Generalized Kubo relations and conditions for anomalous diffusion: Physical insights from a mathematical theorem

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The paper describes an approach to anomalous diffusion within the framework of the generalized Langevin equation. Using a Tauberian theorem for Laplace transforms due to Hardy, Littlewood, and Karamata, generalized Kubo relations for the relevant transport coefficients are derived from the asymptotic form of the mean square displacement. In a second step conditions for anomalous diffusion are derived for the asymptotic forms of the velocity autocorrelation function and the associated memory function. Both spatially unconfined and confined diffusion processes are considered. The results are illustrated with semi-analytical examples. © *2011 American Institute of Physics*. [doi:10.1063/1.3598483]

I. INTRODUCTION

During the last two decades, the theoretical description of diffusion processes has shown a change of paradigm in order to account for the increasing number of manifestations of anomalous diffusion processes in all branches of science. In case of particles diffusing without confinement such processes manifest themselves by a deviation of the time-dependent mean square displacement (MSD) from the linear form for regular Brownian motion,[1–3] $W(t) \equiv \langle [\mathbf{x}(t) - \mathbf{x}(0)]^2 \rangle = 2Dt$, where D is the diffusion constant. One observes instead a diffusion law of the form

$$W(t) = 2D_\alpha t^\alpha, \tag{1}$$

where the regimes $0 < \alpha < 1$ and $1 < \alpha < 2$ are referred to as sub- and superdiffusion, respectively. D_α is the fractional diffusion constant with physical dimension length^2/time$^\alpha$, which includes for convenience the spatial dimension of the diffusion process. Examples for unconfined anomalous diffusion comprise the transport of electrons in porous media,[4] the diffusion of molecules in polar liquids in presence of an external electrical field,[5] and the diffusion of molecules in biological environments.[6–10] In the context of this paper, the key word "unconfined" refers to the physical situation where the diffusing particle can escape to infinity for long times and its MSD is asymptotically unbound, although its motion might be strongly hindered. In reality, some confinement may exist due to the probed system itself[11] or due to the experimental setup,[12] and anomalous diffusion can also be a transient phenomenon.[13] In case of spatially confined motions, anomalous diffusion is associated with a slow, strongly non-exponential decay of the position autocorrelation function. In contrast to confined diffusion processes, the MSD is bound and tends asymptotically to a plateau value. Examples range from turbulence[14] to internal protein dynamics.[15–17]

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A possible approach to anomalous single-particle diffusion in dense media is to consider a tagged particle in interaction with its physical environment, whose dynamics is described by an appropriate explicit physical model. Long time ago Percus has shown[18] that particles in a one-dimensional hard-core fluid, which are driven by independent random forces, exhibit anomalous diffusion with $\alpha = 1/2$, and there are many models explaining anomalous diffusion in polymeric systems.[19,20] Another, more mathematical route to model anomalous diffusion is to consider stochastic non-markovian single particle models. Here only the diffusing particle is explicitly considered and its environment is represented by long time memory effects in the underlying stochastic process. An example for such a process is fractional Brownian motion,[21–23] which is driven by stationary fractional Gaussian noise (FGN). In contrast to normal, "white" Gaussian noise, FGN is characterized by a slowly decaying autocorrelation function. More generally, one can consider long-memory processes which are described by fractional Langevin equations (FLE).[24–26] Here the driving force is again FGN and its autocorrelation function defines a memory kernel which replaces the friction constant in the ordinary Langevin equation. Instead of describing stochastic processes with long memory by stochastic differential equations, one may also consider fractional Fokker-Planck equations (FFPE) for the corresponding transition probabilities.[27–31] FFPEs are generalizations of normal Fokker-Planck equations[32] in which non-markovian long-memory effects are introduced by an additional fractional time derivative. The properties of stochastic processes described by FLEs and FFPEs are, however, not the same. In Refs. 26 and 33 it is pointed out that stochastic processes described by the FLE are ergodic and Refs. 12, 34, and 35 discuss weak ergodicity breaking of stochastic processes described by FFPEs. In this context, the impact of confinement is discussed in Ref. 36. To some extent, a physical interpretation of anomalous diffusion described by FFPEs can be given by deriving the latter from the continuous time random walk model,[30,37] and an illustrative interpretation of the memory kernel in FLEs for the description of subdiffusion in viscoelastic media can be found in Ref. 38.

In this paper, a theoretical description of anomalous diffusion processes is developed which combines a formally exact description of single particle dynamics within the framework of the generalized Langevin equation[39,40] with an asymptotic analysis of the relevant observables for long times. Memory effects enter here naturally through the memory function of the velocity autocorrelation function of the diffusing particle, which is in turn related to the MSD. The aim of the paper is to derive generalized Kubo relations for the relevant transport coefficients, which hold for both normal and anomalous diffusion, and to formulate general conditions for anomalous diffusion, enabling a simple physical interpretation without imposing a particular model.

The paper is organized as follows: Section II treats the derivation of generalized Kubo relations, starting from a theorem for asymptotic analysis which is applied to the MSD of a diffusing particle. In a second step general conditions for anomalous diffusion are derived, where spatially unconfined and confined diffusion are distinguished.

In Sec. III, the results are illustrated with semi-analytical examples and the paper is concluded by a short résumé and an outlook.

II. THEORY

A. Kubo relation for D_α

Kubo relations establish a connection between macroscopic transport coefficients and the microscopic Hamiltonian dynamics of the system under consideration.[41] Each transport coefficient is expressed by an integral over a corresponding time correlation function. In case of diffusion processes one considers the velocity autocorrelation function (VACF), $c_{vv}(t) = \langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$, and the diffusion coefficient is given by the well-known relation

$$D = \int_0^\infty dt\, c_{vv}(t), \tag{2}$$

if one assumes unconfined normal diffusion.

A generalization of expression (2) covering both normal and anomalous diffusion can be derived from an appropriate asymptotic analysis of the MSD. Assuming isotropic diffusion, its asymptotic form may be written as

$$W(t) \overset{t\to\infty}{\sim} 2D_\alpha L(t) t^\alpha \quad (0 \le \alpha < 2), \tag{3}$$

where $L(t)$ fulfills the conditions

$$\lim_{t\to\infty} L(t) = 1, \tag{4}$$

$$\lim_{t\to\infty} t\frac{dL(t)}{dt} = 0. \tag{5}$$

For physical reasons $L(t)$ must be positive. The ballistic asymptotic regime, where $\alpha = 2$, is not considered in the following. By construction, $L(t)$ belongs to the class of slowly varying functions,[42,43] which are defined through the weaker condition $\lim_{t\to\infty} L(\lambda t)/L(t) = 1$, with $\lambda > 0$.

The general asymptotic form (3) of the MSD yields a direct link to a Tauberian theorem due to Hardy, Littlewood, and Karamata (HLK),[42,43] which establishes a relation between slowly growing functions and their Laplace transforms,

$$h(t) \overset{t\to\infty}{\sim} L(t)t^\rho \Leftrightarrow \hat{h}(s) \overset{s\to 0}{\sim} L(1/s)\frac{\Gamma(\rho+1)}{s^{\rho+1}} \quad (\rho > -1). \tag{6}$$

Here $\hat{h}(s) = \int_0^\infty dt\, \exp(-st)h(t)$ $(\Re\{s\} > 0)$ denotes the Laplace transform of $h(t)$. Noting that $\hat{h}(0) = \int_0^\infty dt\, h(t)$, the theorem can be intuitively understood. It states that the divergence of the integral $\int_0^t d\tau\, h(\tau)$ as t approaches infinity is reflected in the divergence of the Laplace transform of $h(t)$, as s approaches zero. From the asymptotic form (3) of the MSD and the HLK theorem one can conclude that

$$\hat{W}(s) \overset{s\to 0}{\sim} 2D_\alpha L(1/s)\frac{\Gamma(\alpha+1)}{s^{\alpha+1}}. \tag{7}$$

The relation of this expression to the VACF of the diffusing particle follows from the convolution relation[44]

$$W(t) = 2\int_0^t dt'\,(t-t')c_{vv}(t'), \tag{8}$$

which translates by Laplace transform into

$$\hat{W}(s) = \frac{2\,\hat{c}_{vv}(s)}{s^2}. \tag{9}$$

Comparison with Eq. (7) shows that

$$\hat{c}_{vv}(s) \overset{s\to 0}{\sim} D_\alpha \Gamma(\alpha+1)L(1/s)s^{1-\alpha}. \tag{10}$$

From expression (10) one can derive a generalized Kubo relation for the fractional diffusion constant which holds for both normal and anomalous diffusion processes. The first step consists in solving Eq. (10) for D_α. Using that $\lim_{s\to 0} L(1/s) = 1$ on account of Eq. (4), one obtains

$$D_\alpha = \lim_{s\to 0} s^{\alpha-1}\hat{c}_{vv}(s)/\Gamma(1+\alpha). \tag{11}$$

In a second step one recognizes that $s^{\alpha-1}\hat{c}_{vv}(s)$ is the Laplace transform of the fractional derivative of order $\alpha - 1$ of $c_{vv}(t)$ with respect to time. Writing $\rho = n - \beta$, where $n = 0, 1, 2, \ldots$ is an integer number and $\beta \ge 0$ is real, the fractional Riemann-Liouville derivative of order ρ of an arbitrary function g is defined through[45]

$${}_0\partial_t^\rho g(t) = \partial_t^{(-)n}\int_0^t dt'\,\frac{(t-t')^{\beta-1}}{\Gamma(\beta)}g(t'). \tag{12}$$

The symbol $\partial_t^{(-)n}$ denotes a normal *left* derivative of order n and negative values of ρ indicate fractional integration. The index "0" in the symbol for the fractional derivative on the left-hand side in Eq. (12) refers to the lower limit in the integral on the right-hand side. Since $\lim_{s\to 0}\hat{g}(s) = \int_0^\infty dt\, g(t)$, one finds that the fractional diffusion coefficient is given by the relation

$$D_\alpha = \frac{1}{\Gamma(1+\alpha)}\int_0^\infty dt\;\; {}_0\partial_t^{\alpha-1}c_{vv}(t). \tag{13}$$

For $\alpha = 1$ the standard Kubo expression (2) for the diffusion constant is retrieved and for the case $\alpha = 0$, which describes spatially limited diffusion where $\lim_{t\to\infty} W(t) = 2D_0$, one obtains

$$D_0 = \lim_{T\to\infty} \int_0^T dt \int_0^t d\tau\, c_{vv}(\tau)$$
$$= \lim_{T\to\infty} \int_0^T d\tau\, (T-\tau) c_{vv}(\tau) = \lim_{T\to\infty} W(T)/2. \quad (14)$$

Since $\lim_{T\to\infty} W(T) = 2\langle \mathbf{u}^2\rangle$, where $\langle \mathbf{u}^2\rangle = \langle \mathbf{x}^2\rangle - \langle \mathbf{x}\rangle^2$ is the mean square position fluctuation of the particle, it follows that

$$D_0 = \langle \mathbf{u}^2 \rangle. \quad (15)$$

B. Generalized fluctuation-dissipation theorem

In the framework of the generalized Langevin equation developed by Zwanzig,[39,40] the motion of a tagged particle in an isotropic solvent is described by an equation of motion of the form

$$\dot{\mathbf{v}}(t) = -\int_0^t dt'\, \kappa(t-t')\mathbf{v}(t') + \mathbf{f}^{(+)}(t), \quad (16)$$

where $\mathbf{v}(t)$ is the velocity of the particle, $\kappa(t)$ is the corresponding memory function, and $\mathbf{f}^{(+)}(t)$ a generalized acceleration fulfilling the orthogonality relation $\langle \mathbf{v}(t)\cdot \mathbf{f}^{(+)}(t')\rangle = 0$. In contrast to a full Hamiltonian description of the system, the solvent is not described explicitly, but both $\kappa(t)$ and $\mathbf{f}^{(+)}(t)$ can be, in principle, expressed by the microscopic dynamical variables describing the full system. They are thus fully deterministic quantities. For details the reader is referred to the monograph by Zwanzig.[40] Due to the orthogonality between $\mathbf{v}$ and $\mathbf{f}^{(+)}$, the time evolution of the VACF is described by the integro-differential equation

$$\partial_t c_{vv}(t) = -\int_0^t dt'\, c_{vv}(t-t')\kappa(t'). \quad (17)$$

The Laplace transform of this integral equation can be solved for the Laplace transformed VACF,

$$\hat{c}_{vv}(s) = \frac{\langle \mathbf{v}^2\rangle}{s + \hat{\kappa}(s)}, \quad (18)$$

which may be inserted into Eq. (9) to yield

$$\hat{W}(s) \overset{s\to 0}{\sim} \frac{\langle \mathbf{v}^2\rangle}{s^2 \hat{\kappa}(s)}. \quad (19)$$

Here $\langle \mathbf{v}^2\rangle = c_{vv}(0)$ and the assumption $s^3 \ll s^2\hat{\kappa}(s)$ has been made, which is correct for $s \to 0$ if ballistic diffusion is excluded. In the latter case one would have $W(t) \overset{t\to\infty}{\sim} t^2$ and therefore $\hat{W}(s) \overset{s\to 0}{\sim} s^{-3}$. Equating expressions (7) and (19) leads then to

$$\hat{\kappa}(s) \overset{s\to 0}{\sim} \frac{\langle \mathbf{v}^2\rangle}{D_\alpha \Gamma(\alpha+1)} \frac{s^{\alpha-1}}{L(1/s)}. \quad (20)$$

Analogously to a fractional diffusion coefficient one can define a fractional relaxation constant through

$$\eta_\alpha = \Gamma(1+\alpha) \lim_{s\to 0} s^{1-\alpha}\hat{\kappa}(s), \quad (21)$$

which becomes in the time domain

$$\eta_\alpha = \Gamma(1+\alpha) \int_0^\infty dt\ {}_0\partial_t^{1-\alpha}\kappa(t), \quad (22)$$

and leads to the fractional version of the fluctuation-dissipation theorem,

$$D_\alpha = \frac{\langle \mathbf{v}^2\rangle}{\eta_\alpha}. \quad (23)$$

It should be noted that the same relation for phenomenological constants D_α and η_α has been found in Ref. 28. For $\alpha = 1$ one retrieves the standard definition $\eta = \int_0^\infty dt\, \kappa(t)$ for the relaxation constant and for spatially confined diffusion one obtains

$$\eta_0 = \int_0^\infty dt\, \partial_t^{(-)}\kappa(t) = \kappa(\infty). \quad (24)$$

Here is has been used that $\partial_t^{(-)}$ is a left derivative and that $\kappa(t) = \theta(t)\kappa(t)$ ($\theta(t)$ is the Heaviside function) since the memory function is causal. On the other hand, it follows from $D_0 = \langle \mathbf{v}^2\rangle/\eta_0 = \langle \mathbf{u}^2\rangle$ that

$$\eta_0 = \kappa(\infty) = \frac{\langle \mathbf{v}^2\rangle}{\langle \mathbf{u}^2\rangle}. \quad (25)$$

C. Conditions for anomalous diffusion in the time domain

A further application of the HLK theorem permits the derivation of conditions for the asymptotic form of the VACF and its memory function in the time domain. To derive these conditions we introduce the functions

$$f(t) = \int_0^t d\tau\, c_{vv}(\tau), \quad (26)$$

$$g(t) = \int_0^t d\tau\, \kappa(\tau). \quad (27)$$

One recognizes that $f(\infty) = D$ and $g(\infty) = \eta$ in case of normal unconfined diffusion. Defining the slowly varying functions

$$L_f(t) = \alpha D_\alpha L(t), \quad (28)$$

$$L_g(t) = \frac{\langle \mathbf{v}^2\rangle}{D_\alpha \Gamma(2-\alpha)\Gamma(\alpha+1)L(t)}, \quad (29)$$

and using that $\hat{f}(s) = \hat{c}_{vv}(s)/s$ and $\hat{g}(s) = \hat{\kappa}(s)/s$, we obtain the following equivalences from Eqs. (10) and (20), and from the HLK theorem (6),

$$\hat{f}(s) \overset{s\to 0}{\sim} L_f(1/s)\frac{\Gamma(\alpha)}{s^\alpha} \Leftrightarrow f(t) \overset{t\to\infty}{\sim} L_f(t) t^{\alpha-1}, \quad (30)$$

$$\hat{g}(s) \overset{s\to 0}{\sim} L_g(1/s)\frac{\Gamma(2-\alpha)}{s^{2-\alpha}} \Leftrightarrow g(t) \overset{t\to\infty}{\sim} L_g(t) t^{1-\alpha}. \quad (31)$$

Note that if $L(t)$ is a slowly varying function, the same is true for $1/L(t)$. On account of Eqs. (26) and (27), differentiation of $f(t)$ and $g(t)$ for large times leads to necessary conditions for the asymptotic forms of the VACF and its memory function.

Observing that $\lim_{t\to\infty} t\, dL/dt = 0$, one obtains

$$c_{vv}(t) \overset{t\to\infty}{\sim} D_\alpha \alpha(\alpha-1)L(t)t^{\alpha-2}, \tag{32}$$

$$\kappa(t) \overset{t\to\infty}{\sim} \frac{\langle \mathbf{v}^2\rangle}{D_\alpha}\frac{\sin(\pi\alpha)}{\pi\alpha}\frac{1}{L(t)}t^{-\alpha}. \tag{33}$$

Applying here the HLK theorem again, one can also conclude that Eq. (10) follows from Eq. (32) if $1 < \alpha < 2$ and that Eq. (20) follows from Eq. (33) if $0 < \alpha < 1$. Therefore, Eq. (32) and Eq. (33) are also sufficient conditions for superdiffusion and subdiffusion, respectively. The relations $c_{vv}(t) \overset{t\to\infty}{\sim} 0$ and $\kappa(t) \overset{t\to\infty}{\sim} 0$, which arise for $\alpha = 0, 1$ in case of the VACF and for $\alpha = 1$ in case of the memory function, indicate the absence of the corresponding algebraic long time tails.

D. Spatially confined diffusion

So far, spatially confined diffusion appears as an extreme case of subdiffusion, where $\alpha = 0$. The fact that the motions of the diffusing particle take place in a restricted volume does, however, certainly not imply that the diffusion process is anomalous. In contrast to unconfined diffusion, where the anomalies refer to a deviation of the MSD from an asymptotically linear regime, the distinction between normal and anomalous confined diffusion must be made on the basis of the function $L(t)$. The latter describes how the MSD and the memory function converge to their respective plateau values $W(\infty) = 2\langle \mathbf{u}^2\rangle$ and $\kappa(\infty) = \langle \mathbf{v}^2\rangle/\langle \mathbf{u}^2\rangle$.

A natural way to define anomalous spatially confined diffusion is to consider the relaxation time of the shifted memory function, $\kappa(t) - \kappa(\infty)$, which is given by

$$\tau_c = \int_0^\infty dt\, \frac{\kappa(t)-\kappa(\infty)}{\kappa(0)-\kappa(\infty)}. \tag{34}$$

Normal diffusion may then be characterized by a finite value of τ_c, whereas an infinite relaxation time indicates long time memory effects leading to anomalous diffusion. In this sense the situation corresponds to unconfined subdiffusion, where $\int_0^t d\tau\, \kappa(\tau) \equiv g(t)$ diverges for $t \to \infty$. To find out if τ_c diverges, it suffices to consider the asymptotic form of $\kappa(t) - \kappa(\infty)$. According to Eq. (33) we have for $\alpha = 0$

$$\kappa(t) \overset{t\to\infty}{\sim} \frac{\langle \mathbf{v}^2\rangle}{\langle \mathbf{u}^2\rangle}\frac{1}{L(t)}, \tag{35}$$

which confirms that $\kappa(t)$ tends to the plateau value of Eq. (25). In view of Eq. (35) τ_c will diverge if

$$\frac{1}{L(t)} - 1 \overset{t\to\infty}{\sim} C\, t^{-\beta} \text{ and } 0 < \beta \le 1, \tag{36}$$

where C is a constant. Any faster decay leads to a finite value for τ_c.

E. Cage model

The asymptotic forms of the VACF and its memory function which have been derived above have a simple physical interpretation in terms of the "cage model" for the dynamics of particles diffusing in liquids.[46] Its meaning is easily understood by considering the extreme case, where the memory function is constant, $\kappa(t) \equiv \Omega^2$. The corresponding VACF has then the form $c_{vv}(t) = \langle \mathbf{v}^2\rangle \cos\Omega t$, reflecting an ongoing "rattling motion" in the persistent cage of nearest neighbors. In real systems, the latter will exist for more or less long time and it depends on its persistence which type of diffusion is seen. The following discussion illustrates this point.

- *Subdiffusion.*
  According to Eqs. (32) and (33) subdiffusion implies a negative long time tail for the VACF and a positive long time tail for the memory function,

$$\left.\begin{array}{ll} c_{vv}(t) \sim t^{\alpha-2},\ c_{vv}(t) & < 0 \\ \kappa(t) \sim t^{-\alpha}, \quad \kappa(t) & > 0 \end{array}\right\}\ 0 < \alpha < 1. \tag{37}$$

  The negative autocorrelations of the particle velocity for large time lags indicate a persistent tendency of the diffusing particle to invert its direction of motion and to stay localized. The classical Kubo relations for D and η evaluate here to $D = 0$ and $\eta = \infty$.
- *Normal diffusion.*
  This type of diffusion occurs whenever the classical Kubo relations for D and η give finite values.
- *Superdiffusion.*
  Here, Eqs. (32) and (33) imply a positive long time tail for the VACF and a negative long time tail for the memory function,

$$\left.\begin{array}{ll} c_{vv}(t) \sim t^{\alpha-2},\ c_{vv}(t) & > 0 \\ \kappa(t) \sim t^{-\alpha}, \quad \kappa(t) & < 0 \end{array}\right\}\ 1 < \alpha < 2. \tag{38}$$

  The asymptotically positive velocity autocorrelation function indicates a preference to delocalize the diffusing particle. Consistently, $\kappa < 0$ for $t \to \infty$ expresses an asymptotically "negative" cage, favoring according to Eq. (17) correlations of the particle's velocity in the same direction. Here, the classical Kubo intergals for D and η yield $D = \infty$ and $\eta = 0$.
- *Spatially confined diffusion.*
  It follows from relation Eq. (33) that the memory function decays to a plateau value, $\kappa(\infty)$, describing a "permanent cage." If Eq. (36) is fulfilled, i.e., if the approach of $\kappa(t)$ to its plateau value is sufficiently slow, the diffusion is anomalous.

III. ILLUSTRATIONS

In the following some examples for spatially unconfined and confined diffusion will be discussed which illustrate how the various asymptotic forms of the MSD can be generated from a simple model for the memory function associated to the VACF, i.e., from different types of "cages."

A. Spatially unconfined diffusion

The memory function for confined diffusion is assumed to have the form

$$\kappa_f(t) = \Omega^2 M(\alpha, 1, -t/\tau), \tag{39}$$

where $M(a, b, z)$ is Kummer's hypergeometric function,[47] Ω has the dimension of a frequency and $\tau > 0$ sets the time scale. The Kummer function is regular in the whole complex plane and it has the properties $M(0, b, z) = 1$ and $M(a, a, z) = \exp(z)$. If α is varied between 0 and 1, the model thus interpolates between a constant and an exponentially decaying memory function. It is worthwhile noting that the latter model has been proposed long time ago by Berne *et al.*[48] to describe qualitatively the VACF of simple liquids obtained from molecular dynamics simulations.[49]

Due to the analytical properties of the Kummer function the Laplace transform of $\kappa_f(t)$ has a particularly simple form,

$$\hat{\kappa}_f(s) = \Omega^2 \left\{ \frac{\tau^\alpha}{s^{1-\alpha}} \frac{1}{(s\tau + 1)^\alpha} \right\}, \quad (40)$$

showing that

$$\hat{\kappa}_f(s) \overset{s\to 0}{\sim} \Omega^2 \tau^\alpha s^{\alpha-1}. \quad (41)$$

From the general form (20) of the Laplace transformed memory function one can thus conclude that α is the exponent for the asymptotic growth of the MSD with time, $W(t) \sim 2D_\alpha t^\alpha$, and that the fractional diffusion constant for the model is given by

$$D_\alpha = \frac{\langle \mathbf{v}^2 \rangle}{\Gamma(1+\alpha)\Omega^2\tau^\alpha}. \quad (42)$$

It follows, moreover, from the asymptotic form of the Kummer function for large arguments z that

$$\kappa_f(t) \overset{t\to\infty}{\sim} \begin{cases} \Omega^2 \frac{(t/\tau)^{-\alpha}}{\Gamma(1-\alpha)}, & \alpha \neq 1, \\ \Omega^2 \exp(-t/\tau), & \alpha = 1. \end{cases} \quad (43)$$

These properties are compatible with condition (33), noting that an exponential decay amounts to saying that $\kappa_f(t) \sim 0$ for large times. Figure 1 shows the normalized model memory function, $\kappa_f(t)/\kappa_f(0)$, for $\alpha = 1/2, 1, 3/2$ (dashed, solid, and dotted line, respectively). One notices the positive long time tail in case of subdiffusion and the negative long time tail in case of superdiffusion. Here and in the following τ is set to one arbitrary time unit.

The VACFs and the MSDs corresponding to Eq. (39) have been computed by inverse Laplace transform of expressions Eqs. (9) and (18), respectively, using computer aided symbolic calculation.[50] For this purpose the analytical expression (40) for $\hat{\kappa}(s)$ was replaced by a Padé approximation,

$$\hat{\kappa}_f(s) \approx \frac{\sum_{k=0}^{M_a} a_k (s - s_0)^k}{\sum_{k=0}^{M_b} b_k (s - s_0)^k}, \quad (44)$$

in order to obtain rational expressions for $\hat{c}_{vv}(s)$ and $\hat{W}(s)$. Choosing $s_0 = 1$ and $M_a = M_b = 7$, the relative error of the inverse Laplace transform of Eq. (44) compared to the exact form (39) is smaller than 5×10^{-3} for $0 \leq t < 50\,\tau$. The calculations were performed with $\Omega = 1.5/\tau$ and $\langle \mathbf{v}^2 \rangle = 1/\tau^2$. Fig. 2 show the results for the VACFs, where the positive long time tail in the VACF corresponding to superdiffusive motion (dotted line) is well visible. The corresponding MSDs are displayed in Figure 3 (solid lines), together with the the limiting forms, $W_\infty(t) = 2D_\alpha t^\alpha$, and the common ballistic short time form, $W_b(t) = \langle \mathbf{v}^2 \rangle t^2$ (dotted lines). The above results demonstrate that the model memory function generates all regimes for unconfined diffusion and that the general conditions Eqs. (32) and (33) for the asymptotic forms of the VACF and the memory function, respectively, are fulfilled.

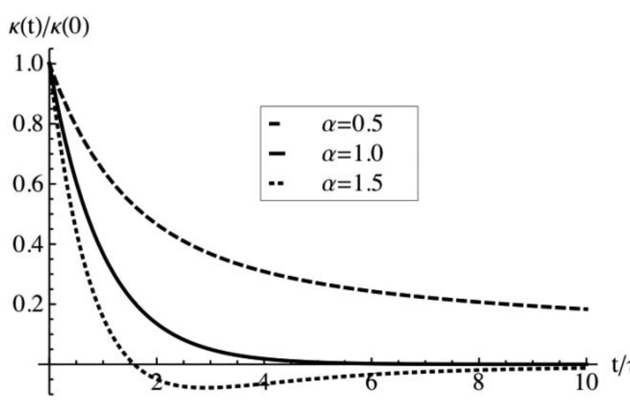

FIG. 1. Normalized memory functions according to model (39) for $\alpha = 1/2, 1, 3/2$ (dashed line, solid line, dotted line).

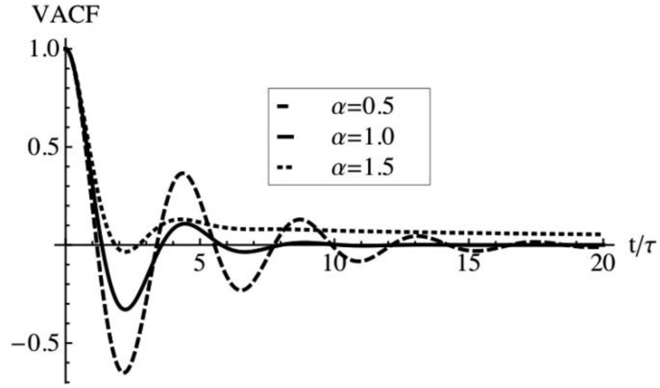

FIG. 2. Normalized VACFs derived from the memory functions shown in Fig. 1.

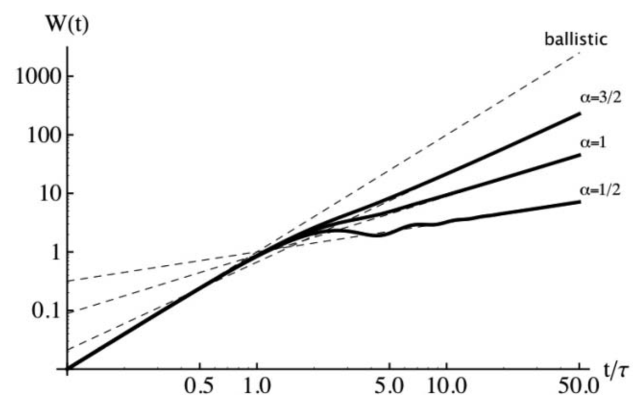

FIG. 3. Log-log plots of the MSDs derived from the memory functions shown in Fig. 1. The dotted lines indicate the asymptotic forms for (from top to bottom) the ballistic regime, $\alpha = 3/2$, $\alpha = 1$, and $\alpha = 1/2$.

B. Spatially confined diffusion

The memory function for spatially confined diffusion is chosen to be

$$\kappa_c(t) = \Omega^2 \left\{r + (1-r)M(\beta, 1, -t/\tau)\right\}, \tag{45}$$

where $0 < r < 1$ and $0 < \beta \leq 1$. It resembles the one for unconfined subdiffusion, but in contrast to the latter it decays to a finite plateau value, $\kappa_c(\infty) = \Omega^2 r$. Its asymptotic form is given by

$$\kappa_c(t) - \kappa_c(\infty) \overset{t\to\infty}{\sim} \begin{cases} \Omega^2(1-r)\frac{(t/\tau)^{-\beta}}{\Gamma(1-\beta)}, & 0 < \beta < 1, \\ \Omega^2(1-r)\exp(-t/\tau), & \beta = 1. \end{cases} \tag{46}$$

For $0 < \beta < 1$ we have thus anomalous diffusion, in the sense that the relaxation constant τ_c introduced in Eq. (34) diverges. Figure 4 displays the normalized model memory function for $\beta = 1$ and $\beta = 1/2$ (solid and dashed line, respectively), fixing $r = 0.3$. The corresponding VACFs and MSDs are shown in Figs. 5 and 6, respectively. They have been calculated in the same way as for unconfined diffusion, setting again $\Omega = 1.5/\tau$ and $\langle \mathbf{v}^2\rangle = 1$. Figure 6 displays in addition the fits of two stochastic models for the MSD: the normal Ornstein-Uhlenbeck (OU) process and the fractional Ornstein-Uhlenbeck (fOU) process. The first one describes the normal, markovian diffusion of a particle in a harmonic potential,[51] and the latter is the corresponding generalization to a non-markovian process.[30] The mean square displacement for both the OU and the fOU process can be expressed by the formula,

$$W_{(\mathrm{f})\mathrm{OU}}(t) = 2\langle \mathbf{u}^2\rangle(1 - E_b(-[t/t_0]^b)), \quad 0 < b \leq 1, \tag{47}$$

where $E_b(z)$ denotes the Mittag-Leffler (ML) function and t_0 is a time scale parameter. The ML function is an entire function in the complex plane and it can be represented by the power series

$$E_b(z) = \sum_{k=0}^{\infty} \frac{z^k}{\Gamma(1+bk)}, \tag{48}$$

which shows that $E_b(z) = \exp(z)$ for $b = 1$. The latter choice for b in Eq. (47) corresponds to the normal Ornstein-Uhlenbeck process, where the MSD converges exponentially to its plateau value. The model (47) has been fitted to the MSDs displayed in Fig. 6, leading to $b = 0.521 \approx \beta$, $t_0 = 5.537\,\tau$ for the fOU process and to $t_0 = 2.126\,\tau$ for the OU process. Both fits represent well the long time form of the MSDs corresponding to model (45) for $\beta = 1/2$ and $\beta = 1$, respectively. In this context, it is worthwhile to compare the L-functions corresponding to the (f)OU process to the one resulting from the memory function (44). It follows from the asymptotic form of the ML function,

$$E_b(-t^b) \overset{t\to\infty}{\sim} \frac{t^{-b}}{\Gamma(1-b)}, \quad (\beta \neq 1), \tag{49}$$

and from $W(t) \overset{t\to\infty}{\sim} 2\langle \mathbf{u}^2\rangle L(t)$ that the function $L_{\mathrm{fOU}}(t)$ is given by

$$L_{\mathrm{fOU}}(t) = \begin{cases} 1 - \frac{(t/t_0)^{-b}}{\Gamma(1-b)}, & \text{if } 0 < b < 1, \\ 1 - \exp(-t/t_0), & \text{if } b = 1. \end{cases} \tag{50}$$

On the other hand, one obtains from Eqs. (35) and (46)

$$L(t) = \begin{cases} 1 - \left(\frac{1-r}{r}\right)\frac{(t/\tau)^{-\beta}}{\Gamma(1-\beta)}, & \text{if } 0 < \beta < 1, \\ 1 - \left(\frac{1-r}{r}\right)\exp(-t/\tau), & \text{if } \beta = 1, \end{cases} \tag{51}$$

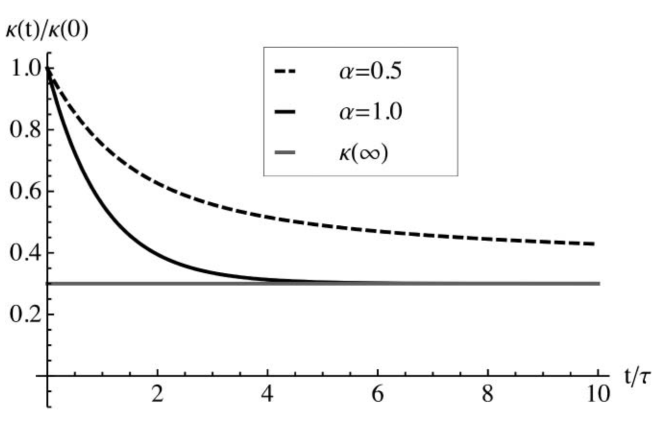

FIG. 4. Normalized memory functions according to model (45) for $\beta = 1/2$ and $\beta = 1$ (dashed line and solid line). The grey horizontal line shows the plateau value.

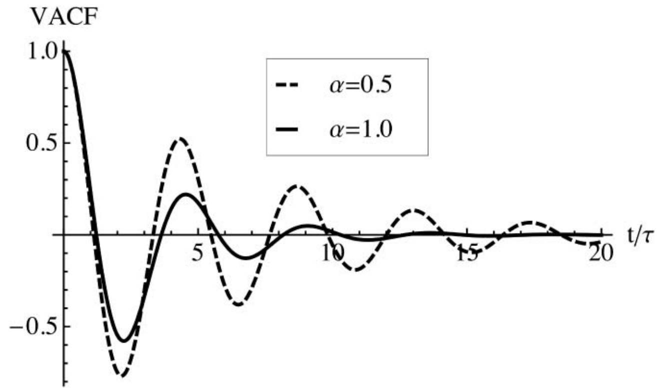

FIG. 5. Normalized VACFs corresponding to the memory functions shown in Fig. 4.

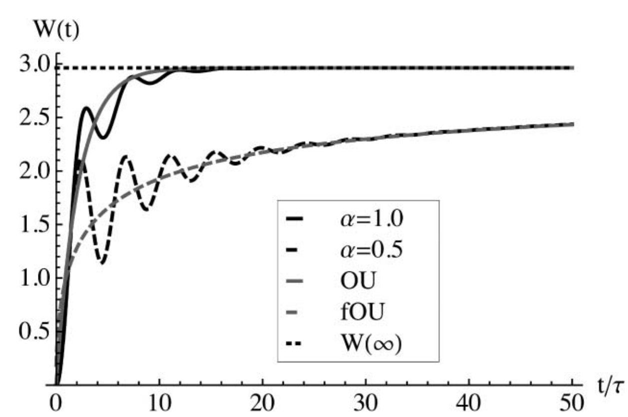

FIG. 6. MSDs derived from the memory functions shown in Fig. 4 (black dashed line for $\beta = 1/2$ and black solid line for $\beta = 1$). In addition the figure displays fits of model (47) for anomalous diffusion (grey dashed line, $\beta_{\mathrm{fOU}} = 0.521$, $\tau_{\mathrm{fOU}} = 5.537\,\tau$) and normal diffusion (grey solid line, $\tau_{\mathrm{OU}} = 2.126\,\tau$). More explanations are given in the text.

where it has been used that $\kappa(\infty) = \langle \mathbf{v}^2 \rangle / \langle \mathbf{u}^2 \rangle = \Omega^2 r$ for the given model. The above considerations show that $L_{\mathrm{fOU}}(t) \approx L(t)$ if $b = \beta$ and t_0 is fitted to match the amplitude of the function $L(t)$.

IV. CONCLUSION AND OUTLOOK

It has been shown that integrating asymptotic analysis into the theoretical description of diffusion processes by the generalized Langevin equation is an interesting route to understand anomalous diffusion from a physical point of view and to obtain generalized Kubo relations for the relevant transport coefficients. The conditions for the long time form of the VACF and its memory function for sub- and superdiffusion derived in this context have a particularly simple physical interpretation in terms of the cage model known from the theory of liquids. The illustrations based on analytical models for the memory function of the VACF demonstrate that stochastic models fit essentially the limiting power law of the MSD, but that they should not be considered as physical models for short times. This problem has been recently addressed by Ilyin *et al.*, who proposed a modified fractional diffusion equation the solution of which yields the correct deterministic form in the ballistic short time regime.[52] It is worthwhile noting that the analytical models for the memory function which have been used for the illustrations in this article can be refined, in order to systematically account for the well-known short time forms of the VACF and related quantities.[44,46] Work in this direction is in progress. As far as the present form of the theory is concerned, the VACF and the MSD are correct in the ballistic short time regime and in the various asymptotic regimes for normal and anomalous diffusion.

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