the anomalous exponent is also expected to be smoothly continuous. On the other hand, in the disorder model, due to the discreteness of the hopping sites, the history of the anomalous exponent is stepwise. For strongly disordered systems, however, the discreteness of the sites might be smeared out to show a smoothly continuous history of the anomalous exponent. Whether the history of the anomalous exponent is stepwise or smoothly continuous is expected to be a matter of the nature of the system, and hence case dependent.

We have also revealed the relation between the disorder model and the MTM [5, 6], which was not stated and remained obscure before. We have shown that the MTM can be expressed as a constrained version of the disorder model, where only hopping to the energy level of the conduction band is allowed. This constraint exactly cancels the factor \(N_R(t)\) in the asymptotic form of the anomalous exponent. Whether the system is better described by the ‘general (unconstrained)’ disorder model or the ‘constrained’ disorder model (i.e. MTM) is expected to be a matter of the nature of the system, and hence case dependent as well.

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References

[1] Scher H and Montroll E W 1975 Phys. Rev. B 12 2455
[2] Mort J and Pai D M 1976 Photoconductivity and Related Phenomena (Amsterdam: Elsevier)
[3] Montroll E W and Scher H 1973 J. Stat. Phys. 9 101
[4] Metzler R and Klafter J 2000 Phys. Rep. 339 1
[5] Tiedje T, Cebula J M, Morel D L and Abeles B 1981 Phys. Rev. Lett. 46 1425
[6] Bisquert J 2003 Phys. Rev. Lett. 91 010602
[7] Scher H and Lax M 1973 Phys. Rev. B 7 4491
[8] Scher H and Lax M 1973 Phys. Rev. B 7 4502
[9] Madan A and Shaw M P 1988 The Physics and Applications of Amorphous Semiconductors (New York: Academic)
[10] Cortis A, Chen Y, Scher H and Berkowitz B 2004 Phys. Rev. E 70 041108
[11] Bässler H 1993 Phys. Status Solidi b 175 15
[12] Fishchuk I I, Kadashchuk A, Bässler H and Nespůrek S 2003 Phys. Rev. B 67 224303
[13] Holstein T 1959 Ann. Phys. 8 343
[14] Seki K, Murayama K and Tachiya M 2005 Phys. Rev. B 71 235212
[15] Arkhipov V I, Emelianova E V, Kodashchuk A, Blonsky I, Nespurek S, Weiss D S and Bässler H 2002 Phys. Rev. B 65 165218
[16] Ambegaokar V, Halperin B I and Langer J S 1971 Phys. Rev. B 4 2612
[17] Miller A and Abrahams E 1960 Phys. Rev. 120 745
[18] Hartenstein B, Bässler H, Jakobs A and Kehr K W 1996 Phys. Rev. B 54 8574
[19] Kivelson S 1980 Phys. Rev. B 21 5755
[20] Uchaikin V V and Sibatov R T 2008 Commun. Nonlinear Sci. Numer. Simul. 13 715
[21] Sokolov I M, Chechkin A V and Klafter J 2004 Acta Phys. Pol. B 35 1323
[22] Toda M, Kubo R, Saito N and Hashtsume N 1991 Statistical Physics II: Nonequilibrium Statistical Mechanics (Springer Series in Solid-State Sciences) (Berlin: Springer)
[23] Watanabe K 2012 unpublished
[24] He Y, Burov S, Metzler R and Barkai E 2008 Phys. Rev. Lett. 101 058101
[25] Barkai E, Garini Y and Metzler R 2012 Phys. Today 65 29
[26] Ariel A, Yuval O and Yoseph I 2010 Phys. Rev. Lett. 105 070601