MITTAG–LEFFLER RELAXATION IN THE LIGHT OF ASYMPTOTIC ANALYSIS

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We show that time autocorrelation functions exhibiting an asymptotic power law decay $\sim t^{-\rho}/\Gamma(1-\rho)$ take the form of a "stretched" Mittag–Leffler function, $E_\rho(-(t/\tau)^\rho)$, if the associated memory function attains its asymptotic form on a time scale which is much shorter than the characteristic time scale of the asymptotic regime itself. The range for the exponent is here restricted to if $0 < \rho < 1$ and we show that the time scale separation can be enforced by downscaling the amplitude of the memory function. Reasoning along the same lines, we demonstrate that the velocity autocorrelation function of an anomalously diffusing particle behaves as $E_{2-\alpha}(-(t/\tau_\mathrm{D})^{2-\alpha})$ if the associated memory function attains its asymptotic form on time scales much shorter than the diffusion time scale, τ_D. The exponent α defines here the asymptotic form of its mean square displacement, $\langle(x(t)-x(0))^2\rangle \sim t^\alpha$, and $0 < \alpha < 2$.

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1. Introduction

Time autocorrelation functions are the basic physical quantities in spectroscopic experiments investigating the atomic and molecular dynamics of condensed matter systems. Their normalized form,

$$\phi(t) = c_{AA}(t)/c_{AA}(0)\,, \tag{1.1}$$

describes the relaxation dynamics of the variable $A(t)$ which is probed in the respective experiment, where $c_{AA}(t) \equiv \langle A(0)A(t)\rangle$ is an equilibrium ensemble average. In complex systems, relaxation functions of the form of (1.1) exhibit a strongly non-exponential long-time decay, reflecting the fact that many dynamical variables with a broad spectrum of time scales are coupled [1–4]. An example is the slow relaxation dynamics of proteins,

whose non-exponential behavior has been investigated for almost 50 years [5–16]. The most commonly used generalization of the exponential relaxation function is the Kohlrausch–Williams–Watt (KWW) function [17, 18]

$$\phi_{\mathrm{KWW}}(t) = \exp(-(t/\tau)^{\rho}) , \qquad \rho > 0 , \tag{1.2}$$

which is often referred to as "stretched" or "compressed" exponential function, depending if $\rho < 1$ or $\rho > 1$, respectively. The KWW function has found many applications, in particular in the field of dielectric relaxation spectroscopy [19, 20]. Another example for a non-exponential relaxation function is the Mittag–Leffler relaxation function [8, 21]

$$\phi_{\mathrm{ML}}(t) = E_{\rho}(-(t/\tau)^{\rho}) , \tag{1.3}$$

where the exponential function in expression (1.2) is replaced by the Mittag–Leffler (ML) function [22–25]. The ML function is an entire function in the complex plane which is represented by the Taylor series

$$E_{\rho}(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(1 + k\rho)} , \tag{1.4}$$

and which has the asymptotic series expansion

$$E_{\rho}(z) = -\sum_{n=1}^{M} \frac{z^{-n}}{\Gamma(1 - n\rho)} + O\left(z^{-(M+1)}\right) , \qquad M = 1, 2, \ldots \tag{1.5}$$

For $0 < \rho < 1$, it decays monotonously and displays an asymptotic power law decay

$$\phi_{\mathrm{ML}}(t) \overset{t\to\infty}{\sim} \frac{(t/\tau)^{-\rho}}{\Gamma(1 - \rho)} , \tag{1.6}$$

whereas the KWW function decays asymptotically faster than any power law term $\sim t^{-k\rho}$, with $k = 1, 2, \ldots$ and $\rho > 0$. Figure 1 shows that it interpolates, in fact, between the ML and the exponential relaxation function. The asymptotic power law form (1.6) of the ML relaxation function expresses asymptotic self-similarity, *i.e.* asymptotic form invariance under a scaling transformation $t \to \mu t$ ($\mu > 0$), which is, for instance, an important property of protein dynamics [8, 16]. We note in this context that $\phi_{\mathrm{ML}}(t)$ is the solution of the fractional differential equation [2, 8]

$$\frac{\mathrm{d}\phi_{\mathrm{ML}}(t)}{\mathrm{d}t} + \tau^{-\rho}\, {}_0\partial_t^{1-\rho} \phi_{\mathrm{ML}}(t) = 0 , \tag{1.7}$$

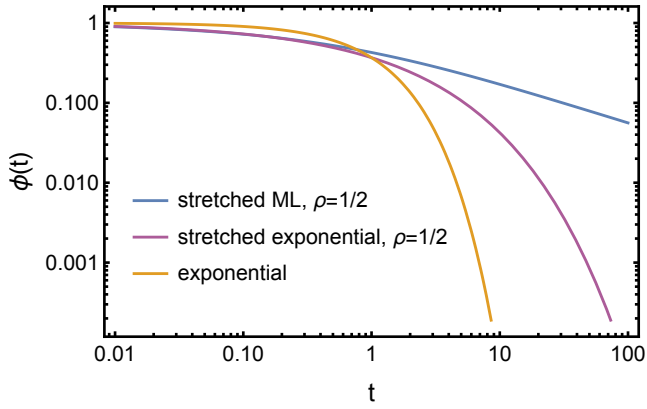

Fig. 1. Log–log plots of $E_{1/2}(-t^{1/2})$ (blue), $\exp(-t^{1/2})$ (magenta), and $\exp(-t)$ (orange).

where the symbol ${}_0\partial_t^{1-\rho}$ denotes a Riemann–Liouville derivative [26] of the order of $1-\rho$

$$ {}_0\partial_t^{1-\rho}\phi_{\mathrm{ML}}(t) \equiv \frac{\mathrm{d}}{\mathrm{d}t}\int_0^t \mathrm{d}t' \, \frac{(t-t')^{\rho-1}}{\Gamma(\rho)}\phi_{\mathrm{ML}}\left(t'\right) \, . \tag{1.8} $$

The convolution integral reflects here long-memory effects which have been extensively discussed in the context of stochastic processes [27, 28] ever since the seminal work of Mandelbrot and Van Ness on fractional Brownian motion [29].

2. Anomalous relaxation

2.1. The memory function of the Mittag–Leffler relaxation function

The basic mathematical tool to be used in the following is the Laplace transform, which is defined as $\hat{f}(s) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} f(t)$ $(\Re\{s\} > 0)$ for an arbitrary function, $f(t)$. The corresponding inverse transform is given by $f(t) = \frac{1}{2\pi i}\oint_C \mathrm{d}s\, \mathrm{e}^{st}\hat{f}(s)$, where C is the Bromwich contour [30]. For the ML relaxation function, one obtains in particular [25]

$$ \hat{\phi}_{\mathrm{ML}}(s) = \frac{1}{s + s(s\tau)^{-\rho}} \, , \tag{2.1} $$

using here the series expansion (1.4) with $z = -(t/\tau)^\rho$ and performing the Laplace transform term by term. Expression (2.1) may now be compared to the general form of a Laplace transformed relaxation function

$$ \hat{\phi}(s) = \frac{1}{s + \hat{\kappa}_{AA}(s)} \, , \tag{2.2} $$

which follows from the Mori–Zwanzig form of the equation of motion for time autocorrelation functions [31–33]

$$\partial_t c_{AA}(t) + \int_0^t \mathrm{d}t' \, \kappa_{AA}\left(t - t'\right) c_{AA}\left(t'\right) = 0 \,. \tag{2.3}$$

The memory function $\kappa_{AA}(t)$ reflects here the interaction of the selected dynamical variable, A, with the dynamical system under consideration and Eq. (2.3) is derived within the theory of the Generalized Langevin Equation (GLE), assuming the framework of classical statistical mechanics. The basic concept here is projection, splitting the space of dynamical variables into a set of variables of interest and a set of "bath variables", which are considered as "noise". Defining the scalar product (A, B) of two variables through the phase-space average $(A, B) \equiv \int\int \mathrm{d}p \, \mathrm{d}q \, \rho_{\mathrm{eq}}(p, q) A(p, q) B(p, q)$, where $\rho_{\mathrm{eq}}(p, q)$ is the equilibrium distribution, the projector on A is given by $\mathcal{P}_A = (A, .)/(A, A)$. If A is the (single) variable of interest, the orthogonal projector, $\mathcal{Q}_A = 1 - \mathcal{P}_A$, projects thus on the space of noise variables. Denoting the generator of an infinitesimal translation in time $\mathcal{L}$, such that $A(t) = \exp(t\mathcal{L})A(0)$, the time autocorrelation function may be written as a scalar product

$$c_{AA}(t) = (A(0), A(t)) \,, \tag{2.4}$$

and the memory function has the form

$$\kappa_{AA}(t) = (A, A)^{-1} \left(f_A^{(Q)}(0), f_A^{(Q)}(t) \right) \,, \tag{2.5}$$

where $f_A^{(Q)}(t)$ is "the projected time derivative"

$$f_A^{(Q)}(t) = \mathrm{e}^{t\mathcal{Q}_A\mathcal{L}} \mathcal{Q}_A \mathcal{L} A \,. \tag{2.6}$$

Equation (2.5) shows that the memory function is itself a time autocorrelation function and it follows from Eq. (2.1) the Laplace transformed memory function of the ML relaxation function has the power law form of

$$\hat{\kappa}_{\mathrm{ML}}(s) = s(s\tau)^{-\rho} \,. \tag{2.7}$$

In the time domain, this corresponds to

$$\kappa_{\mathrm{ML}}(t) = \frac{\tau^{-\rho} t^{\rho-2}}{\Gamma(\rho - 1)} \,, \tag{2.8}$$

which shows that

$$\int_0^t \mathrm{d}t' \, \kappa_{\mathrm{ML}}\left(t - t'\right) c_{AA}\left(t'\right) = \tau^{-\rho}{}_0\partial_t^{1-\rho} c_{AA}(t) \,. \tag{2.9}$$

From a physical point of view, the fractional derivative in the fractional differential equation (1.7) can thus be interpreted as the convolution with a memory function in the sense of the GLE and we note that expressions (2.7) and (2.8) reflect the self-similarity of this memory function in the Laplace and time domain, respectively. It should be noted that the form (2.8) of the memory function cannot be true for $t \to 0$ and it will be shown below that it must be considered as an *asymptotic* form for long times. We also emphasize that the term "Generalized Langevin Equation" is often used in a wider sense, namely for any generalization of the historical Langevin equation [34], where the velocity-dependent friction force, $F_\gamma(t) = -\gamma v(t)$, of a Brownian particle is replaced by a convolution term of the form of $F_\gamma(t) = -\int_0^t \mathrm{d}t'\, v(t-t')\kappa(t')$ (see, for example, Refs. [35–37]). The GLE derived by Mori and Zwanzig has the particular property of being formally an exact "projected" equation of motion, which is in particular time-reversible as the underlying Hamilton's equations of motion from which it is derived. In this context, the description of irreversible phenomena like relaxation implies thus either the assumption of a model for the memory function or the assumption that irreversibility is *de facto* attained in a many-body system with a large number of particles. Molecular dynamics (MD) simulations of liquids and macromolecular systems have given ample of evidence that the latter assumption is, in fact, valid if the observations are restricted to the statistically relevant regime of the analyzed trajectories. This has already been evidenced Rahman's historical computation of the velocity autocorrelation function (VACF) for liquid argon from MD simulation [38], which shows that the VACF of a simple liquid exhibits damped oscillations.

2.2. Asymptotic power law relaxation and weak self-similarity

In the following, we will be working with relaxation functions which have the same asymptotic behavior as $\phi_{\mathrm{ML}}(t)$, namely

$$\phi(t) \overset{t\to\infty}{\sim} \frac{(t/\tau)^{-\rho}}{\Gamma(1-\rho)}\,, \qquad 0 < \rho < 1\,. \tag{2.10}$$

In the context of asymptotic analysis, functions with an asymptotic power law form belong to the class of "regularly varying functions". Karamata [39] defines a regularly varying function, $q(t)$, through the properties $q(t) > 0$ and

$$\frac{q(\lambda t)}{q(t)} \overset{t\to\infty}{\sim} f(\lambda)\,, \qquad \lambda > 0\,, \tag{2.11}$$

where $f(\lambda) > 0$. He shows moreover that $q(t)$ must be of the form of

$$q(t) = L(t)t^a\,, \qquad -\infty < a < +\infty\,, \tag{2.12}$$

and $L(t)$ is a "slowly varying function" fulfilling

$$\frac{L(\lambda t)}{L(t)} \overset{t\to\infty}{\sim} 1\,, \qquad \lambda > 0\,. \tag{2.13}$$

We can thus conclude that any physical relaxation function evolving on a concrete time scale and decaying asymptotically with power law decay of the form of (2.10) can be written in the "weakly self-similar" form

$$\phi(t) = L_\phi(t)\frac{(t/\tau)^{-\rho}}{\Gamma(1-\rho)}\,, \qquad 0 < \rho < 1\,, \tag{2.14}$$

where $L_\phi(t)$ is a slowly varying function fulfilling

$$\lim_{t\to\infty} L_\phi(t) = 1\,. \tag{2.15}$$

Obviously, any positive function approaching a plateau value satisfies condition (2.13) for a slowly varying function. The property "weak self-similarity" expresses that time correlation functions with an asymptotic — self-similar — power law decay approach this regime with some slowly varying function, $L_\phi(.)$, and are for long times "almost self-similar". We have coined this term in Ref. [40] to show that the ML relaxation function is weakly self-similar. We also again refer in this context to Ref. [20], where the asymptotic form of the time correlation function is discussed from the point of view of limiting distributions of waiting times.

We make now use of another theorem by Karamata [41], which relates the asymptotic form of functions of the form of (2.14) in the limit of $t \to \infty$ to the asymptotic form of their Laplace transform for $s \to 0$. The theorem states the equivalence

$$h(t) \overset{t\to\infty}{\sim} L(t)t^\alpha \Leftrightarrow \hat{h}(s) \overset{s\to 0}{\sim} L\left(\frac{1}{s}\right)\frac{\Gamma(1+\alpha)}{s^{1+\alpha}}\,, \tag{2.16}$$

where α is subject to the condition $\alpha > -1$ and the symbol "$\sim$" may be replaced by an equal sign on either side. It thus follows from expression (2.14) that

$$\hat{\phi}(s) \overset{s\to 0}{\sim} L_\phi\left(\frac{1}{s}\right)\frac{1}{s(s\tau)^{-\rho}}\,, \tag{2.17}$$

and for any $\rho > 0$, one then obtains the following asymptotic form of the Laplace transformed memory function

$$\hat{\kappa}_{AA}(s) \overset{s\to 0}{\sim} \frac{s(s\tau)^{-\rho}}{L_\phi\left(\frac{1}{s}\right)}\,. \tag{2.18}$$

Introducing now $u = 1/s$ and noting that $1/L(t)$ is slowly varying if $L(t)$ is slowly varying shows that $\hat{\kappa}_{AA}(1/u)$ is the asymptotic form of a regularly varying function. Since any regularly function can be written as the product of a slowly varying function and a power law (see Eq. (2.12)), there must exist some slowly varying function, $L_{\hat{\kappa}}(t)$, such that $\hat{\kappa}_{AA}(1/u) = u^{-1}(u/\tau)^{\rho}/L_{\hat{\kappa}}(u)$, and consequently

$$\hat{\kappa}_{AA}(s) = \frac{s(s\tau)^{-\rho}}{L_{\hat{\kappa}}\left(\frac{1}{s}\right)}\,. \tag{2.19}$$

For the Laplace transformed relaxation function, we thus have

$$\hat{\phi}(s) = \frac{1}{s + \frac{s(s\tau)^{-\rho}}{L_{\hat{\kappa}}\left(\frac{1}{s}\right)}}\,, \tag{2.20}$$

and comparison to Eq. (2.1) shows that the ML relaxation function is obtained if one can assume that $L_{\hat{\kappa}}(1/s) \approx 1$. Assigning a typical time scale τ^* to $L_{\hat{\kappa}}\,(t)$ via

$$L_{\hat{\kappa}}(t) \equiv L_{\hat{\kappa}}(t/\tau^*) \tag{2.21}$$

shows that this is the case if $\tau^* \to 0$ and, therefore,

$$\phi(t) \overset{\tau^*\to 0}{\sim} E_{\rho}(-(t/\tau)^{\rho})\,, \tag{2.22}$$

which is the central result of the paper.

From a physical point of view, τ^* defines the characteristic time scale describing the approach of the memory function to its asymptotic power law form. The latter is derived by writing

$$\frac{\hat{\kappa}_{AA}(s)}{s} = \frac{(s\tau)^{-\rho}}{L_{\hat{\kappa}}\left(\frac{1}{s\tau^*}\right)}\,,$$

where the r.h.s. can be considered as the Laplace transform of a slowly varying function. We can thus use equivalence (2.16), with equality for $\hat{h}(s)$, to obtain in the time domain

$$\int_0^t \mathrm{d}t'\,\kappa(t') \overset{t\to\infty}{\sim} \frac{1}{L_{\hat{\kappa}}\,(t/\tau^*)}\frac{\tau^{-\rho}t^{\rho-1}}{\Gamma(\rho)}\,.$$

Since $\lim_{t\to\infty} \mathrm{d}L_{\hat{\kappa}}(t/\tau^*)/\mathrm{d}t = 0$, it follows by differentiation that

$$\kappa_{AA}(t) \overset{t\to\infty}{\sim} \frac{1}{L_{\hat{\kappa}}\,(t/\tau^*)}\underbrace{\frac{\tau^{-\rho}t^{\rho-2}}{\Gamma(\rho-1)}}_{\kappa_{\mathrm{ML}}(t)} \tag{2.23}$$

is a refined, asymptotic self-similar form of the memory function $\kappa_{\rm ML}(t)$ which is associated with the ML relaxation function (see Eq. (2.8)). Considering $\tau^* \to 0$ thus means to make the memory function not asymptotically but completely self-similar. This is not compatible with the fact that the memory function is itself a time autocorrelation function (see Eq. (2.5)), which implies in particular $0 < \kappa_{AA}(0) < \infty$. The memory function of the ML relaxation function is, therefore, a mathematical idealization, where only the asymptotic power law form is considered. We note that this algebraic long-time tail vanishes in the limit of $\rho \to 1$, where the memory function becomes a Dirac distribution, $\kappa_{AA}(t) \to \delta(t)/\tau$, and the associated relaxation function a normal exponential function, $\phi(t) \to \exp(-t/\tau)$.

We finally note that the asymptotic form of $L_\phi(t)$ can be read off from Eq. (2.20), writing

$$\hat{\phi}(s) = \underbrace{\left(\frac{1}{\frac{1}{L_{\hat{\kappa}}(1/s\tau^*)} + (s\tau)^\rho} \right)}_{\equiv L_{\hat{\phi}}(1/s)} s^{-1} (s\tau)^\rho \,,$$

where the term in parentheses defines a slowly varying function $L_{\hat{\phi}}(.)$ as a function of $1/s$. This shows that in the time domain,

$$\phi(t) \overset{t\to\infty}{\sim} \underbrace{\left(\frac{1}{\frac{1}{L_{\hat{\kappa}}(t/\tau^*)} + (t/\tau)^{-\rho}} \right)}_{L_\phi(t) \approx L_{\hat{\phi}}(t)} \frac{(t/\tau)^{-\rho}}{\Gamma(1-\rho)} \tag{2.24}$$

is a refined asymptotic form for $\phi(t)$. We note in this context that the limit $\tau^* \to 0$, *i.e.* $L_{\hat{\kappa}}\,(t/\tau^*) \approx 1$, leads to the refined asymptotic form of the ML relaxation function derived in Ref. [40].

2.3. Illustration

As an illustration for the above findings, we construct a model relaxation function from Kummer's hypergeometric function [42], $M(a,b,z) \equiv {}_1F_1(a,b,z)$. We define the Kummer relaxation function as

$$\phi_{\rm K}(t) = {}_1F_1(\rho, 1, -t/\tau) \,, \tag{2.25}$$

and the essential point is that $\phi_{\rm K}(t)$ decays asymptotically as the ML relaxation function, *i.e.*

$$\phi_{\rm K}(t) \overset{t\to\infty}{\sim} \frac{(t/\tau)^{-\rho}}{\Gamma(1-\rho)} \,. \tag{2.26}$$

However, in contrast to the ML relaxation function, $\phi_{\mathrm{M}}(t)$ can be developed into a Taylor series around $t = 0$,

$$\phi_{\mathrm{K}}(t) = 1 - \rho(t/\tau) + \frac{\rho(\rho+1)}{4}(t/\tau)^2 + \frac{\rho(\rho+1)(\rho+2)}{36}(t/\tau)^3 + \dots \quad (2.27)$$

The Laplace transform of the Kummer relaxation function has the simple analytical form

$$\hat{\phi}_{\mathrm{K}}(s) = s^{-1}(s\tau)^{\rho}\,(1+s\tau)^{-\rho}\,, \quad (2.28)$$

which may be written as

$$\hat{\phi}_{\mathrm{K}}(s) = \frac{1}{s + \frac{s(s\tau)^{-\rho}}{L_{\mathrm{K}}(1/s\tau)}}\,, \quad (2.29)$$

where $L_{\mathrm{K}}(t)$ is the slowly varying function

$$L_{\mathrm{K}}(t) = \frac{t^{\rho}}{(t+1)^{\rho} - 1}\,. \quad (2.30)$$

Our model correlation function, $\phi(t)$, will now be defined by replacing $L_{\mathrm{K}}(1/s\tau) \to L_{\mathrm{K}}(1/s\tau^*)$, such that

$$\hat{\phi}(s) \equiv \frac{1}{s + \frac{s(s\tau)^{-\rho}}{L_{\mathrm{K}}(1/s\tau^*)}} \overset{\tau^* \to 0}{\sim} \hat{\phi}_{\mathrm{ML}}(s)\,. \quad (2.31)$$

The inverse Laplace transform $\hat{\phi}(s) \to \phi(t)$ cannot be performed analytically and we resorted to computing it from a Padé approximation of $\hat{\phi}(s)$ (see also Ref. [43])

$$\hat{\phi}(s) \approx \frac{P_m(s - s_0)}{Q_n(s - s_0)}\,, \quad (2.32)$$

where $P_m(.)$ and $Q_n(.)$ are polynomials of degree m and n, respectively. This approach leads by construction to a multi-exponential approximation of $\phi(t)$ which can be computed via the residue theorem, since $\hat{\phi}(s)$ is a rational function in s

$$\phi(t) \approx \frac{1}{2\pi i} \oint_C \mathrm{d}s\, \mathrm{e}^{st} \frac{P_m(s - s_0)}{Q_n(s - s_0)} = \sum_k \mathrm{Res}\left\{ \mathrm{e}^{st} \frac{P_m(s - s_0)}{Q_n(s - s_0)}, s = s_k \right\}.$$

Choosing $s_0 = 0.1$, $m = 10$, and $n = 11$, we found that the approximation is excellent in a time range of approximately $0 \leq t < 40$ and suffices to illustrate the approach of the model relaxation function $\phi(t)$ to the ML relaxation function, which is shown in Fig. 2. We note here that for $\rho = 0.2$, the ratio τ^*/τ must be chosen very small to obtain $\phi(t) \approx \phi_{\mathrm{ML}}(t)$.

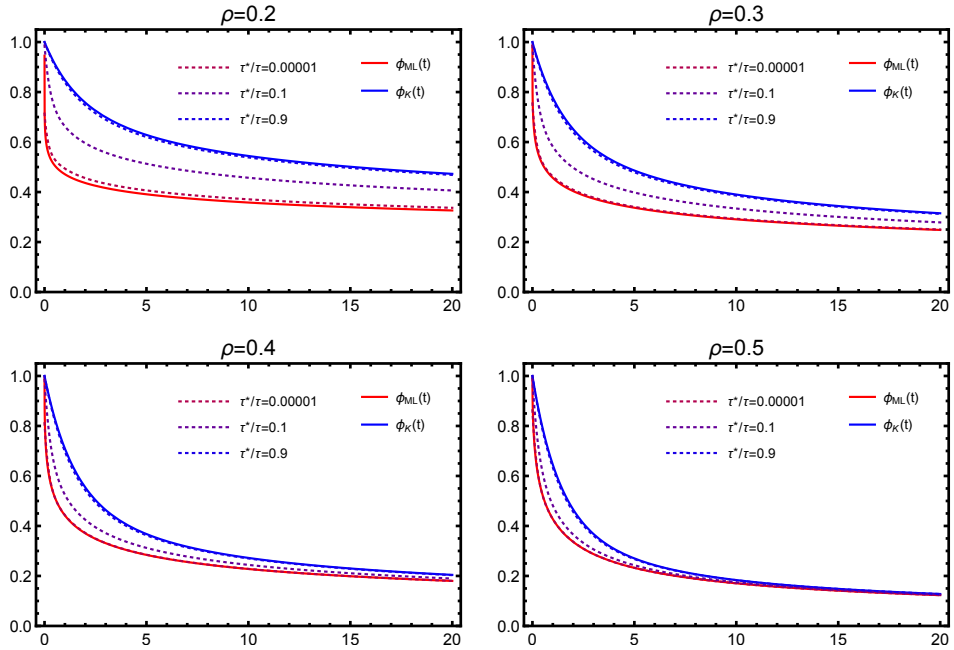

Fig. 2. Model relaxation function $\phi(t)$ for different values of ρ and τ^*/τ (blue dashed lines), together with the exact limiting cases — the Kummer relaxation function (blue solid line) and the ML relaxation function (red solid line).

3. Anomalous diffusion

3.1. Diffusion and velocity autocorrelation function

The Mittag–Leffler relaxation function appears also in the context of anomalous diffusion, where it describes the form of the velocity autocorrelation function under the condition of time scale separation comparing the time evolution of the "slow" velocity autocorrelation function (VACF) of the diffusing particle and the "fast" associated memory function. This has been proven in Ref. [43] by using amplitude scaling of the memory function and we show here that the same result can be obtained more directly, following the reasoning in Section 2.2. In diffusion processes, one considers the mean squared displacement (MSD) of a diffusing particle

$$W(t) = \left\langle (x(t) - x(0))^2 \right\rangle , \tag{3.1}$$

which may be written in the alternative form

$$W(t) = 2 \int_0^t \mathrm{d}t' \, \left(t - t'\right) c_{vv} \left(t'\right) , \tag{3.2}$$

where $c_{vv}(t) = (v(0), v(t))$ is the velocity autocorrelation function (VACF) and $x(t) - x(0) = \int_0^t \mathrm{d}t' v(t')$, with $v = \mathrm{d}x(t)/\mathrm{d}t$. The MSD for an anomalously diffusing particle has the asymptotic form [1, 4]

$$W(t) \overset{t\to\infty}{\sim} 2D_\alpha t^\alpha, \qquad 0 < \alpha < 2\,, \tag{3.3}$$

where $0 < \alpha < 1$ is referred to as "subdiffusion", which is typical for diffusion in crowded environments, $\alpha = 1$ corresponds to normal diffusion according to the Einstein–Smoluchowski law [44, 45] and $1 < \alpha < 2$ to "superdiffusion", which describes diffusion of particles tending to be expelled from their instantaneous positions. The MSD may now be considered as a regularly varying function, and we can write

$$W(t) = 2D_\alpha L_W(t) t^\alpha\,, \qquad 0 < \alpha < 2\,, \tag{3.4}$$

where $L_W(.)$ is a slowly varying function describing the approach of the MSD to the asymptotic regime. The VACF being a classical time correlation function obeys an equation of motion of the form of (2.3),

$$\partial_t c_{vv}(t) + \int_0^t \mathrm{d}t'\, c_{vv}\left(t - t'\right) \kappa_{vv}\left(t'\right) = 0\,, \tag{3.5}$$

and the Laplace transform of this equation may be inserted into the Laplace transform of Eq. (3.2) to give

$$\hat{W}(s) = \frac{2}{s^2} \underbrace{\frac{\langle v^2 \rangle}{s + \hat{\kappa}(s)}}_{\hat{c}_{vv}(s)}\,. \tag{3.6}$$

On the other hand, it follows from the general form (3.4) of the MSD that

$$\hat{W}(s) \overset{s\to 0}{\sim} 2D_\alpha L_W\left(\frac{1}{s}\right) \frac{\Gamma(1+\alpha)}{s^{1+\alpha}}\,, \tag{3.7}$$

and defining the diffusion time scale

$$\tau_\mathrm{D} = \left(\frac{\langle v^2 \rangle}{D_\alpha \Gamma(\alpha+1)}\right)^{\frac{1}{\alpha-2}}\,, \tag{3.8}$$

the asymptotic form of the memory function is found to be

$$\hat{\kappa}_{vv}(s) \overset{s\to 0}{\sim} \frac{s(s\tau_\mathrm{D})^{\alpha-2}}{L_W\left(\frac{1}{s}\right)}\,. \tag{3.9}$$

Therefore, the memory function of the VACF must have the general form of

$$\hat{\kappa}_{vv}(s) = \frac{s(s\tau_{\mathrm{D}})^{\alpha-2}}{L_{\hat{\kappa}}\left(\frac{1}{s}\right)}\,, \tag{3.10}$$

noting that $\lim_{t\to\infty} L_{\hat{\kappa}}(t) = 1$. Introducing now again an explicit time scale τ^* for $L_{\hat{\kappa}}(t)$, *i.e.*

$$L_{\hat{\kappa}}(t) \equiv L_{\hat{\kappa}}(t/\tau^*)\,, \tag{3.11}$$

the Laplace transform of the relaxation function

$$\psi(t) = c_{vv}(t)/c_{vv}(0) \tag{3.12}$$

becomes

$$\hat{\psi}(s) = \frac{1}{s + \frac{s(s\tau_{\mathrm{D}})^{\alpha-2}}{L_{\hat{\kappa}}\left(\frac{1}{s\tau^*}\right)}} \overset{\tau^*\to 0}{\sim} \frac{1}{s + s(s\tau_{\mathrm{D}})^{\alpha-2}}\,, \tag{3.13}$$

and, therefore,

$$\psi(t) \overset{\tau^*\to 0}{\sim} E_{2-\alpha}(-(t/\tau_{\mathrm{D}})^{2-\alpha})\,. \tag{3.14}$$

For an MSD that grows asymptotically as $2D_\alpha t^\alpha$, we thus obtain a VACF in the form of an ML relaxation function of the order of $2-\alpha$ and τ_{D} given by Eq. (3.8) as the characteristic time scale. For the $\alpha = 1$ case, *i.e.* for normal diffusion, we have in particular exponential relaxation

$$\lim_{\alpha\to 1} \psi(t) \overset{\tau^*\to 0}{\sim} \exp(-t/\tau_{\mathrm{D}})\,, \tag{3.15}$$

which characterizes the case of Langevin dynamics. In the Langevin model, τ^* is the time scale of the rapidly varying external forces due to the impact of the solvent molecules, which are modeled as rapidly varying random forces [34].

3.2. Illustration

As an illustration, we take the relaxation function of Section 2.3 as a model for the VACF, replacing $\rho \to 2-\alpha$,

$$\hat{\psi}(s) := \frac{1}{s + \frac{s(s\tau_{\mathrm{D}})^{\alpha-2}}{L_{\mathrm{K}}(1/s\tau^*)}}\,. \tag{3.16}$$

The slowly varying function $L_{\mathrm{K}}(.)$ is here given by Eq. (2.30). We use again a Padé approximation for $\hat{\psi}(s)$ in order to obtain $\psi(t)$ for different values of τ^*/τ_{D} by the inverse Laplace transform, recalling that $\psi(t)$ is then a multi-exponential approximation of the true model relaxation function in

the time domain. Figure 3 shows from top to bottom in the left panels the normalized model VACFs for $\alpha = 0.5, 1, 1.5$, respectively, using different ratios τ^*/τ_D, and in the right panels the respective MSDs, which have been obtained by numerical integration according to Eq. (3.2). In contrast to the case of anomalous relaxation, the index of the ML relaxation function varies

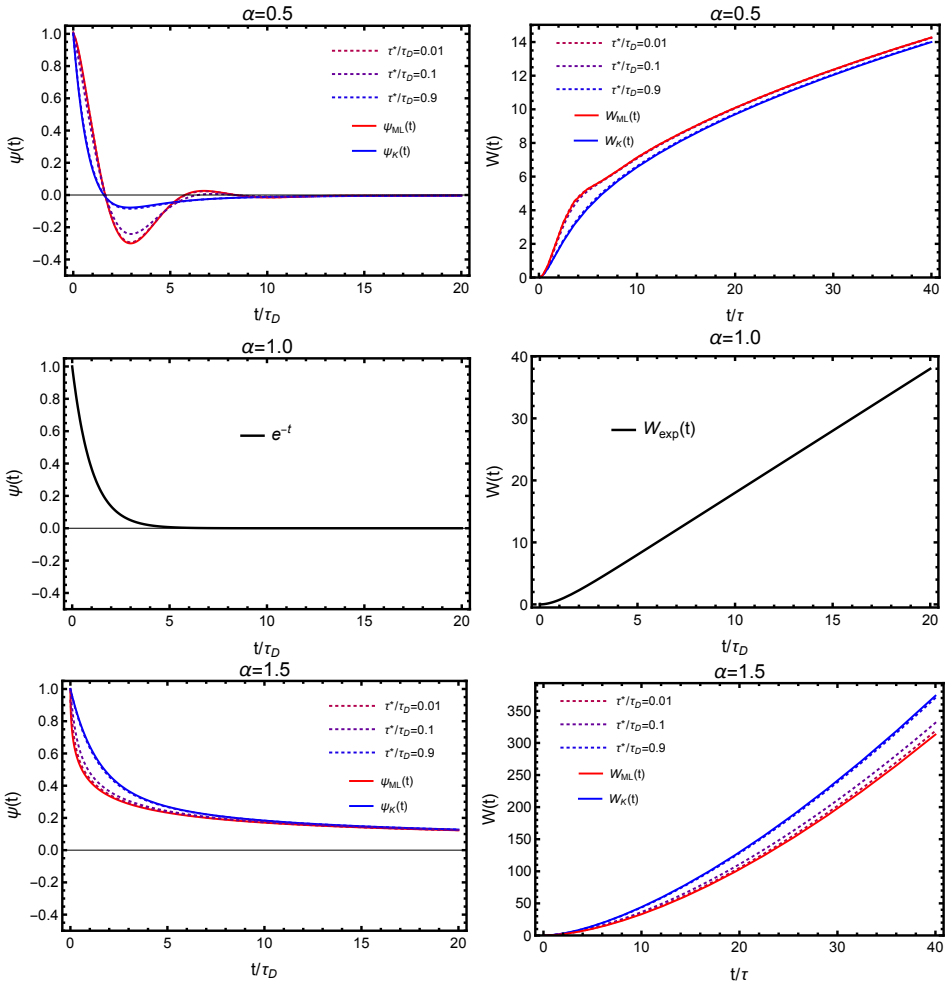

Fig. 3. From top to bottom: Normalized velocity autocorrelation functions (left panel) and mean squared displacements (right panel) for $\alpha = 0.5, 1.0, 1.5$, respectively. For $\alpha = 0.5$ and $\alpha = 1.5$, the dashed lines indicate the normalized model VACFs and the corresponding MSDs for the indicated values of τ^*/τ_D. The blue and red solid lines correspond, respectively, to the $\tau^* = \tau_\mathrm{D}$ and $\tau^*/\tau_\mathrm{D} \to 0$ cases. For $\alpha = 1$, the model VACF and the Mittag–Leffler relaxation function coincide and become an exponentially decaying function, $\psi(t) = \exp(-t/\tau_\mathrm{D})$.

here between 0 and 2. The "subdiffusive" regime, $0 < \alpha < 1$, is characterized by a VACF exhibiting a negative algebraic long-time tail, which indicates a persisting tendency of the diffusing particles to invert their velocity and to return to the point of departure, whereas the VACF corresponding to the "superdiffusive" regime, $1 < \alpha < 2$, exhibits a positive power law long-time tail which indicates a persisting tendency of the diffusing particles to keep their velocity and to escape from the current position [46].

It is important to note that the time scale separation does not lead to an MSD of the form of $W(t) = 2D_\alpha t^\alpha$, *i.e.* to $L_W(.) = 1$. The reason is that $L_W(.)$ and $L_{\hat{\kappa}}(.)$ are only asymptotically equal and the ballistic regime $W(t) \approx \langle v^2 \rangle t^2$ survives the limit of $\tau^*/\tau_\mathrm{D} \to 0$. This follows by the Taylor expansion of expression (3.2) and it can also be seen in Fig. 3, which shows that all MSDs start with a quadratic ballistic regime.

4. Memory function scaling

4.1. Anomalous relaxation

It follows from the asymptotic forms (2.15) and (2.17) of the slowly varying function $L(.)$ and the Laplace transformed relaxation function, respectively, that the relaxation time scale τ is given by

$$\tau = \left(\lim_{s \to 0} s^{\rho - 1} \hat{\kappa}_{AA}(s) \right)^{-1/\rho} = \eta_\rho^{-1/\rho} , \qquad 0 < \rho < 1 , \tag{4.1}$$

where $\eta_\rho = \lim_{s \to 0} s^{\rho-1} \hat{\kappa}_{AA}(s)$ can be expressed as the fractional Kubo integral [46]

$$\eta_\rho = \int_0^\infty \mathrm{d}t \, \partial_t^{\rho - 1} \kappa_{AA}(t) . \tag{4.2}$$

The fractional time derivative of the memory function is here defined through

$$\partial_t^{\rho-1} \kappa_{AA}(t) = \frac{\mathrm{d}}{\mathrm{d}t} \int_0^t \mathrm{d}t' \, \frac{(t - t')^{1-\rho}}{\Gamma(2 - \rho)} \kappa_{AA}\left(t'\right) .$$

In the case of normal relaxation, where $\rho \to 1$, we have $\tau = 1/\eta$ and $\eta = \int_0^\infty \mathrm{d}t \, \kappa_{AA}(t)$. With these preliminaries, one sees immediately that the scaling

$$\kappa_{AA}(t) \to \lambda \kappa_{AA}(t) \tag{4.3}$$

entails a scaling of the time scale τ through

$$\tau \to \tau(\lambda) = \lambda^{-1/\rho} \tau , \tag{4.4}$$

such that $\lim_{\lambda\to 0}\tau^*/\tau(\lambda) = 0$ and

$$\phi(t) \overset{\lambda\to 0}{\sim} E_\rho(-\lambda(t/\tau)^\rho) \tag{4.5}$$

becomes the ML relaxation function.

4.2. Anomalous diffusion

In the case of anomalous diffusion, we have simply to replace

$$A \to v \quad \text{and} \quad \rho \to 2-\alpha\,, \quad \text{where} \quad 0<\alpha<2\,. \tag{4.6}$$

This leads to a diffusion time of the form of

$$\tau_{\mathrm{D}} = \left(\lim_{s\to 0} s^{1-\alpha}\hat{\kappa}_{vv}(s)\right)^{\frac{1}{\alpha-2}} = \eta_\alpha^{\frac{1}{\alpha-2}}\,, \tag{4.7}$$

where the fractional relaxation rate is given by

$$\eta_\alpha = \int_0^\infty \mathrm{d}t\, \partial_t^{1-\alpha}\kappa_{vv}(t)\,. \tag{4.8}$$

The fractional derivative of the order of $1-\alpha$ reads here explicitly

$$\partial_t^{1-\alpha}\kappa_{vv}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\int_0^t \mathrm{d}t'\,\frac{(t-t')^{\alpha-1}}{\Gamma(\alpha)}\kappa_{vv}\left(t'\right)\,,$$

and the scaling $\kappa_{vv}(t) \to \lambda\kappa_{vv}(t)$ entails here a change of the diffusion time scale τ_{D} as

$$\tau_{\mathrm{D}} \to \tau_{\mathrm{D}}(\lambda) = \lambda^{\frac{1}{\alpha-2}}\tau_{\mathrm{D}}\,. \tag{4.9}$$

Therefore, $\lim_{\lambda\to 0}\tau^*/\tau_{\mathrm{D}}(\lambda) \to 0$ and

$$\psi(t) \overset{\lambda\to 0}{\sim} E_{2-\alpha}\left(-\lambda(t/\tau_{\mathrm{D}})^{2-\alpha}\right) \tag{4.10}$$

are in agreement with Ref. [43]. The physical argument for scaling the memory function is here an increase of the mass of the diffusing particle according to $m \to m/\lambda$. The mass scaling argument was already used some time ago [47] by one of us (G.R.K.) to explain the approach $\psi(t) \to \exp(-\lambda(t/\tau_{\mathrm{D}}))$, for $\lambda \to 0$, which is characteristic for the Brownian motion and which has been found empirically by molecular dynamics simulations of a tracer particle of increasing mass, $m \to m/\lambda$, in a solvent of identical "solvent particles" of mass m [48].

5. Conclusion and discussion

We have shown that any time correlation function displaying an asymptotic slow power law decay $\sim t^{-\rho}/\Gamma(1-\rho)$, with $0 < \rho < 1$, takes the form of a Mittag–Leffler relaxation function, $E_\rho(-(t/\tau)^\rho)$, if there is a separation between the time scale τ^*, describing the approach of the memory function to its asymptotic form, and the relaxation time scale τ describing its asymptotic regime, in the sense of $\tau^* \ll \tau$. The essential point was to use that time correlation functions with an asymptotic power law decay and their associated memory functions are regularly varying functions in the sense of asymptotic analysis, and that such functions can be written as a product of a slowly varying function, $L(t)$, tending to a plateau value, and a power law function $\sim t^{-\rho}$. The Mittag–Leffler relaxation function appears also as a limiting case of the velocity autocorrelation function of an anomalously diffusing particle, $\langle v(0)v(t)\rangle \sim E_{2-\alpha}(-(t/\tau_\mathrm{D})^{2-\alpha})$, if the time scale τ^* describing the approach of the associated memory function to its asymptotic regime is much shorter than the diffusion time scale, τ_D, where $0 < \alpha < 2$ defines the asymptotic form of the mean squared displacement, $\langle (x(t) - x(0))^2\rangle \sim t^\alpha$.

The derivation of the ML relaxation function in the framework of asymptotic analysis shows an alternative route to the scaling method for the memory function used in earlier work [43], and gives a clearer physical picture of the transition to the asymptotic regime. We finally remark that numerical illustrations have been produced with Wolfram's Mathematica package [49].

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