Fractional Diffusion in the Multiple-Trapping Regime and Revision of the Equivalence with the Continuous-Time Random Walk

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We investigate the macroscopic diffusion of carriers in the multiple-trapping (MT) regime, in relation with electron transport in nanoscaled heterogeneous systems, and we describe the differences, as well as the similarities, between MT and the continuous-time random walk (CTRW). Diffusion of free carriers in MT can be expressed as a generalized continuity equation based on fractional time derivatives, while the CTRW model for diffusive transport generalizes the constitutive equation for the carrier flux.

Electronic transport in disordered semiconductors may occur by hopping between localized states, by displacement through extended states, or by a combination of both mechanisms. Microscopic models of the individual electronic transitions, such as trapping and detrapping, in conjunction with assumptions about the system's statistical properties, provide equations of motion that describe the evolution of macroscopic carrier densities under required conditions, such as those of the time-of-flight measurements.

A major representative of this approach is the continuous-time random walk (CTRW) model, which describes electronic transport in a wide variety of disordered materials [1–3]. This model is based on the idea that the lengths of jump in the transitions from one localized state to another as well as the waiting time between two jumps are broadly distributed quantities. The multiple-trapping (MT) model is another very important approach to the motion of electrons in disordered systems [4,5]. In this model the displacement of conduction band electrons is limited by the rates of trapping and release from the broad, usually exponential distribution of localized states. Recently, there has been a renewed interest in these kinds of models in relation with nanoscaled semiconductor networks [6,7], where the presence of a highly conductive phase, such as a liquid electrolyte, that permeates the nanoporous network, implies that the electronic transport is mainly driven by diffusion, instead of the drift in the electrical field.

The features of macroscopic diffusion in the CTRW formalism have been amply studied [8–14] and the main results will be outlined below. It has been shown that the waiting time distribution characteristic of CTRW, $w(t) \propto t^{-(1+\alpha)}$, leads to an extension of the Fick equation that can be expressed in terms of fractional derivatives as follows:

$$\frac{\partial}{\partial t} f(x, t) = K_\alpha \left(D_{0+}^{1-\alpha} \frac{\partial^2 f}{\partial x^2} \right)(x, t). \quad (1)$$

Here, f is a probability distribution and K_α is a generalized diffusion coefficient. The fractional derivative operator, denoted as D_{0+}^α, is the Riemann-Liouville operator of order α and with lower limit $a \in$ R. It is defined as [11]

$$(D_{a+}^\alpha f)(x) = \frac{1}{\Gamma(\alpha)} \frac{d}{dx} \int_a^x (x - y)^{\alpha-1} f(y) dy. \quad (2)$$

Less attention has been paid to macroscopic diffusion equations in the MT regime, despite the widespread recognition of the significance of this model [6]. In part, this may be due to the influence of a particular equivalence between MT and CTRW. Schmidlin, Noolandi, and others [3,15–17] showed that the models, under certain conditions, yield similar results [15]. But the general structure of diffusion equations in the MT model has not been derived yet, and this is the main purpose of this Letter.

A significant point of difference between the models is the distinction between free and trapped charges in MT, which has no counterpart in CTRW. In fact the defining feature of MT is that only free electrons in transport states can diffuse [17]. It is important to realize that free and trapped charges can be distinguished experimentally in nanoscaled semiconductors by light absorption techniques [18]. Therefore the main goal of this paper is to reduce the complete set of kinetic equations of the MT model to a diffusion equation for the free electrons. We will show that diffusion of free carriers in the MT regime can be represented by a fractional diffusion equation (FDE) of the type

$$D_{0+}^\alpha f(x, t) = C_\alpha \frac{\partial^2 f(x, t)}{\partial x^2}. \quad (3)$$

This last equation is obtained directly by replacing the time derivative $\partial/\partial t$ in the Fick equation with a fractional time derivative. Interestingly, this formal extension has been considered in the literature [10,13,14,19,20], besides Eq. (1), but several authors doubted its validity because the $f(x, t)$ is not a normalized function [10,14]. Here, by constructing Eq. (3) from a kinetic model we will be able to explain the meaning of this feature.

The fact that the FDEs (1) and (3) cannot be converted one to the other was pointed out by Hilfer [13]. This fact implies a significant difference of the diffusion process in the MT and CTRW models, which leads us to study the extension of the continuity and constitutive diffusion equations in both models. Finally, the classical analogy based on a generalized master equation will be briefly discussed.

We consider the MT diffusion of carriers in extended states, affected by a continuous distribution of localized states of the exponential form

$$g(E) = \frac{N_L}{k_B T_c} \exp[(E - E_c)/k_B T_c], \qquad (4)$$

where N_L is the total density of localized sites, E_c is the lower band edge energy, k_B is Boltzmann's constant, and T_c characterizes the broadening of the distribution, with $\alpha = T/T_c < 1$ at temperature T. The model is defined by the kinetic equations for free (conduction band) electrons

$$\frac{\partial n}{\partial t} = -\frac{\partial J}{\partial x} - \int_{-\infty}^{E_c} \{\beta(E)n[1 - f_L(E)] \\ - g(E)\varepsilon(E)f_L(E)\}dE, \qquad (5)$$

and for trapped electrons

$$g(E)\frac{\partial f_L(E)}{\partial t} = \beta(E)n[1 - f_L(E)] - g(E)\varepsilon(E)f_L(E). \qquad (6)$$

In Eqs. (5) and (6) n is the density of conduction band electrons. It can be written also $n = N_c f$, where N_c is the total density and f the fractional occupancy of conduction band states (classical distribution). $f_L(E)$ is the fractional occupancy of the localized level at energy E. The probabilities of trapping and release are determined by the principle of detailed balance: $\beta(E) = g(E)\nu_0/N_c$; $\varepsilon(E) = \nu_0 \exp[-(E_c - E)/k_B T]$, where ν_0 is an attempt-to-escape frequency of order 10^{12} s^{-1}. $J = N_c j$ is the diffusive flux of conduction band electrons, which may be stated as

$$j = -K_0 \frac{\partial f}{\partial x}, \qquad (7)$$

where K_0 is the free electrons diffusion coefficient.

It should be noted that Eq. (6) represents an infinite set of equations for the different trap levels characterized by E. Often we do not need to resolve separately the occupancies in the different trap levels: the interest lies in the evolution of free carriers as affected by the traps, for example, when describing the diffusive flux of free electrons. It is important therefore to reduce the complete set of equations, (5)–(7), to a single generalized diffusion equation. This reduction will be carried out using Laplace-Fourier transforms of the MT equations. We will denote the Fourier or Laplace transform of a function by explicitly showing the dependence on the respective variable, q or u.

As an introductory step let us consider the ordinary diffusion through extended states in a trap-free system. The normal conservation equation can be written

$$uf(x, u) - f_0(x) = -\frac{\partial j(x, u)}{\partial x}. \qquad (8)$$

In terms of the random walk formalism, ordinary diffusion can be described by a finite characteristic time and jump length variance. Then the Laplace and Fourier transforms of the jump length, $\lambda(x)$, and waiting time distributions, $w(t)$, are of the forms: $w(u) \approx 1 - u\tau_0$, $\lambda(q) \approx 1 - \sigma^2 q^2$, so that $K_0 = \sigma^2 \tau_0^{-1}$ [11]. From Eqs. (7) and (8) we obtain in this case

$$f(q, u) = \frac{f_0(q)}{u + \sigma^2 \tau_0 q^2}. \qquad (9)$$

We now derive an expression like Eq. (9) for the free carriers in MT diffusion. We assume a low occupancy of traps, $f_L(E) \ll 1$ and the initial condition $f_L(E, x, 0) = 0$, i.e., electrons are initially injected to the conduction band (as in the transient photoconductivity technique [5]). From Eq. (6) we obtain a relationship between the occupancy of localized and conduction band states

$$f_L(E, x, u) = \frac{\beta(E)}{g(E)[u + \varepsilon(E)]} N_c f(x, u). \qquad (10)$$

Using Eq. (10), the Laplace transform of Eq. (5) gives

$$u\varphi(u)^{-1} f(x, u) - f_0(x) = -\frac{\partial j(x, u)}{\partial x}, \qquad (11)$$

where $f_0(x)$ is the initial occupancy of the extended states and we have introduced the quantity

$$\varphi(u) = \left(1 + \int_{-\infty}^{E_c} \frac{\beta(E)}{u + \varepsilon(E)} dE\right)^{-1}. \qquad (12)$$

The term 1 in Eq. (12) leads to ordinary diffusion, Eq. (8), and will be neglected. The integral in Eq. (12) can be evaluated readily with the change $y = (\nu_0/u)e^{(E-E_c)/k_B T}$. For the case of interest, $|u| \ll \nu_0$, the reflection formula of the Gamma function gives the following solution:

$$\int \frac{\beta(E)}{u + \varepsilon(E)} dE = \tau_\alpha^{\alpha-1} u^{\alpha-1}, \qquad (13)$$

where the characteristic time is defined as

$$\tau_\alpha = \left(\frac{\alpha}{\pi \sin(\pi\alpha)} \frac{N_L}{N_c}\right)^{1/\alpha} \nu_0^{-1}. \qquad (14)$$

Therefore, Eq. (11) yields

$$\tau_\alpha^{\alpha-1} u^\alpha f(x, u) - f_0(x) = -\frac{\partial j(x, u)}{\partial x}. \qquad (15)$$

From Eqs. (7) and (15) we obtain the diffusion equation of the MT model

$$\tau_\alpha^{\alpha-1} u^\alpha f(x, u) - f_0(x) = K_0 \frac{\partial^2 f(x, u)}{\partial x^2}. \qquad (16)$$

The Fourier transformation of Eq. (16) gives

$$f(q, u) = \frac{f_0(q)}{\tau_\alpha^{\alpha-1} u^\alpha + \sigma^2 \tau_0 q^2}. \qquad (17)$$

Recently, Hilfer showed [13] that Eq. (17) can be obtained from the FDE indicated in Eq. (3). The solutions of Eqs. (3) and (17) are given in Ref. [13]. Our analysis shows that the new FDE suggested by Hilfer, Eq. (3), is obtained from the MT model for an exponential distribution of localized states. Comparing Eqs. (3) and (17) it follows that the generalized diffusion coefficient is $C_\alpha = \sigma^2 \tau_0^{-1} \tau_\alpha^{1-\alpha}$.

By taking the zeroth moment of the distribution in Eq. (17), Hilfer [13] noted that the occupancy function decays as

$$f(q = 0, t) \propto t^{(\alpha-1)}. \qquad (18)$$

It was thereby pointed out that f cannot be a probability density because its normalization would depend on t. In fact Eq. (18) may be related to a nonstationary stochastic signal, i.e., one in which not even the first and second moments of the distribution are independent of time [21], or to fractional stationarity, $D_{0+}^\alpha f = 0$ [19]. The derivation from the MT model provides a simple interpretation for the seemingly counterintuitive [10,14,22,23] behavior of the carrier density in Eqs. (3) and (18). In a transient experiment the total concentration of conduction band electrons, $\int dx N_c f(x, t)$, decreases with time because the electrons injected initially to the conduction band (i.e., by a light flash) are falling into traps. In fact, the decay law of Eq. (18) is observed in the time decay of photoconductivity [5] and it constitutes the signature of an exponential distribution of localized states in the material.

For the sake of comparison let us review the macroscopic diffusion in the CTRW model. If the jump length and waiting time distribution are independent random variables the jump probability distribution function is $\psi(x, t) = w(t)\lambda(x)$. The expression of the probability density in the Fourier-Laplace domain for a CTRW diffusion is well known (see, e.g., [11]) and has the form

$$f(q, u) = \frac{1 - w(u)}{u} \frac{f_0(q)}{1 - \lambda(q)w(u)}. \qquad (19)$$

The distribution of waiting times, $w(t) \propto t^{-(1+\alpha)}$, gives the form $w(u) = 1 - (\tau_\alpha u)^\alpha$. Using $\lambda(q) = 1 - \sigma^2 q^2$, as above, Eq. (19) yields

$$f(q, u) = \frac{f_0(q)}{u + \sigma^2 \tau_\alpha^{-\alpha} q^2 u^{1-\alpha}}. \qquad (20)$$

Rearranging terms and taking the Fourier transform in Eq. (20), we can write the CTRW diffusion equation in the Laplace domain

$$u f(x, u) - f_0(x) = -K_\alpha u^{1-\alpha} \frac{\partial^2 f(x, t)}{\partial x^2}, \qquad (21)$$

where $K_\alpha = \sigma^2 \tau_\alpha^{-\alpha}$. The FDE in Eq. (1) is obtained from Eq. (21). The exact equivalence is shown in Ref. [8]. An additional term required in Eq. (21) for the consistency of the Laplace transformation is pointed out in Ref. [12].

The contrast between the MT and CTRW diffusion formalisms can be recognized by comparing Eqs. (16) and (21). Both equations appear to be the same, because transforming one to the other is a matter of shifting a factor $u^{\alpha-1}$ to either side of the equation. However, this manipulation changes the time dependence of the initial condition (as pointed out clearly by Hilfer [13]), giving different time-dependent solutions. In fact in Eq. (21) the probability density $f(x, t)$ of being at point x at time t maintains the normalization at all the times, which is not the case in Eq. (16). According to our interpretation this is because Eq. (21) is obeyed by all the carriers in the system and (16) only by the free carriers, as commented before.

Let us discuss separately the conservation and constitutive equations in each formalism. In MT the constitutive equation is given by the ordinary Eq. (8). The conservation equation takes the form of Eq. (15), which can be expressed, in the time domain, as [19]

$$D_{0+}^\alpha f(x, t) = -\frac{\partial j(x, t)}{\partial x}. \qquad (22)$$

This generalized continuity equation represents a reduction of the system of Eqs. (5) and (6) that maintains the essential information on the evolution of free carrier concentration.

For the CTRW model, the flux can be defined [20] as

$$j(x, t) = l \int_0^t dt' \int_{-\infty}^x P(x', t - t')\psi(x - x', t')$$
$$- l \int_0^t dt' \int_x^\infty P(x', t - t')\psi(x - x', t'), \qquad (23)$$

where $P(x, t)$ is the probability density of arriving at x exactly at time t, so that $f(x, t) = \int_0^t dt' P(x, t - t')\Psi(t')$; $\Psi(t)$ is the probability of waiting at least a time t at a site, and $l = \sigma\sqrt{\pi}/2$. Compte and Metzler [20] showed that Eq. (23), when Fourier-Laplace transformed, gives

$$j(q, u) = -i\sigma^2 \frac{uw(u)}{1 - w(u)} q f(q, u), \qquad (24)$$

and with $w(u) = 1 - (\tau_\alpha u)^\alpha$ we obtain the constitutive equation in the CTRW model

$$j(q, u) = -iK_\alpha u^{1-\alpha} q f(q, u), \qquad (25)$$

which may be written also as [20]

$$j(x, t) = -K_\alpha \left(D_{0+}^{1-\alpha} \frac{\partial f}{\partial x} \right)(x, t). \qquad (26)$$

On the other hand, in this model the conservation equation takes the normal form, Eq. (8), which together with Eq. (25) recovers the CTRW relation of Eq. (21). This analysis reveals the main difference between MT and CTRW models. Both of them can be formulated as the combination of a conservation equation and a diffusion equation, but each model generalizes a *different* equation, and only one, to a fractional time derivative.

Finally we revise the classical analogy between MT and CTRW [3,15–17]. More precisely, this result establishes that total charge in MT obeys the CTRW diffusion equation. The total density of carriers in MT is given by

$$\rho = N_c f + \int_{-\infty}^{E_c} g(E) f_L(E) dE. \qquad (27)$$

Using Eqs. (10) and (12) we obtain the relationship

$$\rho(x, u) = \varphi(u)^{-1} N_c f(x, u), \qquad (28)$$

so that Eq. (11) gives

$$u N_c^{-1} \rho(x, u) - f_0(x) = -\frac{\partial j(x, u)}{\partial x}. \qquad (29)$$

Applying Eqs. (7) and (28) we can write

$$u \rho(x, u) - \rho_0(x) = K_0 \varphi(u) \frac{\partial^2 \rho(x, u)}{\partial x^2}. \qquad (30)$$

With the particular form given in Eq. (13), $\varphi(u) = \tau_\alpha^{1-\alpha} u^{1-\alpha}$, Eq. (30) for ρ takes the expression of the CTRW FDE, Eq. (1). In general, the trap distribution defines a waiting time distribution $w(u) = [1 + u \tau_0 \varphi^{-1}]^{-1}$ so that Fourier transform of Eq. (30) can be written as the CTRW expression of the probability density in Eq. (20). An alternative expression of this result is obtained transforming Eq. (30) to the generalized master equation [17]

$$\frac{\partial}{\partial t} \rho(x, t) = \int_0^t \varphi(t - \tau) K_0 \frac{\partial^2}{\partial x^2} \rho(x, \tau) d\tau. \qquad (31)$$

Just as we have reduced above the full set of MT equations to the generalized continuity equation for the free carriers, Eq. (22), the constraint in Eq. (31) over the total carrier density in MT represents a further reduction of the system of Eqs. (5)–(7). Equation (31) may be useful to treat some problems [15], but it has the disadvantage that it loses the distinction between free and trapped carriers that is essential in many applications. As a simple example, consider the injection of a homogeneous number of excess free carriers. Equation (22) gives the rele-

vant decay law, Eq. (18), as already discussed. On the other hand Eq. (31) only indicates that $\partial \rho / \partial t = 0$ for this experiment, which of course is correct, because the total carrier concentration will be conserved in the process of decay to traps, but it is not informative.

In summary, macroscopic diffusion of free carriers in the MT regime can be described by an extension of the continuity equation where the time derivative $\partial / \partial t$ generalizes to a fractional time derivative. The resulting FDE is irreducible to that of the CTRW, and the reason for this is that CTRW generalizes instead the constitutive equation of diffusion. But the evolution of total carrier density in MT does obey a CTRW, as has been known for a long time.

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[1] H. Scher and E.W. Montroll, Phys. Rev. B **12**, 2455 (1975).
[2] H. Scher, M. F. Shlesinger, and J.T. Bendler, Phys. Today **26**, No. 1, 26 (1991).
[3] G. Pfister and H. Scher, Adv. Phys. **27**, 747 (1978).
[4] T. Tiedje and A. Rose, Solid State Commun. **37**, 49 (1981).
[5] J. Orenstein and M. Kastner, Phys. Rev. Lett. **46**, 1421 (1981).
[6] P. E. de Jongh and D. Vanmaekelbergh, Phys. Rev. Lett. **77**, 3427 (1996).
[7] J. Nelson, Phys. Rev. B **59**, 15 374 (1999).
[8] R. Hilfer and L. Anton, Phys. Rev. E **51**, R848 (1995).
[9] A. Compte, Phys. Rev. E **53**, 4191 (1996).
[10] R. Metzler, E. Barkai, and J. Klafter, Phys. Rev. Lett. **82**, 3563 (1999).
[11] R. Metzler and J. Klafter, Phys. Rep. **339**, 1 (2000).
[12] B. I. Henry and S. L. Wearne, Physica (Amsterdam) **276A**, 448 (2000).
[13] R. Hilfer, J. Phys. Chem. B **104**, 3914 (2000).
[14] E. Barkai, Phys. Rev. E **63**, 046118 (2001).
[15] F.W. Schmidlin, Phys. Rev. B **16**, 2362 (1977).
[16] J. Noolandi, Phys. Rev. B **16**, 4474 (1977).
[17] F.W. Schmidlin, Philos. Mag. B **41**, 535 (1980).
[18] G. Franco, J. Gehring, L. M. Peter, E. A. Ponomarev, and I. Uhlendorf, J. Phys. Chem. B **103**, 692 (1999).
[19] R. Hilfer, Fractals **3**, 549 (1995).
[20] A. Compte and R. Metzler, J. Phys. A **30**, 7277 (1997).
[21] A. Ambrózy, *Electronic Noise* (McGraw-Hill, New York, 1982).
[22] G. Jumarie, J. Math. Phys. (N.Y.) **33**, 3536 (1992).
[23] E. Barkai, R. Metzler, and J. Klafter, Phys. Rev. E **61**, 132 (2000).