Thoughts about Anomalous Diffusion: Time-dependent Coefficients versus Memory Functions

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Abstract

Relations between two natural generalizations of the standard diffusion equation, one involving memory functions and the other time-dependent coefficients, are investigated. It is shown that while the two descriptions are by no means equivalent to each other, each is equivalent to a spatially nonlocal generalization of the other. Explicit prescriptions to bridge the two formalisms are provided and illustrated in two physical transport situations. Experimental relevance of these considerations is also briefly discussed, one in the context of NMR microscopy, the other in that of transient gratings in molecular crystals.

1 Introduction and the Two Descriptions

Electrons and holes in a semiconducting device [1], interstitial atoms injected into a solid [2], molecules in a gas container, ink droplets in a glass of liquid, mice carrying the deadly Hantavirus over a landscape [3], all of these entities engage in a common activity: they diffuse. The study of diffusion has, therefore, been fundamental, important, and active in diverse disciplines. Famous thinkers who have made primary and oft-used contributions to such a study include not only the physicist Einstein [4] but the financial expert Bachelier [5], the former in his research on Brownian motion, the latter during his investigations of markets and stock movements. In the present manuscript, the authors report thoughts and calculations regarding two manners of the generalization of the fundamental process of diffusion. Such generalization becomes necessary when the mechanism of motion is more complex than in normal diffusion and may involve coherence, spatial restrictions, trapping, and similar features.

Non-equilibrium statistical mechanics in general, with transport theory as might be represented by diffusion processes as a sub-area, has benefitted from the early work [6] of Professor Gerard Emch on Master equations. One of the present authors (VMK) has

mentioned some of that work in another festschrift article [7] written thirty years ago. He remembers fondly the years of overlap with Gerard as a friend and colleague in Rochester in the seventies. He thanks Gerard for much he taught him by example, including kindness, integrity and punctuality. It is with pleasure that he dedicates the present article, with the consent of his co-author (FJS), to Gerard on the occasion of his seventieth birthday.

One simple manner of describing standard diffusion is via the diffusion equation. The latter states that the time-rate of change of density P of whatever is diffusing (including the probability of a random walker) equals the product of the diffusion constant D and the Laplacian of P at the spatial location under consideration: $\frac{\partial P}{\partial t} = D\nabla^2 P$. From here onwards let us consider 1-dimensional systems for the sake of simplicity. The two manners of generalization of the diffusion equation that we wish to explore in the present paper are, respectively,

$$\frac{\partial P(x,t)}{\partial t} = D\chi(t)\frac{\partial^2 P(x,t)}{\partial x^2}, \tag{1}$$

$$\frac{\partial P(x,t)}{\partial t} = D\int_0^t ds\,\phi(t-s)\frac{\partial^2 P(x,s)}{\partial x^2}. \tag{2}$$

The first introduces time-dependence into the diffusion coefficient whereas the second injects temporal non-locality. Both reduce to standard diffusion in the respective limits $\chi(t) = 1$ and $\phi(t) = \delta(t)$.

Our interest is in studying the connections, if any, between the above mentioned two alternatives to the description of non-standard diffusion. Clearly, the quantities $\chi(t)$ and $\phi(t)$ need to be related to each other before any connection can be discussed. It is possible to show [8, 9], through a study of the underlying processes not discussed here, that a sensible relationship is

$$\chi(t) = \int_0^t ds\,\phi(s). \tag{3}$$

The precise source of this relation will become clearer below, but we can notice at once that it leads to *exactly* the same evolution for the mean square displacement from the two Eqs. (1), (2). Thus, multiplying each equation by x^2, integrating over x from $-\infty$ to $+\infty$, and assuming that the probability decays at $x = \pm\infty$ sufficiently fast, following standard procedures, we get the respective evolution for the mean square displacement

$$\langle x^2(t)\rangle = \langle x^2\rangle_0 + 2D\int_0^t ds\,\chi(s), \tag{4}$$

from the χ-formalism, and

$$\langle x^2(t)\rangle = \langle x^2\rangle_0 + 2D\int_0^t dt'\int_0^{t'} ds\,\phi(s) \tag{5}$$

from the ϕ-formalism. It is immediately clear that the two evolutions give identical results provided that $\chi(t)$ is the time integral of the memory $\phi(t)$, *i.e.*, that relation (3) is true.

We will assume that relation for the rest of the paper. Additionally, for simplicity, we will take the initial value of all moments such as $\langle x^2 \rangle_0$ to vanish.

2 Higher Moments, Differences and Relations

What happens with higher moments of $P(x,t)$ in Eqs. (1) and (2)? It is straightforward to show that the χ-formalism gives, for the n-th moment (n is a positive integer) defined as $\langle x^n(t) \rangle = \int_{-\infty}^{\infty} dx x^n P(x,t)$,

$$\frac{d\langle x^n(t) \rangle}{dt} = Dn(n-1)\chi(t)\langle x^{n-2}(t) \rangle. \tag{6}$$

For the evolution of the same quantity, the ϕ-formalism gives

$$\frac{d\langle x^n(t) \rangle}{dt} = Dn(n-1)\int_0^t ds\, \phi(t-s)\langle x^{n-2}(s) \rangle. \tag{7}$$

Both formalisms connect the evolution of the n-th moment to the lower, $(n-2)$-th moment, the χ-formalism to its instantaneous value through a multiplicative factor containing $\chi(t)$, the ϕ-formalism to its values at all times s in the past through the memory function $\phi(t-s)$. Iterating Eqs. (6) and (7) over n down to $n = 2$, using the explicit solutions (4) and (5) for the second moment, and focusing attention only on the even moments $\langle x^{2n} \rangle$, we have

$$\langle x^{2n}(t) \rangle = \frac{(2n)!}{n!}\,[D\tau]^n \tag{8}$$

for the χ-formalism and

$$\widetilde{\langle x^{2n} \rangle}(\epsilon) \rangle = \frac{(2n)!}{\epsilon^{n+1}}\left[D\tilde{\phi}(\epsilon)\right]^n \tag{9}$$

for the ϕ-formalism. In Eq. (8), we have defined a new time $\tau = \int_0^t ds \chi(s)$. In Eq. (9), tildes denote Laplace transforms and ϵ is the Laplace variable; thus, for instance, $\tilde{\phi}(\epsilon) = \int_0^{\infty} dt e^{-\epsilon t}\phi(t)$.

When Eq. (3) holds, $\phi(t)$ and $\chi(t)$ are related in Laplace domain as $\tilde{\chi}(\epsilon) = \tilde{\phi}(\epsilon)/\epsilon$. Therefore, by comparing (8) with (9) we obtain the result mentioned above that the second moments are exactly the same as predicted by the two formalisms. On the other hand, higher moments differ. Note as an illustration that the 4-th moment is given by

$$\langle x^4(t) \rangle = 12D^2\left[\int_0^t ds\, \chi(s)\right]^2 \tag{10}$$

from the χ-formalism, and thus is not the same as

$$\langle x^4(t) \rangle = 24D^2\int_0^t ds \int_0^s du\, \chi(s-u)\chi(u), \tag{11}$$

which is the result of the ϕ-formalism, given relation (3). Clearly, Eqs. (10) and (11) yield different results for the fourth moment for all cases except that of standard (not anomalous) diffusion in which $\chi(t) = 1$.

The importance of demonstrating explicitly the perhaps obvious fact that the two formalisms are not equivalent to each other stems from the wide use that each has found in practical applications to situations in which diffusion is suspected to be anomalous. The χ-formalism is associated [10] with the phrase "fractional Brownian motion" if $\chi(t)$ is a power of t, while the ϕ-formalism has been called the generalized master equation (GME) approach and used widely [11] for the description of coherence. The clear difference in the higher moments along with the exact congruence of the second moment leads us to ask what the precise relation between the two formalisms is. An inspection of Eqs. (1)-(2) or of (6)-(7) shows the following. If the exact description happens to be that given by the memory function formalism, the description provided by the χ-formalism emerges as the so-called *half-Markoffian approximation*. This terminology appeared decades ago in the study of exciton motion [11]. The Markoffian approximation (see, e.g., ref. [7]) on a time non-local term such as $\int_0^t ds\phi(s)b(t-s)$ is made if the memory $\phi(s)$ varies so rapidly that the slower b may be taken out of the integral as $b(t)$. The full Markoffian approximation normally made, for instance, to convert the GME into the Pauli Master equation further assumes that $\phi(t)$ may be replaced by a δ-function times the time integral of $\phi(t)$ over all time:

$$\int_0^t ds\ \phi(s)b(t-s) \approx b(t)\int_0^\infty ds\ \phi(s).$$

The other, weaker and less-used Markoffian approximation [12] stops at taking b out of the integral, does not take the upper limit of the integral of the memory to be infinity, and has the form

$$\int_0^t ds\phi(s)b(t-s) \approx b(t)\int_0^t ds\phi(s) = b(t)\chi(t).$$

This partial Markoffian approximation, applied to the ϕ-formalism, can be said to be the content of the χ-formalism.

The above discussion should by no means imply that the χ-formalism always provides a more approximate description than does the ϕ-formalism. It is possible that the underlying dynamics of a given system may be precisely that given by Eq. (1). In such a case, it will be Eq. (2) that will be the approximation. To make this clear, let us compare the exact solutions of the two equations. Because there are no preferred points in space in the systems considered in this paper, the solution of Eq. (1) may be computed straightforwardly in Fourier space. It is given by the Gaussian

$$\frac{\hat{P}(k,\tau)}{\hat{P}(k,0)} = \exp\left[-Dk^2\int_0^t ds\chi(s)\right], \tag{12}$$

where k is the Fourier variable and the circumflex denotes the Fourier transform through

$\hat{P}(k) = \int_{-\infty}^{\infty} dx P(x) e^{ikx}$. Equation (2), on the other hand, may be solved in the Fourier-Laplace domain as

$$\frac{\tilde{P}(k,\epsilon)}{\tilde{P}(k,0)} = \frac{1}{\epsilon + D\tilde{\phi}(\epsilon)k^2}. \tag{13}$$

Surely, it is impossible to find a $\phi(t)$ that would make the right hand side of Eq. (13) identical to the Laplace transform of the right hand side of Eq. (12) for *arbitrary* $\chi(t)$. The reverse is also true: it is impossible to find a $\chi(t)$ that would make the Laplace transform of the right hand side of Eq. (12) identical to the right hand side of Eq. (13) for *arbitrary* $\phi(t)$. Is there then no hope of finding a bridge between the two descriptions? One of the present authors has argued in the course of his study of stress distribution in granular materials [8] that a useful bridge might be constructed by generalizing one or the other of these two formalisms to include *spatially non-local* situations. To understand that argument, let us promote the χ-formalism by replacing the multiplicative factor $D\chi(t)$ in Eq. (1) by a spatial convolution:

$$\frac{\partial P(x,t)}{\partial t} = \int_{-\infty}^{\infty} dx' \, \mathfrak{D}_\chi(x - x', t) \frac{\partial^2 P(x',t)}{\partial x'^2} \tag{14}$$

The time rate of change of $P(x,t)$ is now connected to its second spatial derivative (Laplacian) not only at x but at all locations x' through the connecting function $\mathfrak{D}_\chi(x - x', t)$ which incorporates, in addition, the time dependence of the simpler $\chi(t)$ in a non-separable form. One recovers Eq. (1) from Eq. (14) if $\mathfrak{D}_\chi(x - x', t) = D\chi(t)\delta(x - x')$. Let us similarly generalize the ϕ-formalism by replacing the factor $D\phi(t - s)$ in Eq. (2) by a spatial convolution involving the new connecting function $\mathfrak{D}_\phi(x - x', t - s)$:

$$\frac{\partial P(x,t)}{\partial t} = \int_{-\infty}^{\infty} dx' \int_0^t ds \, \mathfrak{D}_\phi(x - x', t - s) \frac{\partial^2 P(x',s)}{\partial x'^2}. \tag{15}$$

We see that Eq. (2) is recovered from Eq. (15) if $\mathfrak{D}_\phi(x - x', t - s) = D\phi(t - s)\delta(x - x')$.

Whereas it was true that the spatially local equations of the χ- and ϕ- formalisms could not be put into equivalence, we now see that their generalizations can be. Equating the ratio $\frac{\tilde{P}(k,\epsilon)}{\hat{P}(k,0)}$ as predicted by the two equations, we find that equivalence can be established provided

$$\int_0^\infty e^{-k^2 \int_0^t \mathfrak{D}_\chi(k,s) ds} e^{-\epsilon t} dt = \frac{1}{\epsilon + k^2 \tilde{\mathfrak{D}}_\phi(k,\epsilon)}. \tag{16}$$

Equation (16) constitutes a practical bridge to pass between the two formalisms. Assume the (spatially local) χ-formalism to be correct, i.e., that the system evolution obeys the original equation (1). An entirely equivalent description is then provided by the *spatially non-local* ϕ-formalism given by Eq. (15) in which

$$\tilde{\mathfrak{D}}_\phi(k,\epsilon) = \frac{1}{k^2} \left\{ \frac{1}{\mathcal{L}\left[e^{-Dk^2 \int_0^t \chi(s) ds} \right]} - \epsilon \right\}. \tag{17}$$

Thus, spatially non-locality in the ϕ-formalism is essential to describe a spatially local χ situation. Equation (17) is the explicit prescription through which we can find the key ϕ-quantity, viz., $\mathfrak{D}_\phi(k,\epsilon)$, for *an arbitrarily given* $\chi(t)$.

Conversely, if the (spatially local) ϕ-formalism provides the correct description, i.e., the system evolution obeys the original equation (2), a fully equivalent description is provided by the *spatially non-local* χ-formalism given by Eq. (14), the key quantiy $\mathfrak{D}_\chi(k,t)$ being computed for *any given* $\phi(t)$ by

$$\mathfrak{D}_\chi(k,t) = \frac{d}{dt}\left\{-\frac{1}{k^2}\ln\left|\mathcal{L}^{-1}\left(\frac{1}{\epsilon + k^2 D\tilde{\phi}(\epsilon)}\right)\right|\right\}. \tag{18}$$

In the prescriptions (17) and (18) the symbols $\mathcal{L}$ and $\mathcal{L}^{-1}$ stand, respectively, for the direct and inverse Laplace transforms, and the argument of the logarithm is the absolute value as shown.

3 Applications of the General Formalism

In this Section, we present an illustrative application of the prescription we have developed above in one physical instance in which the spatially local ϕ-formalism provides the exact description of the system. We will also mention briefly an instance of the opposite situation.

3.1 ϕ to χ: Memory Functions from a Railway-track Model

Coherence issues in exciton transport [13, 14] led to a great deal of work based on memory functions in the seventies [11, 14]. The specific form of the memory functions often arose from quantum features in the dynamics of excitons [14]. To dispel an incorrect notion held by some that an underlying quantum layer was essential to memory functions, one of the present authors introduced a trivially simple model that showed how memory functions could arise purely classically.[1] Because the model leads easily to Eq. (2), we study it here along with its equivalent spatially nonlocal χ-description.

For reasons that should be obvious, we call it the railway-track model. Let $P^{\rightarrow}$ ($P^{\leftarrow}$) be the probability that a particle moves to the right (left) with rate c ($-c$). The particle is subject to scattering at rate $\mathcal{Q}$, the only effect of scattering being to change the direction of motion from right to left and vice-versa. This system is depicted in Fig. 1 and analyzed through the coupled equations

$$\frac{\partial P^{\rightarrow}(x,t)}{\partial t} = c\frac{\partial P^{\rightarrow}(x,t)}{\partial x} + \mathcal{Q}[P^{\leftarrow}(x,t) - P^{\rightarrow}(x,t)], \tag{19}$$

$$\frac{\partial P^{\leftarrow}(x,t)}{\partial t} = -c\frac{\partial P^{\leftarrow}(x,t)}{\partial x} + \mathcal{Q}[P^{\rightarrow}(x,t) - P^{\leftarrow}(x,t)]. \tag{20}$$

[1] The utter simplicity of the model meant that there was no need to publish it–it was only discussed at conferences and private discussions. Its simplicity also means that it has been probably invoked by others before or since.

Note the Markoffian nature of equations (19), (20). By defining $P(x,t) \equiv P^{\rightarrow} + P^{\leftarrow}$ and

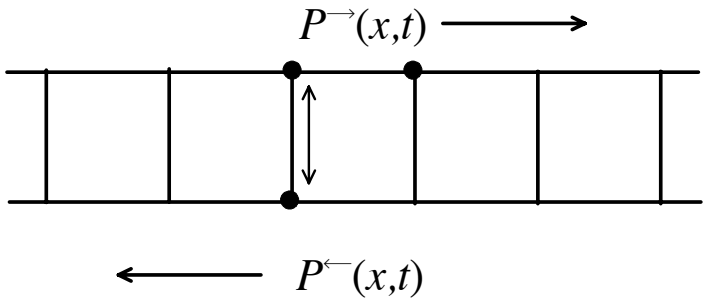

Figure 1: Pictorial description of the "railway-track" model naturally addressed via the ϕ-formalism.

$R(x,t) \equiv P^{\rightarrow} - P^{\leftarrow}$, we get

$$R(x,t) = R(x,0)e^{-2\mathcal{Q}t} + c\int_0^t ds\, e^{-2\mathcal{Q}(t-s)}\frac{\partial}{\partial x}P(x,s). \tag{21}$$

For the initial condition $\partial P(x,t)/\partial t|_{t=0} = 0$, $P(x,t)$ satisfies

$$\frac{\partial P(x,t)}{\partial t} = c^2\int_0^t ds\, e^{-2\mathcal{Q}(t-s)}\frac{\partial^2 P(x,s)}{\partial x^2}. \tag{22}$$

Equation (22) is exactly of the ϕ form of Eq. (2) with $D = c^2/2\mathcal{Q}$, the memory $\phi(t)$ being equal to the exponential $2\mathcal{Q}e^{-2\mathcal{Q}t}$. This trivial but clear example shows how a memory function description arises from coarsegraining involved in seeking the evolution of the *combination* $P(x,t) = P^{\rightarrow} + P^{\leftarrow}$ without interest in how much of rightward motion versus leftward motion there is. Needless to say, we have here a caricature of a system in which particles move and scatter among various velocity states, only 2 such states being considered in this caricature system.

The solution to the memory equation (22) with initial condition $P(x,t) = \delta(x)$ is given explicitly by [8]

$$P(x,t) = e^{-\mathcal{Q}t}\left[\frac{\delta(x+ct)+\delta(x-ct)}{2} + T(x,t)\right], \tag{23}$$

where $T(x,t)$ vanishes identically for $ct \leq |x|$ and equals

$$T(x,t) = \left(\frac{\mathcal{Q}}{2c}\right)\left[I_0\left(\frac{\mathcal{Q}}{c}\sqrt{c^2t^2-x^2}\right) + \frac{ct}{\sqrt{c^2t^2-x^2}}I_1\left(\frac{\mathcal{Q}}{c}\sqrt{c^2t^2-x^2}\right)\right] \tag{24}$$

for $ct > |x|$, $I_\nu(z)$ being the modified I Bessel function of order ν and argument z. We point out in passing that the moments of $P(x,t)$ may be computed by just knowing the

Laplace transform of the memory function and using (9). Inverting the Laplace transform, we find

$$\langle x^{2n}(t)\rangle = (ct)^{2n}\, M(n, 2n+1, -2\mathcal{Q}t), \tag{25}$$

where $M(a,b,z) = 1 + \frac{az}{b} + \frac{a(a+1)z^2}{b(b+1)2!} + ... + \frac{a(a+1)\cdots(a+n-1)z^n}{b(b+1)\cdots(b+n-1)n!} + ...$ is the Kummer confluent hypergeometric function of argument z [15].

Our purpose in introducing the "railway-track" model here is to examine how one may pass from the ϕ-formalism to the spatially non-local χ-formalism via our prescription (18). A straightforward evaluation after replacing $\tilde{\phi}(\epsilon)$ by $2\mathcal{Q}/(\epsilon + 2\mathcal{Q})$ leads to

$$\mathfrak{D}_\chi(k,t) = \left(\frac{c^2}{\mathcal{Q}}\right) \frac{\sin\left(\mathcal{Q}t\sqrt{k^2c^2/\mathcal{Q}^2 - 1}\right)}{\sin\left(\mathcal{Q}t\sqrt{k^2c^2/\mathcal{Q}^2 - 1}\right) + \sqrt{k^2c^2/\mathcal{Q}^2 - 1}\cos\left(\mathcal{Q}t\sqrt{k^2c^2/\mathcal{Q}^2 - 1}\right)}. \tag{26}$$

The Fourier inverse of this expression, $\mathfrak{D}_\chi(x - x', t)$, when substituted in Eq. (14), allows us to write the desired spatially nonlocal χ-description.

What new insights does the combination of Eqs (14) and (26) yield? One answer is that (14) may now be inverted explicitly as an infinite sum of local terms:

$$\frac{\partial P(x,t)}{\partial t} = D_0(t)\frac{\partial^2}{\partial x^2}P(x,t) + \frac{D_2(t)}{2!}\frac{\partial^4}{\partial x^4}P(x,t) + \frac{D_4(t)}{4!}\frac{\partial^6}{\partial x^6}P(x,t)..., \tag{27}$$

where the factors $D_{2n}(t)$ may be computed as $(-1)^n \left.\dfrac{\partial^{2n}\mathfrak{D}_\chi(k,t)}{\partial k^{2n}}\right|_{k=0}$. The first three factors are

$$D_0(t) = D(1 - e^{-2\mathcal{Q}t}), \tag{28}$$

$$D_2(t) = \frac{D^2}{\mathcal{Q}}\left[4\mathcal{Q}te^{-2\mathcal{Q}t} - (1 - e^{-4\mathcal{Q}t})\right], \tag{29}$$

$$D_4(t) = \frac{6D^3}{\mathcal{Q}^2}\left[2 + e^{-2\mathcal{Q}t}(1 - 4\mathcal{Q}t - 8\mathcal{Q}^2t^2) - 2e^{-4\mathcal{Q}t}(1 + 4\mathcal{Q}t) - e^{-6\mathcal{Q}t}\right], \tag{30}$$

where and henceforth we suppress the symbol c and use $D = c^2/2Q$ in addition to Q.

If we truncate (27) by keeping only the first term, the local χ-description emerges:

$$\frac{\partial P(x,t)}{\partial t} = D\left[\int_0^t ds\, \phi(s)\right]\frac{\partial^2}{\partial x^2}P(x,t), \tag{31}$$

since $D_0(t) = D\chi(t) = D\int_0^t ds\, \phi(s)$. The solution to Eq. (31) is given by the Gaussian

$$\frac{\mathcal{Q}^{1/2}}{\left[2\pi D\left(2\mathcal{Q}t - (1 - e^{-2\mathcal{Q}t})\right)\right]^{1/2}} e^{-\frac{\mathcal{Q}x^2}{2\pi D\left(2\mathcal{Q}t - (1 - e^{-2\mathcal{Q}t})\right)}},$$

and leads, as mentioned above, to precisely the same $\langle x^2(t)\rangle$ as the exact solution. However, it predicts, for the *next higher* moment,

$$\langle x^4(t)\rangle = \frac{3D^2}{\mathcal{Q}^2}\left[2\mathcal{Q}t - (1-e^{-2\mathcal{Q}t})\right]^2, \tag{32}$$

which is only an approximation (see Fig. 1) to the exact fourth moment

$$\langle x^4(t)\rangle = \frac{6D^2}{\mathcal{Q}^2}\left[3 - 4\mathcal{Q}t + 2\mathcal{Q}^2t^2 - e^{-2\mathcal{Q}t}(3+2\mathcal{Q}t)\right] \tag{33}$$

computed from (9). Any moment from the spatially-nonlocal χ-formalism may be computed from the infinite series (27). Note that not all the higher order terms are necessary to compute a given moment. Thus, the infinite series collapses into only the first two terms when computing $\langle x^4(t)\rangle$:

$$\langle x^4(t)\rangle = 12\int_0^t ds\, D_2(s) + 12\left[\int_0^t ds\, D_0(s)\right]^2. \tag{34}$$

In Fig. 2 we show the fourth moment as function of time along with its half-Markoffian approximation. [2]

3.2 Time Dependent Diffusion Constant, a Sketch

Obviously, the local ϕ-formalism does not provide the more appropriate description in every physical system. A case in which the χ-formalism appears is in the Master equation description [16] of the effects of vibrational relaxation on intermolecular transfer of electronic excitation. Time-dependent transfer rates occur naturally there. The probability of occupation of vibrational levels as well as of site occupation, denoted by $P_m^M(t)$, where M and m refer to site and vibrational state respectively, obeys

$$\frac{d}{dt}P_m^M(t) = \sum_n[\gamma_{m,n}P_n^M(t) - \gamma_{n,m}P_m^M(t)] + \sum_N[F_m^{M,N}P_m^N(t) - F_m^{N,M}P_m^M(t)]. \tag{35}$$

When the use of a specific form for the relaxation rate $\gamma_{m,n}$ and the assumption of nearest-neighbor transfer rates $F_m^{M,N} = F_m(\delta_{M+1,N} + \delta_{M-1,N})$ are made, an effective transfer

[2] It might be interesting to observe that the recursive relation for the even moments in the spatially-local ϕ-formalism, Eq. (6), the $2n$-th moment depends on the previous one $2(n-1)$-th while in the spatially-non-local χ-formalism, described by (27), the $2n$-th moment depends on all the previous non-vanishing moments, the explicit relation is given by

$$\frac{d}{dt}\langle x^{2n}(t)\rangle = \sum_{m=1}^{n}\frac{(2n)!}{(2n-2m)!(2m-2)!}D_{2m-2}(t)\langle x^{2n-2m}\rangle.$$

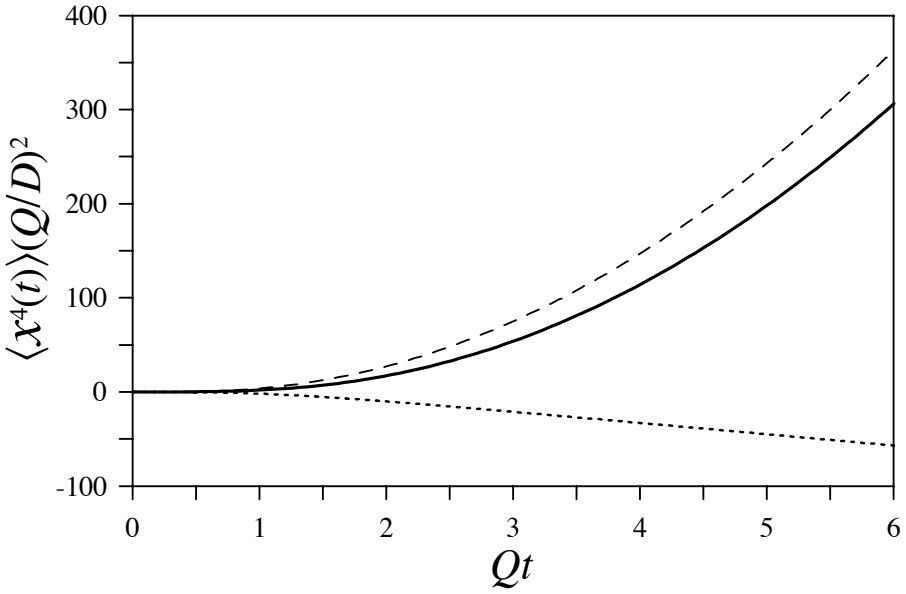

Figure 2: Fourth moment $\langle x^4(t)\rangle$ in units of $(D/\mathcal{Q})^2$ as function of the dimensionless time $\mathcal{Q}t$. We compare the exact fourth moment of (23) in the ϕ-formalism (solid-line) with the one given by the local χ-formalism, i.e., the "half-Markoffian" approximation (dashed-line). The exact curve lies entirely below the approximate curve. The lower curve (dotted-line) gives the correction provided by just the second term of the infinite series (27). The dashed and the dotted curves add up precisely to the solid curve.

equation is seen to emerge which is precisely of the form of the local χ-description. It is possible to convert that time dependence into appropriate expressions for quantities such as $\mathfrak{D}_\chi(x-x',t)$ of Eq. (14) and cast the problem into a spatially non-local ϕ mould. We refrain from showing any of the details here for want of space.

4 Concluding Remarks

If the phrase "anomalous diffusion" is taken to represent any process that has some basic features of standard diffusion but also has significant departures from the latter, one can state confidently that one encounters anomalous diffusion in a rich variety of physical situations. Quantum mechanical (quasi)particles, such as Frenkel excitons in photosynthetic units and photo-injected electrons in molecular crystals, obey GME's [11] whose features are in some regimes similar to those of the standard diffusion equation but in others sharply different as when coherence is substantially present. A description via memory functions

[17], i.e., via the ϕ-formalism of Eq. (2), is natural in that case. In another extreme example of anomalous diffusion, one encounters animal movements [3] that are said to be an example of *fractional Brownian motion*, which is nothing but Eq. (1) representative of the χ-formalism with a power dependence of $\chi(t)$ on t [10]. There is a large number of other instances where it is not clear which of the descriptions is appropriate. Prior to 1973, it had been thought that continuous time random walks represented a description that was fundamentally different from that provided by memory functions. This viewpoint held previously (even by some of the originators of one of those descriptions) was found [7, 14, 18] to be incorrect and led to a trivially simple but important clarification. Because the demonstration of such an equivalence between methods of investigation or description can typically save much unnecessary theoretical labor, we thought it worthwhile to make that enquiry in the context of the χ- and the ϕ-formalisms. This enquiry, begun in part by one of the present authors in the context of the stress distribution of granular compacts [8], has been extended much further in the present paper.

The previous observation [8] that, as stated (i.e., in their *spatially* local form), the two descriptions cannot be generally equivalent, except in the trivial case when both describe standard diffusion, has been made transparently clear in the present paper by Eqs. (4), (5) for the mean square displacement. The latter is formally similar in the two formalisms but sharply different in content for general $\phi(t)$ or $\chi(t)$. The earlier indication [8] that each of the two formalisms is equivalent to a spatially non-local form of the other has been extended here through the complete and practical prescriptions (17) and (18). These prescriptions allow one, given an arbitrary form of $\phi(t)$ or $\chi(t)$, to obtain, at least in principle, the corresponding non-local quantities $\mathfrak{D}_\chi(x,t)$ and $\mathfrak{D}_\phi(x,t)$ in the other formalism. The prescriptions are given in k-space and the Laplace domain and are to be followed by a final Fourier-Laplace inversion if necessary.

We have also examined, in detail, a physical case in which the (spatially local) ϕ-formalism (i.e., memory functions) provides the accurate description. We have explicitly shown how our prescription developed in Eq. (26) is applied and how the spatially non-local character develops in the χ-formalism (see Eq. (27)). This is the elucidation of the railway-track model. We have also pointed out how, the reverse situation, a natural description in terms of the χ-formalism, arises in the theory of vibrational relaxation of molecular excitations in the presence of motion [16]. To avoid lengthy calculations we have refrained from showing the detail of that opposite situation.

Because the spatial shape of the propagator in the local χ-formalism is always Gaussian (for instance in fractional Brownian motion), only a generalization from the time t to $\tau = \int_0^t ds\chi(s)$ being necessary (see Eq. (12)), one may tend to believe that the χ-formalism is not as rich as the ϕ-formalism since the latter allows more freedom in the shape of the propagator. This is, however, not an appropriate statement. Indeed, there exists a certain "symmetry in richness" as we move from the Laplace domain to the time domain. For instance, an equation such as (1) will appear as a convolution equation in the Laplace domain.

Since it may not be clear by inspection which of the two formalisms may be providing a correct description for a given system, we comment in passing about probing this question experimentally. We draw the attention of the reader to two observational set-ups in two widely different areas of study: transient grating observations in molecular crystals (TGO) [11, 19] and nuclear magnetic resonance microscopy (NMRM) [20, 21]. Both are sensitive not merely to the mean square displacement of the moving entities but to the entire Fourier transform of the probability density $P(x,t)$. The TGO involve crossed laser beams that are used to create a sinusoidal spatial distribution of electronic excitations. The decay of the amplitude of that distribution is measured and information is thereby extracted about the motion of the excitations. The NMRM uses the so-called pulsed-gradient spin echo technique [22]. In the limit of very short duration pulses, that technique, just as does the TGO, probes directly the Fourier transform of $P(x,t)$ and not its moments. Clearly, both experiments should be able, in principle, to discriminate between whether a local χ or local ϕ formalism is appropriate. More details will be presented elsewhere.

We have restricted attention in the present paper to spatially homogeneous (not the same as spatially non-local or local) systems only. Fourier transformation therefore diagonalizes the relevant matrices and there is no $k-k'$ interaction. If spatial locations were not all equivalent, we would have terms such as $\mathfrak{D}_\chi(x,x',t)$ and $\mathfrak{D}_\phi(x,x',t)$ in Eqs. (14) and (15) and the difference nature of the spatial kernels would be destroyed. Transformation via $\exp(ikx)$ would be useless and the problem would become quite complicated. Because situations where the diffusion coefficient itself may be spatially varying occur often in physical and biological applications, it is important to extend our analysis to incorporate them. We plan to do that in a future study.

We acknowledge fruitful discussions with Dr. Luca Giuggioli. This work was supported in part by the NSF under Grant no. INT-0336343, by NSF/NIH Ecology of Infectious Diseases under Grant no. EF-0326757 and by DARPA under Grant no. DARPA-N00014-03-1-0900.

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