Generalization of the Kubo relation for confined motion and ergodicity breakdown

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A time-dependent generalized Kubo relation is derived by introducing the notion of a diffusion function for a particle confined in a harmonic potential. The relation reduces to the standard Kubo relation as a special case but holds for anomalous diffusion, nonergodic processes, and bounded motion. We analyze in detail the behaviors of the diffusion and memory functions and report a generalized Stokes-Einstein relation concerning anomalous diffusion. Furthermore, we demonstrate that when a high finite-frequency cutoff is imposed on the noise spectral density, a breakdown in ergodicity accompanied by the appearance of nonstationarity in the velocity autocorrelation function occurs in forced systems. This breakdown is taken as explicit evidence for either decay-spring-memory or recovering-force effects leading to nonexponential relaxation kinematics.

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I. INTRODUCTION

One of the fundamental expressions in Brownian motion theory is the famous Kubo relation, which links the diffusion constant D with the velocity autocorrelation function (VACF) $C_v(t)$ for a particle undergoing force-free Brownian motion, that is, $D = \int_0^\infty C_v(t)dt$ [1]. The former is an observable in experiments; the latter, an obtainable, is easily computed from molecular dynamics simulations and amenable to direct measurement [2]. This relation has been widely applied in the study of chemical physics [3–5], soft matter [6], and quantum physics [7], but nonetheless is only valid for normal diffusion. There are many formalisms that describe anomalous diffusion [8–10], although the details of the analysis differ depending on which of the various models was adopted. Correspondence between the models is possible [6]. A theoretical description of diffusion processes has initiated a change in paradigm to account for the numerous manifestations of anomalous diffusion and nonergodic processes. In this circumstance, the generalized Langevin equation (GLE) provides a powerful coarsened multitimescale approach to particle dynamics in a fluid environment. The practical applications of the GLE entail adopting a statistical model for the random forces.

If the experimental curves cannot be fitted by expressions obtained by solving a diffusion equation with a constant diffusion coefficient, one assumes that the effective diffusion coefficient depends on the timescale and tries to fit the data using essentially the same expressions that now contain a time-dependent diffusion coefficient $D(t)$ [6,11]. Sokolov investigated the time-dependent Kubo relation pertinent to nonstationary velocity processes for free Brownian motion [6]. It is certainly interesting to generalize the Kubo relation to other time-dependent processes, including novel correlated effects.

Furthermore, when the motion is bounded because of the experimental setup, for example, for a polymer solution interacting according to the dumbbell model, a fluid modeled using fluctuating linearized hydrodynamics theory [12], or the motion of particles in liquids for which the dynamics is influenced by the surrounding cage formed by the nearest neighbors [5,13], the mean-square displacement (MSD) of the tagged particle becomes stable with the diffusion constant falling to zero after an initial rise related to the transient anomalous diffusion. This is a specific result that is induced by the so-called cage effect [14]. From the fluctuation-dissipation theorem, this effect may be compatible with thermal equilibrium in time-independent bounded confining potentials. However, using the standard Kubo relation to extract dissipative characteristics is difficult [15].

More importantly, for spatially confined motion, the relaxation kinematics associated with the VACF may arise either in oscillatory behavior or in strongly nonexponential decay [13]. The usual expectation suggests that a bounded potential should help the system become ergodic and subsequently approach thermal equilibrium. However, surprisingly, we show the contrary to be true. Only a small number of prior studies have considered the consequences of the underlying oscillations in view of the ergodicity breakdown of forced systems [16]. It has been stressed that further theoretical investigations must be conducted on this issue [17].

The problem addressed in this paper is to extend the Kubo relation to account for situations in which a tagged particle is subject to a harmonic potential. This relation does not exhaust the subject because diffusion in various environments and external fields is a fundamental transport phenomenon being the starting point of many different formalisms. We highlight the effect of memory possessing a decay-spring behavior and demonstrate a condition that leads to ergodicity breakdown. The remainder of the paper is organized as follows. Section II discusses the significance of the time-dependent diffusion function and summarizes the physical restrictions imposed on the related memory function. In Sec. III we derive a time-

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dependent generalized Kubo relation and analyze the scaling behavior of the diffusion function subject to non-Ohmic type noise. We also report an alternative form of the Stokes-Einstein formula. In Sec. IV we identify a condition that leads necessarily to ergodicity breaking for a forced system and analyze a self-oscillation phenomenon. A summary is given in Sec. V.

II. DIFFUSION AND MEMORY FUNCTIONS

To analyze at best the diffusive (dispersion) behavior of a system of interest undergoing a stochastic process, it is convenient to introduce the time-dependent diffusion function $D(t)$ as a time derivative of a position variance [3,18,19], defined by

$$D(t) = \frac{1}{2}\frac{d}{dt}\langle \Delta x^2(t)\rangle, \tag{1}$$

where $\langle \Delta x^2(t)\rangle = \langle x^2(t)\rangle - \langle x(t)\rangle^2$, when combined with the average position, fully describes a Gaussian-type function that gives the probability density of finding a particle at position x at time t. This occurs in the motion described by a linear GLE subjected to Gaussian noise. Here the time-dependent diffusion function is indeed an effective notion and determines the temporal rate of change of the spatial spread for the system. For the problem of Brownian motion in a periodic potential, which arises in several fields of science, and for long enough times, the particles are then distributed over many potential wells. This diffusion can be described by an effective diffusion constant [20–22]. The same notion also holds for a finite position variance at any time, for instance, a bounded potential such as a harmonic potential imposed on the system or from the experimental setup directly.

Previously, several authors have defined a time-dependent diffusion function associated with a time-varying slope of the position variance, i.e., $D(t) = \langle \Delta x^2(t)\rangle/2t$ [21–23]. Note that a time-decreasing $D(t)$ at long times corresponds to subdiffusion whereas a time-increasing $D(t)$ at long times corresponds to superdiffusion. For $D(t) = \text{const}$, asymptotically one is dealing with normal diffusion. We stress that only in the asymptotic long-time regime is a finite diffusion coefficient D found, i.e., $D = \lim_{t\to\infty} D(t) < \infty$. L'Hôpital's second rule reduces Eq. (1) to align with the standard result of normal diffusion. The present definition for $D(t)$ behaves as a generalization that is also suitable for transitive processes because the original expression used in the asymptotic regime has been replaced by the temporal variation of the position variance. Note that Eq. (1) retains its practical advantage in estimating the transition time of a system from an initial state to a stationary state. In the Monte Carlo simulations, one can stop time evolution when either the $D(t)$ function arrives at a stable value or a scaling law emerges (see Sec. III C and Appendix A).

The approach by means of the temporal variation of particle position to study the diffusive behavior of a system has been widely used in the literature in recent decades. For instance, in using the fractional Riemann-Liouville time derivative of order α $(0 < \alpha < 2)$ to get the scaling coefficient prepower law of time for anomalous diffusion, Kneller and Stackura determined the coefficient of fractional diffusion, which is equal to a constant in the long-time limit [14,24,25]. Moreover, another scheme, specifically, $D(t) = \frac{1}{2}\frac{d}{dt}\langle x^2(t)\rangle$, was used to determine the time-dependent diffusion function by calculating the MSD [5]. At the initial stages, the diffusion function is found to be proportional to time. In the preparation of the particle, the initial velocity is set to a specific value, i.e., the particle is initially not at rest but undergoes thermalization as $\{v^2(0)\}_{\text{th}} = k_B T/m$ [26]. The force-free situation is discussed in Appendix B.

We begin with Zwanzig's GLE [27] for a particle of mass m moving in a potential $U(x)$ and a friction kernel $\gamma(t)$. Specifically, we have

$$\dot{x} = v(t), m\dot{v} = -m\int_0^t \gamma(t-t')v(t')dt' - U'(x) + \varepsilon(t). \tag{2}$$

Here x and v denote the particle's position and velocity, respectively, and $\varepsilon(t)$ denotes Gaussian noise having statistical properties $\langle \varepsilon(t)\rangle = 0$ and $\langle v(0)\varepsilon(t)\rangle = 0$ (here $\langle\cdots\rangle$ indicates an ensemble average). The fluctuation-dissipation theorem provides a relation for the correlation function of a random force in terms of the memory function $\langle \varepsilon(t)\varepsilon(t')\rangle = mk_B T\gamma(|t-t'|)$, where k_B denotes the Boltzmann constant and T the temperature.

To ensure that the analysis of the function of the present model yields a maximization, we consider a linear GLE; specifically, the external potential is set to $U(x) = \frac{1}{2}m\Omega_0^2 x^2$ as a recovering-force structure. This describes a number of physical problems, e.g,, the dynamics of a Brownian oscillator. Equation (2) is easily solved using the Laplace transform technique [12,28], which yields

$$v(t) = v(0)h(t) - \Omega_0^2 x(0)H(t) + \frac{1}{m}\int_0^t h(t-t')\varepsilon(t')dt', \tag{3}$$

$$x(t) = x(0)G(t) + v(0)H(t) + \frac{1}{m}\int_0^t H(t-t')\varepsilon(t')dt', \tag{4}$$

where $x(0)$ and $v(0)$ denote the initial position and velocity of the particle, respectively, and $G(t) = 1 - \Omega_0^2\int_0^t H(t')dt'$. The Laplace transforms of $h(t)$ and $H(t)$ are given as

$$\hat{h}(s) = \frac{s}{s^2 + s\hat{\gamma}(s) + \Omega_0^2}, \quad \hat{H}(s) = s^{-1}\hat{h}(s), \tag{5}$$

where $\hat{\gamma}(s)$ denotes the Laplace transform of the memory kernel $\hat{\gamma}(s) = \int_0^\infty \gamma(t)\exp(-st)dt$ and $h(t)$ the velocity relaxation function; $H(t) = \int_0^t h(t')dt'$ behaves as a relaxation time for the velocity degrees of freedom.

One of the key features of the GLE is the fact that it contains a time-dependent function $\gamma(t)$, termed a memory function. In this work we assume that thermal colored noise as well as the memory function meets all requirements necessary so that the phenomenological GLE remains physical [1,29–31]. The conditions are as follows.

(i) The memory function vanishes in the long-time limit $\lim_{t\to\infty}\gamma(t) = 0$. This is always the case provided the random force (noise) is irreversible in the sense that the noise correlation function and the memory function vanish as $t \to \infty$ [30].

(ii) The noise spectral density (NSD) is non-negative. The energy considerations require that the NSD must be positive on the real axis, i.e., $\rho(\omega) \geqslant 0$ for $\omega \geqslant 0$. The condition of positivity is of fundamental physical importance [29].

(iii) The magnitude of the memory function at any time is not larger than its initial value $\gamma(t) \leqslant \gamma(0)$ [30]. This is because $\gamma(t)$ is essentially the correlation function of the stationary random force $\varepsilon(t)$, which satisfies the inequality

$$\langle[\varepsilon(0)-\varepsilon(t)]^2\rangle = 2\langle\varepsilon^2(0)\rangle - 2\langle\varepsilon(0)\varepsilon(t)\rangle \geqslant 0, \\ \Rightarrow \langle\varepsilon(0)\varepsilon(t)\rangle \leqslant \langle\varepsilon^2(0)\rangle. \tag{6}$$

The property that is being invoked here is, by definition, the stationarity of the random force.

(iv) The Laplace transform of the memory function obeys $\lim_{s\to\infty}\hat{\gamma}(s)/s = 0$ in the large-s limit, s being the Laplace variable. This last condition is more difficult to handle than the other three; here we have the aid of the initial-value and linear-response theorems. Starting from Eq. (3), we know that the velocity relaxation function $h(t)$ satisfies $h(0) = 1$ at the initial time. Given the example of $\Omega_0^2 = 0$, this leads to the relation $h(0) = \lim_{s\to\infty}\{s/[s+\hat{\gamma}(s)]\} = 1$. We give a simply proof of this property using the Laplace transform of $h(t)$, i.e.,

$$\hat{h}(s) = \int_0^\infty h(t)\exp(-st)dt = -\frac{1}{s}\int_0^\infty h(t)d\exp(-st) \\ = \frac{1}{s}\left(h(0) + \int_0^\infty \exp(-st)dh(t)\right). \tag{7}$$

We then have

$$\lim_{s\to\infty}[s\hat{h}(s)] = h(0) = 1 \Rightarrow \lim_{s\to\infty}\left(\frac{s}{s+\hat{\gamma}(s)}\right) = 1, \\ \Rightarrow \lim_{s\to\infty}\hat{\gamma}(s)/s = 0. \tag{8}$$

In brief, we have demonstrated the properties of the memory function and in terms of their physical significance emphasized the conditions for the validity of the GLE.

III. GENERALIZED KUBO RELATION

A. Derivation of the generalized Kubo relation

Given the Kubo relation [1], the normal diffusion coefficient is calculated by the integral over the VACF $C_v(t)$ or, equivalently, by the velocity's power spectrum at zero frequency: $D = \int_0^\infty C_v(\tau)d\tau = \frac{1}{2}S_v(\omega = 0)$. This is a simple interpretation of the zero-frequency theory [32]. With the present definition of the diffusion function as a temporal time derivative of the position variance, the work reported in this paper is mainly concerned with the generalized Kubo relation in connection with the VACF and is time dependent. Thus, a frequency-dependent diffusive theory should be established within the framework of the function $D(t)$. The Kubo relation then has a time dependence similar to its standard form, in which infinite time is replaced formally by a finite time. However, realistic transitive features do not emerge from an arbitrary initial preparation. That is, a term is lacking in the time-dependent Kubo relation, which we will identify explicitly in Eq. (11) below.

Diffusion is characterized by the variance of the particle position $x(t)$. To elucidate the physical meaning of the time-dependent diffusion function, we employ a generic form for this variance for a particle in a harmonic potential,

$$\langle\Delta x^2(t)\rangle = \frac{k_BT}{m\Omega_0^2}\left[1 - G^2(t) - \Omega_0^2H^2(t)\right]. \tag{9}$$

It includes the result for force-free motion, i.e., taking the limit $\Omega_0^2 \to 0$ [33,34] (see Appendix B).

Differentiating Eq. (9) with respect to time and using Eq. (1), we derive a strictly rigorous relation between the temporal diffusion function $D(t)$ and the time-dependent functions related to the VACF,

$$D(t) = \frac{k_BT}{m}[G(t) - h(t)]H(t). \tag{10}$$

A connection with the Kubo relation can be made. Multiplying both sides of Eq. (3) by $v(0)$ and using the statistical properties of noise and assuming $\{x(0)v(0)\} = 0$, we obtain as a consequence the velocity relaxation function $h(t)$ given by $h(t) = \langle v(t)v(0)\rangle/\{v^2(0)\}$. Hence, Eq. (10) is rewritten as

$$D(t) = \frac{k_BT}{m}\left(1 - \tilde{C}_v(t) - \Omega_0^2\int_0^t dt'\int_0^{t'}\tilde{C}_v(t'')dt''\right) \\ \times \int_0^t \tilde{C}_v(t')dt', \tag{11}$$

where $\tilde{C}_v(t) = C_v(t)/\{v^2(0)\} = h(t)$ is the normalized VACF and $\{v^2(0)\}$ is required to be finite. Herein we denote by $\{\cdots\}$ the average with respect to the initial preparation of the state variables, i.e., an average over their initial values.

Equation (11) is referred to as the generalized time-dependent Kubo relation, which is independent of initial preparation. In particular, for force-free motion ($\Omega_0^2 = 0$) under the conditions (i) $C_v(t \to \infty) = 0$, (ii) $D(t)$ approaches a constant when the upper limit of the integral is set to infinity (i.e., normal diffusion), and (iii) $\{v^2(0)\} = \frac{k_BT}{m}$, Eq. (11) reduces to the standard Kubo relation [1]. Moreover, it is not limited to just Markovian diffusion. For non-Markovian normal diffusion, the effective Markovian friction strength $\hat{\gamma}(0) = \int_0^\infty \gamma(t)dt$ can be used to replace the coefficient of friction in Markovian diffusion. Nevertheless, if the process considered is not ergodic, i.e., $C_v(t \to \infty) \neq 0$, the term $1 - \tilde{C}_v(t)$ taking the place of unity needs to be added to the time-dependent Kubo relation.

B. Alternative version of the Stokes-Einstein formula

There are two ingredients involved in diffusion that have become prototypical in the connection between the correlation function and the transport coefficient. The first is a consequence of the Langevin theory [35] and gives an exponential decay for the VACF of a sphere $\langle v(t)v(0)\rangle = \frac{k_BT}{m}\exp(-t/\tau)$, in which τ is the relaxation time given by the Stokes law $\tau = m/6\pi\eta R$, where η is the fluid viscosity and R is the sphere radius. The second ingredient is the Green-Kubo formula connecting the diffusion constant D with the VACF, $D = \int_0^\infty\langle v(t)v(0)\rangle dt = k_BT/6\pi\eta R$, which is also written in an equivalent form $\frac{D}{\tau} = \frac{k_BT}{m}$ [36]. This expression was already obtained by Einstein [37], which holds only for normal diffusion but can be modified to cover non-Markovian cases. There have been a number of attempts to calculate

the transport coefficients of apparently dissipative systems and the Fourier transform of the VACF was widely used in semiphenomenological spectral studies of fluids, magnets, and other systems. Its generalization to a measurable approach for arbitrary frequency-dependent friction is a challenge.

Furthermore, starting from Eq. (10) or (11) and assuming the process is ergodic, we find the limit of the ratio of the diffusion function to the relaxation time for the velocity degrees of freedom; the behavior may be regarded as a generalized Stokes-Einstein relation

$$\lim_{t\to\infty}\left(\frac{D(t)}{H(t)}\right)=\begin{cases}\frac{k_BT}{m}, & \Omega_0^2=0\\ 0, & \Omega_0^2\neq 0.\end{cases} \tag{12}$$

We stress that the above expression is more generic because it is valid for anomalous diffusion and is independent of the scale α. The two varying functions modifying the kinetic behavior of diffusion and relaxation harmonize in the ratio entering the limit on the right-hand side.

In several previous papers, the Stokes-Einstein formula was expressed in different forms. The diffusion constant was computed from the memory function or the VACF as $D=\frac{k_BT}{m}[\int_0^\infty \gamma(t)dt]^{-1}$ [5] or $D=\frac{k_BT}{m}\int_0^\infty \tilde{C}_v(t)dt$ [13]. However, both are only valid for normal diffusion. This is because the value at infinity of the integral of $\gamma(t)$ either diverges for subdiffusion or vanishes for superdiffusion. Moreover, the opposite results occur for the integral of $C_v(t)$. Recently, a generalized asymptotic Einstein relation applying to anomalous diffusion was expressed in the form $\lim_{t\to\infty}[D(t)\gamma(t)]=2C(0)/m^2\Gamma(\alpha)\Gamma(2-\alpha)$ [3], where $C(0)$ denotes the noise intensity; however, no connection was made with the velocity relaxation time of an underlying process.

C. Example and scaling analysis

We discuss next an example that can be solved analytically. The expression for the diffusion function at large times makes it possible to identify an asymptotic regime in the scaling behavior of the system. According to the Wiener-Khintchine theorem, the memory function related to the NSD reads

$$\gamma(t)=\frac{2}{\pi}\int_0^\infty \rho(\omega)\cos(\omega t)d\omega. \tag{13}$$

Once the NSD is known, the GLE is capable of describing, within a unified framework, all types of anomalous diffusions and relaxations.

We do not study all possible limiting behaviors of the memory function. Instead we consider a very general model, i.e., the non-Ohmic friction model [18,19,38,39], which takes the form

$$\rho(\omega)=\gamma_\alpha(\omega/\tilde{\omega})^{\alpha-1}f(\omega)\quad(0<\alpha<2), \tag{14}$$

where $\tilde{\omega}$ denotes a reference frequency, the constant γ_α allows for the GLE (2) to have the correct dimension, and $f(\omega)$ is a frequency modulate function. Note that the small-ω behavior of the NSD obeys a power law characterized by the exponent $\alpha-1$. Because $0<\alpha<2$, one can safely set $f(\omega)=1$ in the theory [18,19]. The Laplace transform of the memory function is given by $\hat{\gamma}(s)=\omega_\alpha^{2-\alpha}s^{\alpha-1}$, where $\omega_\alpha^{2-\alpha}=\gamma_\alpha\tilde{\omega}^{\alpha-1}\sin^{-1}(\alpha\pi/2)$. At this stage, the velocity relaxation function for the force-free particle is given by the Mittag-Leffler function $h(t)=E_{2-\alpha}[-(\omega_\alpha t)^{2-\alpha}]$ [18,38].

Unfortunately, solving the GLE having a harmonic potential and a memory function with a long-time tail exactly is much more complex. This particular case is referred to as the non-Markovian Brownian oscillator and the quadrature has to be approximated to obtain the anomalous relaxation behavior. The necessary condition for the existence of a long-time tail in the relaxation dynamics of a diffusing particle has been found by the author in Ref. [34], i.e., $\hat{\gamma}(e^{\pi i})\neq\hat{\gamma}(e^{-\pi i})$. This is also valid for the harmonic potential case. Here we report an interesting result: The diffusion functions vary with time for the linear GLE for the two different asymptotes

$$D(t)\sim\begin{cases}A_\alpha t^{\alpha-1}, & \Omega_0^2=0\\ B_\alpha t^{-2\alpha-1}, & \Omega_0^2\neq 0,\end{cases} \tag{15}$$

where the two α-dependent coefficients are evaluated to be

$$A_\alpha=\begin{cases}\frac{k_BT}{m}\frac{\sin[(1-\alpha)\pi]}{\pi\omega_\alpha^{2-\alpha}}\Gamma(1-\alpha), & 0<\alpha<1\\ \frac{k_BT}{m}\frac{\sin[(\alpha-1)\pi]}{\pi\omega_\alpha^{2-\alpha}}\frac{\Gamma(2-\alpha)}{\alpha-1}, & 1<\alpha<2\end{cases} \tag{16}$$

and

$$B_\alpha=\frac{k_BT\left(\omega_\alpha^{2-\alpha}\right)^2}{m\pi^2\Omega_0^6}\sin^2[(1-\alpha)\pi]\Gamma(\alpha)\Gamma(1+\alpha). \tag{17}$$

The derivation of these expressions is outlined in Appendix A. In comparison with the force-free and harmonic potential cases, Eq. (15) displays for both an opposite dependence on the exponent α. In particular, the normal diffusion does not result in a long-time tail asymptotic behavior and cannot be described by Eq. (15).

We next calculate numerically the diffusion function using the VACF approach. Multiplying both sides of Eq. (2) by $v(0)$ and performing the ensemble average using the statistical properties of the noise $[\langle v(0)\varepsilon(t)\rangle=0]$, we get a homogeneous integro-differential equation for the VACF $C_v(t)$. In addition, we define the cross-correlation function as $C_{xv}(t)=\langle x(t)v(0)\rangle=C_{vx}(t)=\langle v(t)x(0)\rangle$. A set of coupled differential equations obtains

$$\dot{C}_{xv}(t)=C_v(t), \tag{18}$$

$$\dot{C}_v(t)=-\Omega_0^2C_{xv}(t)-\int_0^t\gamma(t-t')C_v(t')dt', \tag{19}$$

where $C_v(0)=\{v^2(0)\}$ and $C_{xv}(0)=0$. Once the memory function is determined, Eqs. (18) and (19) are then solved numerically, from which all the quantities can be evaluated.

In Figs. 1 and 2 we depict the diffusion functions in the presence of non-Ohmic memory friction modulated by $f(\omega)=f_1(\omega)=\exp(-\omega/\omega_c)$ and two kinds of potential. A comparison is made between the diffusion functions for particles in the force-free and harmonic potentials. All quantities represented therein, and in the forthcoming text, are dimensionless (i.e., $k_BT=1$, $m=1$, and $\tilde{\omega}=1$). In this figure we still use the Monte Carlo method to calculate the time-dependent diffusion function and compare the numerical result with the theoretical prediction. Because colored noise with a non-Ohmic spectrum cannot be simulated directly, we make use of the fast Fourier transform technique [40] to

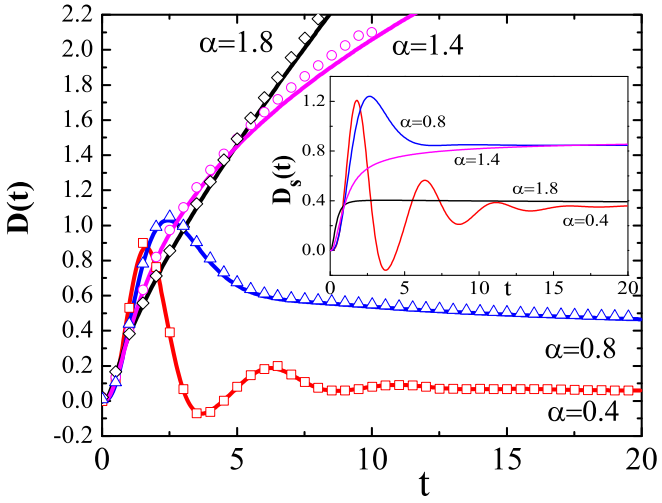

FIG. 1. Diffusion function $D(t)$ and its scaled function $D_s(t) = t^{1-\alpha}D(t)$ in the force-free case. The solid lines and points correspond to theoretical and Monte Carlo results, where $f_1(\omega)$, $\omega_c = 4.0$, and $\gamma_\alpha = 1.0$ are used.

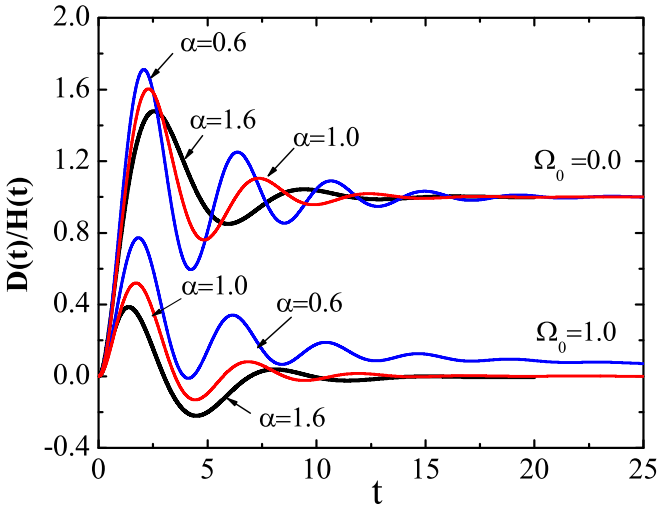

FIG. 3. Ratio of the diffusion function to the velocity relaxation time for various α in which $f_1(\omega)$ is employed. The top and bottom sets of lines correspond to $\Omega_0^2 = 0.0$ and $\Omega_0^2 = 1.0$, respectively. The parameter settings used are $\gamma_\alpha = 1.0$ and $\omega_c = 2.0$.

generate the required noise and then the estimate-corrected stochastic algorithm is used to simulate the GLE [41]. As expected, we observe for the harmonic potential a vanishing of the diffusion function in the long-time limit. Moreover, the scaled diffusion functions $D_s(t) = t^{1-\alpha}D(t)$ for the force-free case (Fig. 1) and $D_s(t) = t^{2\alpha+1}D(t)$ for the harmonic potential case (Fig. 2) are plotted in the insets; they approach different constants at large times. This is certainly evidence that the Monte Carlo simulation offers a quantitative verification of the present analytical results.

As for the transport properties of the bounded system, the diffusion function determines the rate of change in width of the Gaussian spatial distribution for the tagged particle; hence, $D(t)$ may become negative and indeed reflects a recovering-force effect caused by the harmonic potential. Note that the

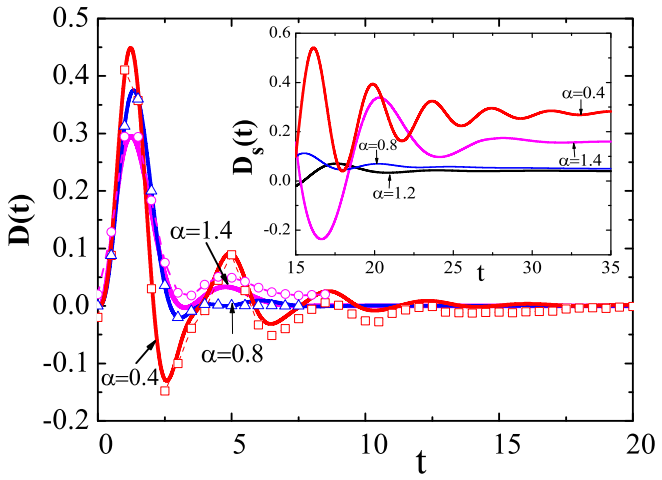

FIG. 2. Diffusion function $D(t)$ and its scaled function $D_s(t) = t^{2\alpha+1}D(t)$ in the harmonic potential case. The solid lines and points correspond to theoretical and Monte Carlo results, where $f_1(\omega)$, $\omega_c = 4.0$, $\Omega_0^2 = 1.0$, and $\gamma_\alpha = 1.0$ are used.

diffusion functions for a particle in the absence of a potential [6] and in a harmonic potential emerge with the opposite dependence for α over long-time intervals. With regard to the above interesting results, we remark that there exists a competing effect between colored noise and memory friction. The presence of a long-time tail for the noise correlation function ($0 < \alpha < 1$) indicates that the random force varies slowly and persists, driving the particle in the same direction. In contrast, for larger values of α ($1 < \alpha < 2$), the memory of the particle's motion is weaker. Nevertheless, when a bounded potential such as a harmonic potential is present, the relaxation kinetics is compensated, thereby decreasing the randomness of the fluid particles. Therefore, for bounded motion and large α, the diffusion function of a particle subject to non-Ohmic friction decays rapidly.

In Fig. 3 we verify numerically relation (12) and the different situations are contrasted. We stress that Eq. (12) is more generic because it is valid for anomalous diffusion and scale (α) independence. From below Eq. (5) we know that $H(t)$ is actually the relaxation time for the velocity degrees of freedom. Indeed, the two varying functions modifying the kinetic behavior of diffusion and relaxation harmonize in the ratio entering the limit on the right-hand side of Eq. (12).

IV. ERGODICITY BREAKING IN NON-MARKOVIAN DYNAMICS

A. Forced system situation

The ergodic hypothesis states that the time and ensemble averages of phase variables exist and are equal. The strong discrepancy between the ensemble and moving time averages implies nonergodicity of such systems [42]. This hypothesis is crucial for the proof of the basic theorems in statistical physics. Explicitly, the Khinchin theorem considers stationary processes and gives the condition for ergodicity, which requires the correlation function to decay to zero [43]. We consider the GLE and following the Khinchin theorem check

the conditions under which the process is ergodic because the irreversibility condition is a necessary and sufficient condition for the validity of the ergodic hypothesis in non-Markovian dynamics [44]. The expectation then is that bound potentials coax the particle velocity to become ergodic when the NSD has zero weight at low frequency [45]. Let us address this problem in terms of the present solvable model.

Using the initial-value formula of relaxation functions $h(0) = 1$, $H(0) = 0$, and $G(0) = 1$, we write down the formal expression for the VACF $C_v(t) = \{\langle v(t)v(0)\rangle\}$ of a particle in a harmonic potential [28],

$$C_v(t) = \{v^2(0)\}L^{-1}\left(\frac{s}{s^2 + s\hat{\gamma}(s) + \Omega_0^2}\right) - \{x(0)v(0)\}\Omega_0^2 L^{-1}\left(\frac{1}{s^2 + s\hat{\gamma}(s) + \Omega_0^2}\right), \quad (20)$$

where L^{-1} denotes the inverse Laplace transform operation. From the spectral analysis, we identify a condition that necessarily leads to breaking of ergodicity for a forced system. The Laplace transform of the memory function is determined by the NSD $\rho(\omega)$,

$$\hat{\gamma}(s) = \frac{2}{\pi}\int_0^\infty \frac{\rho(\omega)s}{s^2 + \omega^2}d\omega. \quad (21)$$

Suppose that the NSD is the cutoff at a high finite frequency ω_c and reads $\rho(\omega) = \rho_0(\omega)f_2(\omega)$, where $\rho_0(\omega)$ is a function of the frequency and $f_2(\omega) = \Theta(\omega_c - \omega)$ is the Heaviside function, equaling unity when $\omega \leqslant \omega_c$ and vanishing when $\omega > \omega_c$. We perform an integration by parts for Eq. (21) to render explicit the dependence of $\hat{\gamma}(s)$ on s,

$$\hat{\gamma}(s) = \frac{2}{\pi}\left[\rho_0(\omega_c)\arctan\left(\frac{\omega_c}{s}\right) - \int_0^{\omega_c}\arctan\left(\frac{\omega}{s}\right)\rho_0'(\omega)d\omega\right]. \quad (22)$$

With $\arctan(\omega/s) = \frac{1}{2i}\ln[(s + i\omega)/(s - i\omega)]$ on the complex plane, the characteristic equation $s^2 + s\hat{\gamma}(s) + \Omega_0^2 = 0$ may have a pair of pure complex roots $s = \pm ia$ once this term enters $\hat{h}(s)$, satisfying

$$-a^2 + a\frac{1}{\pi}\left[\rho_0(\omega_c)\ln\left(\frac{a + \omega_c}{a - \omega_c}\right) - \int_0^{\omega_c}\ln\left(\frac{a + \omega}{a - \omega}\right)\rho_0'(\omega)d\omega\right] + \Omega_0^2 = 0. \quad (23)$$

The implication is that a necessarily exceeds the cutoff frequency. Under this condition proposed here, the VACF contains a function of $\cos(at)$ and does not vanish in the long-time limit. It follows that the nonstationary case obtained here is nonergodic by the basic theorem. This behavior is characteristic of ergodicity breaking of another type [16,31]. It is concluded that the relation (11) is always suitable for such nonergodic process, specifically, the VACF given in Eq. (20) does not vanish at late times.

There exists a vast literature describing the nonexponential behavior of the correlation functions for systems ranging from plasmas to hydrated proteins [46–49]. The present study disentangles a source of anomalous relaxation within the framework of the GLE. In Fig. 4 we plot the memory function varying with time for various values of α using the modulating function $f(\omega) = f_2(\omega)$ and comparing it with $f(\omega) = f_1(\omega)$. High cutoff frequencies of signals are treated in many fields of physics. In two instances, the memory functions decay and vanish at long times. The decay of the sub-Ohmic memory function ($0 < \alpha < 1$) is slower than that for the super-Ohmic case ($1 < \alpha < 2$); the latter, moreover, may become negative. If the NSD is cut off at a high finite frequency [i.e., $f_2(\omega)$ is used], $\gamma(t)$ does not stabilize but instead diminishes with time. This plays the role of an effective decay-spring-memory behavior in the dynamics.

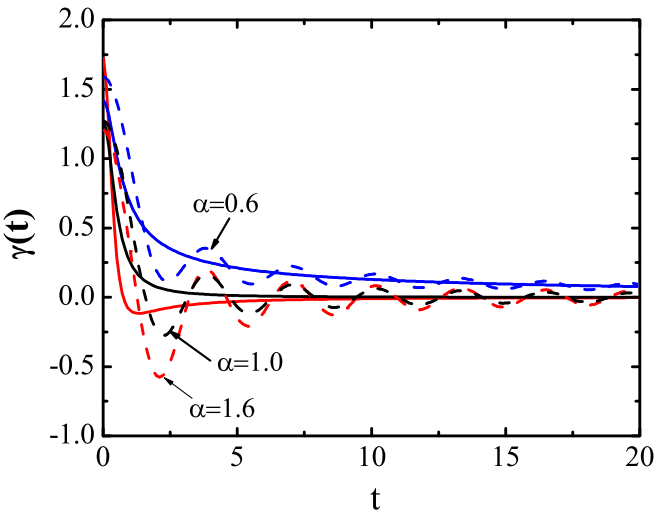

FIG. 4. Memory function for two kinds of frequency-modulated functions. The solid and dashed lines correspond to the results using $f_1(\omega)$ and $f_2(\omega)$, respectively. The parameter settings used are $\gamma_\alpha = 1.0$, $\omega_c = 2.0$, and (from top to bottom) $\alpha = 0.6$ (blue),1.0 (black), and 1.6 (red).

Figure 5 shows the VACF of the particle in a harmonic potential that helps us to extend the theory of ergodicity by focusing on the asymptotic behavior of the VACF. Clearly, it does not factorize and, for a zero-centered process, does not vanish in the long-time limit when the NSD of the driving noise is cut off at high finite frequencies. The expectation is that a bounded potential promotes ergodicity [16,45]. Surprisingly, we find the contrary to be true. Similar results were found for the force-free Brownian motion driven by a generalized Debye-type noise [27,47,48]. The long-time tail of the oscillation around zero appearing in the VACF implies that the particle tends to reverse its direction of motion frequently relative to its initial step. This also arises because the driven noise lacks sufficiently high frequencies. Therefore, our result highlights the existence of different types of nonergodicity.

So far, we have discussed the mathematical origin of ergodicity breakdown. Let us examine the physics behind it. The situation considered is that of a tagged particle coupled to its environment which constitutes a heat bath; the initial particle velocities are sampled with probabilities they would have in an equilibrium or stationary state. In this regard, two influences of the heat bath upon the system have to be distinguished [16,31,45,49]. An exploration of the first type relates to infinite oscillators, followed by our measurement

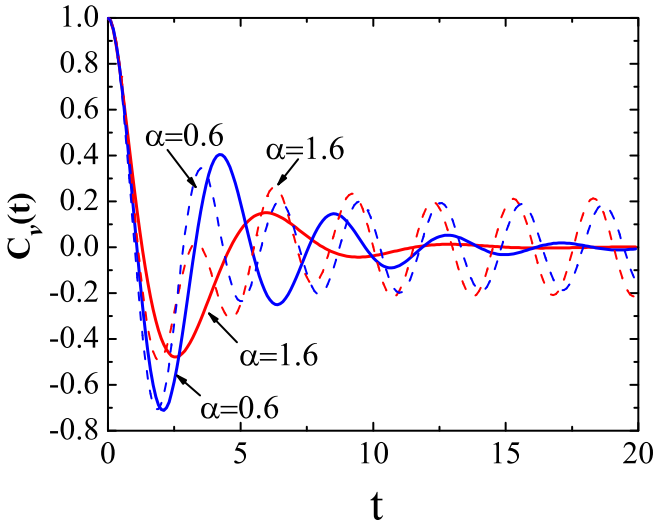

FIG. 5. VACF in the unit of $\{v^2(0)\}$ of a particle in a harmonic potential for different values of α. The solid and dashed lines correspond to results obtained with $f_1(\omega)$ and $f_2(\omega)$, respectively. The parameters used are $\Omega_0^2 = 1.0$, $\gamma_\alpha = 1.0$, and $\omega_c = 2.0$.

appliance. The other exploration corresponds to a different situation: a spectral distribution the lacks some frequencies [16,31,45,49]. Whereas this second situation corresponds to a behavior where the system oscillates with time near an equilibrium state, the first may be close to equilibrium independent of how far the equilibrium distribution in the system is from the initial one.

B. Self-oscillation phenomenon

The diffusion function along with the MSD for the force-free motion of a particle subjected to non-Ohmic memory friction modulated by $f_2(\omega)$ features the emergence of an anomalous diffusion (see Fig. 6). Specifically, the asymptotic MSD is a time-varying power-law function. Nevertheless, the diffusion function still oscillates with time for the three types of diffusion. Because the leading term in the MSD exceeds

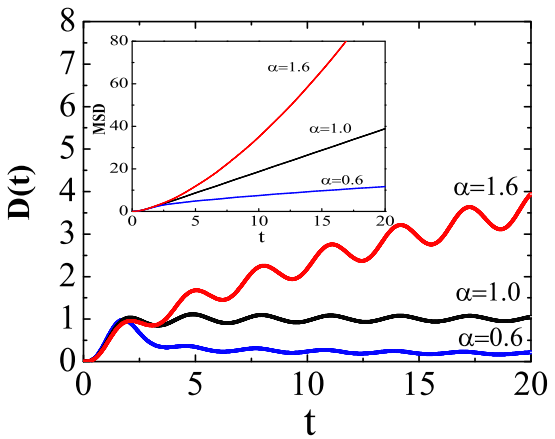

FIG. 6. Diffusion function and MSD for the force-free motion of a particle for various α in which $f_2(\omega)$ is employed. The parameter settings used are the same as in Fig. 4.

the oscillatory contribution, the MSD of the force-free particle motion is proportional to some power of time (see the inset of Fig. 6), but its time derivative still oscillates with time. Hence, the conclusion that the standard Kubo relation holds true is not a necessary condition for the system undergoing normal diffusion. The reason for this is that using the time-dependent diffusion function may give an adequate description for a process with nonstationary increments, if we concentrate on the dispersion behavior of spatial distribution relative to its center.

In practice, the NSD corresponding to $f_2(\omega)$ causes ergodicity breaking, being rooted in the vanishing weight at high frequencies. Driven by such noise, the present model is treated as a generalized Debye Brownian oscillator. Moreover, in the limit $\omega \to \infty$, any realistic spectral density of noise decays because physical quantities seemingly should not diverge. Both of these conditions imply that noise is colored with a limiting high-filtration behavior at high frequencies. Noise of this kind induces nonstationary behavior.

V. SUMMARY

The notion of a diffusion function has provided a characteristic associated with the statistical properties of the time evolution of many systems in fluids arising from the experimental setup. As demonstrated in the present study, it depends on memory features. This quantity is based on a definition that allows the effects of long-tail and decay-spring memory for the dynamics to be extracted. The standard Kubo relation was found not to be a necessary condition for normal diffusion because diffusive motion exists that is accompanied by local oscillations. We have shown that when thermal fluctuations combine with decay-spring-memory effects, the time-dependent diffusion function for the harmonic potential begins at zero, increases with time, then decays, and may become negative in value, assuming that it vanishes in the asymptotic limit.

The second objective was to ascertain whether ergodicity is broken for forced Brownian motion subject to colored noise with a high finite-frequency cutoff. This leads to a time-oscillating VACF for the particle; therefore, a time-dependent reduced term needs to be added that modifies the generalized Kubo relation. We believe that the present study provides useful information regarding the Brownian motion of a particle in a viscoelastic bounded fluid including aftereffects. This conclusion suggests applications in the analysis of complex systems or self-oscillatory particle transport.

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APPENDIX A: RELAXATION FUNCTIONS WITH LONG-TIME TAIL BEHAVIOR

Applying the residue theorem to the Laplace inversion of Eq. (5) [50], we write the solution in two parts as $h(t) = h_e(t) + h_p(t)$, in which $h_e(t)$ denotes the exponent-dependent

fast decaying part and $h_p(t)$ is the power-law term. We now find the leading long-time behavior of $h(t)$ by first observing that the integral term, which arises from the branch point at the origin, is

$$\begin{aligned} h_p(t) &= -\frac{1}{2\pi i}\left(\int_{L_1}+\int_{L_2}\right)\hat{h}(s)\exp(st)ds \\ &= \frac{1}{2\pi i}\int_0^\infty re^{-rt}\left[\frac{1}{r^2-r\hat{\gamma}(re^{\pi i})+\Omega_0^2}\right. \\ &\quad \left.-\frac{1}{r^2-r\hat{\gamma}(re^{-\pi i})+\Omega_0^2}\right]dr \\ &= \frac{\omega_\alpha^{2-\alpha}}{\pi}\sin[(\alpha-1)\pi]\int_0^\infty \frac{r^{\alpha+1}}{\Delta(r)}e^{-rt}dr, \end{aligned} \tag{A1}$$

where L_1 and L_2 denote the integral paths along the positive and negative directions of the negative real axis, respectively, and $\Delta(r)=r^4+r^{2\alpha}+2r^2\Omega_0^2-2(r^{\alpha+2}+r^\alpha\Omega_0^2)\cos[(\alpha-1)\pi]+\Omega_0^4$.

Indeed, when $t\to\infty$, the principal contribution of the integral at long times comes from r around zero. Therefore, we have approximately

$$\begin{aligned} h_p(t) &\approx \frac{\omega_\alpha^{2-\alpha}}{\pi\Omega_0^4}\sin[(\alpha-1)\pi]\int_0^\infty r^{\alpha+1}\exp(-rt)dr \\ &= \frac{\omega_\alpha^{2-\alpha}}{\pi\Omega_0^4}\sin[(\alpha-1)\pi]\Gamma(2+\alpha)t^{-\alpha-2} \end{aligned} \tag{A2}$$

as $t\to\infty$. Likewise, from the Laplace inverse of $\hat{H}(s)$, we find that

$$\begin{aligned} H_p(t) &= \frac{1}{2\pi i}\int_0^\infty\left(-\frac{1}{r^2-r\hat{\gamma}(re^{\pi i})+\Omega_0^2}\right. \\ &\quad \left.+\frac{1}{r^2-r\hat{\gamma}(re^{-\pi i})+\Omega_0^2}\right)\exp(-rt)dt \\ &\sim \frac{\omega_\alpha^{2-\alpha}}{\pi\Omega_0^4}\sin[(1-\alpha)\pi]\int_0^\infty r^\alpha\exp(-rt)dr \\ &= \frac{\omega_\alpha^{2-\alpha}}{\pi\Omega_0^4}\sin[(1-\alpha)\pi]\Gamma(\alpha+1)t^{-\alpha-1}. \end{aligned} \tag{A3}$$

The Laplace transform of $G(t)$ is given by

$$\begin{aligned} \hat{G}(s) &= \frac{1}{s}-\Omega_0^2\frac{1}{s}\frac{1}{s^2+s\hat{\gamma}(s)+\Omega_0^2} \\ &= \frac{s+\hat{\gamma}(s)}{s^2+s\hat{\gamma}(s)+\Omega_0^2}. \end{aligned} \tag{A4}$$

The power-law part of its inverse Laplace transform yields

$$\begin{aligned} G_p(t) &= \frac{1}{2\pi i}\int_0^\infty\left(-\frac{-r+\hat{\gamma}(re^{\pi i})}{r^2-r\hat{\gamma}(re^{\pi i})+\Omega_0^2}\right. \\ &\quad \left.+\frac{-r+\hat{\gamma}(re^{-\pi i})}{r^2-r\hat{\gamma}(re^{-\pi i})+\Omega_0^2}\right)\exp(-rt)dr \\ &\sim \frac{\omega_\alpha^{2-\alpha}}{\pi\Omega_0^2}\sin[(1-\alpha)\pi]\int_0^\infty r^{\alpha-1}\exp(-rt)dr \\ &= \frac{\omega_\alpha^{2-\alpha}}{\pi\Omega_0^2}\sin[(1-\alpha)\pi]\Gamma(\alpha)t^{-\alpha}. \end{aligned} \tag{A5}$$

In the absence of a potential, we obtain straightforwardly the power-law term from Eq. (A1) by setting $\Omega_0^2=0$; e.g., the velocity relaxation function is given by

$$\begin{aligned} h_p(t) &= \frac{1}{2\pi i}\int_0^\infty\left[\frac{\exp(-rt)}{r-\hat{\gamma}(re^{\pi i})}-\frac{\exp(-rt)}{r-\hat{\gamma}(re^{-\pi i})}\right]dr \\ &= \frac{\omega_\alpha^{2-\alpha}}{\pi}\int_0^\infty\frac{\sin[(\alpha-1)\pi]r^{\alpha-1}e^{-rt}dr}{r^2+r^{2(\alpha-1)}-2r^\alpha\cos(\alpha-1)\pi} \\ &\sim \frac{\omega_\alpha^{2-\alpha}}{\pi}\sin[(\alpha-1)\pi]\int_0^\infty r^{-\alpha+1}\exp(-rt)dr \\ &= \frac{\omega_\alpha^{2-\alpha}}{\pi}\sin[(\alpha-1)\pi]\Gamma(2-\alpha)t^{\alpha-2}. \end{aligned} \tag{A6}$$

We can test that Eq. (A6) is in agreement with the known result.

APPENDIX B: DIFFERENCE BETWEEN TWO DEFINITIONS OF THE DIFFUSION FUNCTION

The MSD for force-free motion of a particle can be also found from Eq. (9) by setting Ω_0^2 to zero, for which

$$\begin{aligned} \lim_{\Omega_0^2\to0}\frac{1-G^2(t)}{\Omega_0^2} &= \lim_{\Omega_0^2\to0}\frac{1-\left(1-\Omega_0^2\int_0^t H(t')dt'\right)^2}{\Omega_0^2} \\ &= 2\int_0^t H(t')dt'. \end{aligned} \tag{B1}$$

The average position of the particle is $\{\langle x(t)\rangle\}=\{x(0)\}+\{v(0)\}H(t)$. The MSD of the force-free particle is expressed in the general form

$$\begin{aligned} \{\langle x^2(t)\rangle\} &= \{\langle x(t)\rangle^2\}+\{\langle\Delta x^2(t)\rangle\} \\ &= \{x^2(0)\}+2\{x(0)v(0)\}H(t)+\{v^2(0)\}H^2(t) \\ &\quad -\frac{k_BT}{m}H^2(t)+\frac{2k_BT}{m}\int_0^t H(t')dt'. \end{aligned} \tag{B2}$$

The sum of the first three terms represents the square of the average position and the sum of the latter two terms is the position variance. Note that the position variance is independent of the initial preparation of particle.

The original Kubo relation is associated with free Brownian motion. For anomalous diffusion, the previous treatment to a large degree requires that the diffusion constant D be replaced by $D(t)$ defined by $D(t)=\int_0^t C_v(\tau)d\tau$; however, it may not be simply accepted. We have found that the time-dependent diffusion functions, calculated by taking the time derivative of the position variance and the MSD, are different. If the particle is confined initially at the origin $x(0)=0$ and its velocity obeys the Maxwell equilibrium distribution with $\{v^2(0)\}=k_BT/m$ rather than rest, using Eq. (B2) and $H(t)=\int_0^t h(t')dt'=\frac{k_BT}{m}\int_0^t\tilde{C}_v(t')dt'$, the MSD is expressed as

$$\{\langle x^2(t)\rangle\}=\frac{2k_BT}{m}\int_0^t dt'\int_0^{t'}d\tau\,\tilde{C}_v(\tau). \tag{B3}$$

Therefore, the diffusion function obtained by differentiating Eq. (B3) yields $D(t)=\int_0^t C_v(\tau)d\tau$ with $C_v(t)=\frac{k_BT}{m}\tilde{C}_v(t)$. This is specifically an expression of the time-dependent Kubo relation encountered in the literature [6,26].

Evidently, from (B2), this makes no difference if the particle starts statically from the origin [i.e., $x(0) = 0$ and $v(0) = 0$]. However, the resulting generalized Kubo relation differs from the previous form [1,3]. Note that for an arbitrary initial velocity preparation, the position variance is given by

$$\langle x^2(t)\rangle - \langle x(t)\rangle^2 = \frac{2k_BT}{m}\int_0^t H(t')\,dt' - \frac{k_BT}{m}H^2(t). \quad \text{(B4)}$$

Taking the time derivative on both sides of Eq. (B4), we obtain the diffusion function as Eq. (10), letting $\Omega_0^2 = 0$ for the generalized free Brownian motion. This implies that the previous time-dependent Kubo relation was presented under a special assumption, specifically that the initial velocity has a Maxwellian distribution.

In addition, from the identity $\dot{x} = v(t)$, we have $x(t) = x(0) + \int_0^t v(t')dt'$. Then the second moment of the position of a diffusing particle has the alternative form

$$\begin{aligned}\langle x^2(t)\rangle &= x^2(0) + \int_0^t\int_0^t \langle v(t_1)v(t_2)\rangle dt_1 dt_2 \\ &= x^2(0) + 2\int_0^t dt_1 \int_0^{t_1} \langle v(t_1)v(t')\rangle dt'. \quad \text{(B5)}\end{aligned}$$

We note that Eq. (B5) cannot obviously reveal the initial velocity dependence. Nevertheless, one can formally define the time-dependent diffusion function to match the behavior of $\langle x^2(t)\rangle$ in Eq. (B5) by taking $D(t) = \frac{1}{2}\frac{d}{dt}\langle x^2(t)\rangle = \int_0^t \langle v(t)v(t')\rangle dt'$. This evaluated diffusion function is quite restricted.

During the transitive state or the late oscillating process, the VACF at any two times may be different from the velocity at time t correlated with $v(0)$. Specifically, the translation invariance of time for the VACF does not hold in general, i.e.,

$$\int_0^t \langle v(t')v(0)\rangle dt' \neq \int_0^t \langle v(t)v(t')\rangle dt'. \quad \text{(B6)}$$

Therefore, the diffusion function determined from the MSD [Eq. (B2)] yields a different result in comparison with that of the time derivative of Eq. (B4) despite the initial velocity preparation.

To clearly distinguish the difference between the diffusion functions determined by the time derivative with respect to the position variance and the MSD, we consider the simplest case, specifically, the normal diffusion described by the Markovian Langevin equation. This is essentially not a realistic physical model but a fitting means, which must be taken with care because it is often used. The equation of motion of a particle is $m\ddot{x} + m\gamma_0\dot{x} = \xi(t)$, where $\xi(t)$ denotes Gaussian white noise obeying $\langle\xi(t)\rangle = 0$ and $\langle\xi(t)\xi(t')\rangle = 2m\gamma_0 k_BT\delta(t - t')$, where γ_0 describes the friction strength. The MSD of the diffusing particle was obtained previously,

$$\begin{aligned}\langle x^2(t)\rangle = \langle x(t)\rangle^2 + \frac{2k_BT}{m\gamma_0}\Bigg(t - \frac{2}{\gamma_0}[1 - \exp(-\gamma_0 t)] \\ + \frac{1}{2\gamma_0}[1 - \exp(-2\gamma_0 t)]\Bigg), \quad \text{(B7)}\end{aligned}$$

where the average particle's position yields $\langle x(t)\rangle = x(0) + \frac{v(0)}{\gamma_0}[1 - \exp(-\gamma_0 t)]$.

We now express Eq. (B7) as a Taylor series for short times ($t < \gamma_0^{-1}$),

$$\begin{aligned}\langle x^2(t)\rangle = v^2(0)t^2 + \frac{2k_BT}{m\gamma_0}\Bigg(t - 2t + \gamma_0 t^2 + t - \gamma_0 t^2 \\ + \frac{1}{3}\gamma_0^2 t^3 + \cdots\Bigg). \quad \text{(B8)}\end{aligned}$$

Performing the time derivative of the MSD, the leading term of the diffusion function at the initial time yields

$$D(t) = \frac{1}{2}\frac{d}{dt}\langle x^2(t)\rangle \sim v^2(0)t. \quad \text{(B9)}$$

In contrast, using the present definition [Eq. (1)], we establish a superballistic behavior [51] at the initial time,

$$D(t) = \frac{1}{2}\frac{d}{dt}\langle \Delta x^2(t)\rangle \sim \frac{k_BT}{m}\gamma_0^2 t^2. \quad \text{(B10)}$$

The expressions (B9) and (B10) tell us that, during the initial time periods, the diffusion of a force-free particle induced by thermal fluctuations is slower than that arising from its initial velocity. Therefore, in this sense, the diffusion within the GLE should be of thermal type.

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