Generalized Einstein relations and conditions for anomalous relaxation

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The generalized Einstein relation (GER) for nonergodic processes is investigated within the framework of the generalized Langevin equation. The conditions for anomalous relaxation such as long-tail decay and non-vanishing velocity autocorrelation function (VAF) are proposed and distinguished. For the stationary nonergodic process, if the initial preparation of the particle velocity is non-thermal, an asymptotic GER occurs in a departure from the usual result. It is shown that the GER holding is a necessary condition rather than a full condition for the system being close to equilibrium. For the nonergodic process of the second type due to cutoff of high frequencies, the VAF oscillates with time, the GER holds but the equilibrium fails in the long-time limit. Applications to some practical examples confirm the present theoretical findings.

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I. INTRODUCTION

Brownian motion, as a theory describing the random impact of a resting fluid on a suspended particle, has played a substantial role in statistical mechanics. For normal diffusion, the diffusion constant D is related to the friction coefficient γ experienced by the Brownian particle of mass m in the fluid and the temperature T of the fluid by $D = \frac{k_B T}{m\gamma}$, where k_B is the Boltzmann constant. This is the normal Einstein relation [1]. The generalized Einstein relation (GER) [2,3] establishes a connection between the fluctuation of the particle position in the absence of a potential and the average displacement of a biased Brownian motion subjected to a constant force F, i.e.,

$$\langle x^2(t)\rangle_0 = R(t)\frac{2k_BT}{F}\langle x(t)\rangle_F, \tag{1}$$

where $\langle x^2(t)\rangle$ and $\langle x(t)\rangle$ are the time-dependent mean square displacement (MSD) and average displacement (AD) of the particle, the subscripts "0" and "F" in $\langle\cdots\rangle$ denote instances when an external driving force applied to the particle is absent and present, respectively. Clearly, the generalization of the original Einstein relation stems from a time-dependent process that can be described by a generalized Langevin equation (GLE) and creates a link with mobility and diffusion.

According to the Einstein relation, Eq. (1), $R(t)$ is expected to be time independent satisfying $R(t) = 1$ for diffusion and relaxation close to thermal equilibrium [4]. This has been proved by experimental results in polymeric systems [5,6]. This relation is significant in describing transport for both short and long times, and can be regarded moreover as a probe to determine the diffusive behavior of the system through calculating the mobility of a biased particle. It is not limited however to normal diffusion [7–10], which assumes that the underlying process is stationary. Recently, anomalous diffusion has been a topic of interest as it occurs in the process described by a generalized or fractional Langevin equation.

In a previous article, Barkai and Fleurov [11] reported a departure from the GER using the Scher-Lax-Montroll model, in which a finite constant force influences the scale index of time for the AD of a biased particle. Therefore, $R(t)$ varies with time and even diverges asymptotically. Here, we want to investigate modification of the GER, in which the processes considered are nonergodic. Because the mobility and diffusion should be dependent on the initial preparation, $R(t)$ also depends on the initial conditions but approaches a constant in the long-time limit. We shall show that, for a stationary nonergodic process, the GER is modified by a factor; however, if the resulting process is non-stationary, the situation becomes complex. To the best of our knowledge, the violation of the GER for nonergodic processes has not been discussed, and only a small number of prior studies have emerged on the long-time results of nonergodic systems.

The subject that we address in this paper is whether the GER can be violated in systems that are driven by non-Markovian processes, or, the GER holding implies that the system is close to thermal equilibrium? Because decay dynamics are currently of central importance in nonequilibrium statistical mechanics, and there are several grounds for doubt, it needs to allay these doubts in some detail. To find and distinguish rigorously the conditions for non-standard relaxation and nonergodicity is the other purpose. Furthermore, we apply to various physical situations for which the theory should be explicitly discussed.

The paper is organized as follows. Section II derives the GER starting from a phenomenological GLE using the Laplace transform and the velocity autocorrelation function (VAF) approach. In Sec. III, the types and conditions for ergodicity breaking are distinguished. In Sec. IV, we calculate numerically $R(t)$ of either band-passing noise or Debye-type noise driven system using the VAF approach. A summary is given in Sec. V.

II. GER AND GENERAL REMARK

One of the fundamental approaches to stochastic dynamics is provided by the phenomenological GLE with a frictional

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memory kernel $\gamma(t)$, reading

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

where $v(t)$ and $x(t)$ denote the velocity and position of a particle of mass m, respectively, $U(x)$ the potential. Here, the initial particle velocity-independent $\varepsilon(t)$ is a Gaussian zero-mean random force that is related to the memory kernel by the second fluctuation-dissipation theorem (FDT) $\langle\varepsilon(t)\varepsilon(t')\rangle = mk_BT\gamma(|t-t'|)$.

Remarkably, this model (GLE plus FDT) can be derived from a Hamiltonian dynamics of a particle that bilinearly couples to a thermal bath of harmonic oscillators. This is general and leads to a non-Markovian process of the particle dynamics with linear memory friction and Gaussian random force. In the absence of any potential, the variance of the particle's position will grow with time limiting to the ballistic diffusion [12]. Moreover, due to the FDT it is compatible with thermal equilibrium in confining, time-dependent bounded potential. This happens if the precess obeys: (i) the second FDT, (ii) the stationary form of GLE, (iii) the VAF $C_v(t)$ of the particle decays asymptotically to zero. Nevertheless, the presence of the memory kernel allows us to study a large number of correlated processes. It is also stressed that further investigations have to be made on the issue [13].

In what follows, we shall consider that the driving noise meets all the requirements as necessary conditions so that the phenomenological GLE (2) becomes physical [2,14,15]. The conditions are: (i) the memory function should vanishing in the long time limit, $\lim_{t\to\infty}\gamma(t) = 0$, (ii) the noise spectral density (NSD) must be non-negative, (iii) the magnitude of the memory function is smaller than the initial value, $\gamma(t) < \gamma(0)$, and (iv) the Laplace transform of the memory function becomes finite in the large-s limit, where s is the Laplace variable.

The connection to ergodic properties is given by Khinchin's theorem [16], which states that the stationary variable $v(t)$ is an ergodic one if the VAF factorizes to zero in the long-time limit. Although in Mori-Zwanzig's GLE [17,18] the random force $\varepsilon(t)$ and therefore the velocity variable in the absence of a potential, are not necessary stationary and zero centered [19], we shall assume that these properties do hold. The finial-value theorem $\lim_{t\to\infty} C_v(t) = \lim_{s\to 0}[s\hat{C}_v(s)]$ gives the condition of ergodicity breaking [see Eq. (22)], where the symbol "ˆ" denotes the Laplace transform. It is possible to construct the memory function $\gamma(t)$ that vanishes as long times, but the corresponding VAF of the particle does not have a long time limit. The condition for nonergodicity of this type will be reported in Eq. (23).

A. Derivation of GER

When the external potential is linear, $U(x) = -Fx$, we deal with a biased Brownian motion. The solution of Eq. (2) with arbitrary memory kernel through the Laplace transform has a long history starting from the well-known paper by Adelman [20]. Here, the formal solution of the linear GLE can be expressed in the form

$$x(t) = x(0) + v(0)H(t) + \frac{1}{m}\int_0^t H(t-t')[\varepsilon(t') + F]dt', \quad (3)$$

$$v(t) = v(0)h(t) + \frac{1}{m}\int_0^t h(t-t')[\varepsilon(t') + F]dt' \quad (4)$$

with $x(0)$ and $v(0)$ being the initial position and velocity of the particle, $h(t)$ is the velocity relaxation function. The Laplace transforms of $h(t)$ and $H(t)$ are given by $\hat{h}(s) = [s + \hat{\gamma}(s)]^{-1}$ and $\hat{H}(s) = s^{-1}\hat{h}(s)$, respectively, where $\hat{\gamma}(s)$ is the Laplace transform of the memory kernel, i.e., $\hat{\gamma}(s) = \int_0^\infty \gamma(t)\exp(-st)dt$. The relation between $H(t)$ and $h(t)$ reads $H(t) = \int_0^t h(t')dt'$.

The AD of the particle subjected to an external bias F emerges as

$$\{\langle x(t)\rangle\}_F = \{x(0)\} + \{v(0)\}H(t) + \frac{F}{m}\int_0^t H(t')dt'. \quad (5)$$

In unbiased situations, we derive the MSD of the force-free particle in a generic form

$$\begin{aligned}\{\langle x^2(t)\rangle\}_0 = {} & \{x^2(0)\} + \left(\{v^2(0)\} - \frac{k_BT}{m}\right)H^2(t) \\ & + 2\{x(0)v(0)\}H(t) \\ & + \frac{2}{m}\int_0^t dt' H(t-t')\{\langle x(0)\varepsilon(t')\rangle\} \\ & + \frac{2k_BT}{m}\int_0^t H(t')dt'. \end{aligned} \quad (6)$$

The probability density function of the particle position $x(t)$ in Eq. (3) is also Gaussian, i.e.,

$$P(x,\{x(0)\},t) = \frac{1}{\sqrt{2\pi\sigma_x^2}}\exp\left(-\frac{[x - \{\langle x(t)\rangle\}]^2}{2\sigma_x^2(t)}\right), \quad (7)$$

where $\sigma_x^2(t)$ is the position variance. Herein, we indicate by $\{\cdots\}$ the average with respect to the initial preparation of the state variables, i.e., an average over their initial values, and $\langle\cdots\rangle$ the noise average. It has been observed by Ferrari [21] that, sometimes, the two types of averages are usually confused. Hence, we shall take the two averages separately.

Starting from Eq. (1) and assuming that $x(0) = 0$, $\{v(0)\} = 0$, $\{x(0)v(0)\} = 0$ as well as $\{\langle x(0)\varepsilon(t)\rangle\} = 0$, we present the ratio of Eq. (6) to Eq. (5) and thus obtain an expression for the initial velocity preparation-dependent $R(t)$ as

$$R(t) = 1 + \frac{m}{2k_BT}\left(\{v^2(0)\} - \frac{k_BT}{m}\right)\frac{H^2(t)}{\int_0^t H(t')dt'}. \quad (8)$$

It is observed that $R(0) = \{v^2(0)\}(k_BT/m)^{-1}$, because $\lim_{t\to 0}[H^2(t)/\int_0^t H(t')dt'] = 2h(0) = 2$. In further, while the initial velocity preparation of the particle is set to a special case, i.e., the particle is initially not at rest but undergoes thermalization as $\{v^2(0)\}_{\rm th} = k_BT/m$, $R(t) = 1$ holds for all times. Therefore,

$$\{R(t)\}_{\rm th} \equiv 1; \tag{9}$$

$$\lim_{t\to\infty} R(t) = 1 + b\left(\frac{m}{k_B T}v^2(0) - 1\right) \tag{10}$$

with $b = h(t \to \infty) = (1 + \hat{\gamma}'(0))^{-1}$.

It is worth noting, Eq. (10) is evidence that, if the asymptotic result of $h(t)$ exists and does not decay to vanishing and the initial preparation of the particle velocity is non-thermal, an asymptotic GER occurs in a departure from the usual result. This expression is obtained under the precondition of VAF being assumed to be stationary, so that the Tauberian theorem is valid. By the way, the present results can be applied to deal with the fractional Langevin equation [7].

The usual expectation would be that $R(t) = 1$ implies the system being close to equilibrium [11]. However, surprisingly we find the contrary to be true. It will be demonstrated in Sec. IV B that if the velocity of a force-free particle is not ergodic, namely, its VAF does not freeze but keeps oscillating at long times, the asymptotic value of $R(t)$ can become unity, however, in the velocity space the system does not arrive at equilibrium.

B. Evaluating velocity relaxation function

Presuming that the characteristic equation $s + \hat{\gamma}(s) = 0$ has no pure imaginary roots, the forever time-oscillation term in $h(t)$ does not arise. The resulting process is treated as stationary. In this situation, $h(t)$ as a key quantity can be obtained by the inverse Laplace transform of $\hat{h}(s)$,

$$h(t) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} \hat{h}(s)\exp(st)ds. \tag{11}$$

The contour for evaluating the above integral can be found in Ref. [15], however, the position of the pole point at the coordinate origin was not considered. If $\hat{h}(s)$ is a signal-value and continuous analytical function in the region inside the curve C_R except at isolated singular points, the residue theorem [22] may be used to calculate this contour fully, i.e.,

$$\int_{c-iR}^{c+iR} + \int_{C_R^+} + \int_{C_R^-} + \int_{L_1} + \int_{L_2} + \int_{C_r^+} + \int_{C_r^-} + \int_{C_0} = 2\pi i \sum_{k=1}^{2K} \mathrm{res}[\hat{h}(s_k)]\exp(s_k t), \tag{12}$$

where c is a positive constant and R denotes the contour radius. In addition, the upper limit of the summation in Eq. (12) is written as an even number because $h(t)$ is a real-valued function of time.

To understand the contour integral of Eq. (12), we plot here a figure, i.e., Fig. 1, as a guide to evaluating the inverse Laplace transform of $\hat{h}(s)$. The contributions from C_R^+ and C_R^- vanish when R goes to infinity. In principle, the characteristic equation $s + \hat{\gamma}(s) = 0$ could have simple poles on the left complex plane and the imaginary axis as well as at the origin. However, we do not consider instances of poles situated on the imaginary axis arising from a high-frequency cutoff of the spectral density for noise. With the contributions from C_R^+ and C_R^- vanishing in the limit as R goes to infinity, we arrive at the expression for $h(t)$,

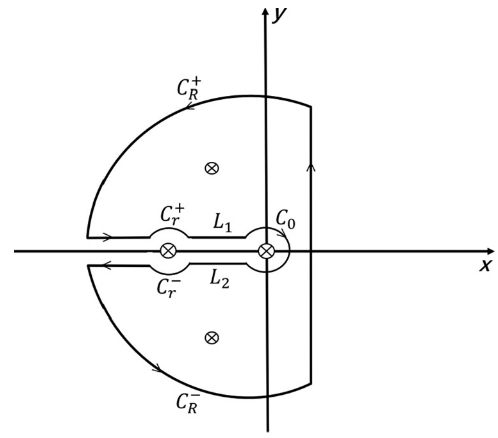

FIG. 1. Contour to evaluate Eq. (11) to obtain the relaxation function $h(t)$ in the time domain.

$$\begin{aligned} h(t) = &-\frac{1}{2\pi i}\lim_{r\to 0}\left(\int_{C_r^+} + \int_{C_r^-}\right)\hat{h}(s)\exp(st)ds \\ &+ \sum_{k=1}^{2K}\mathrm{res}[\hat{h}(s_k)]\exp(s_k t) \\ &- \frac{1}{2\pi i}\lim_{\varepsilon\to 0}\int_{C_\varepsilon}\hat{h}(s)\exp(st)ds \\ &- \frac{1}{2\pi i}\left(\int_{L_1} + \int_{L_2}\right)\hat{h}(s)\exp(st)ds. \end{aligned} \tag{13}$$

Here, the four terms in Eq. (13) indicate in turn the exponential relaxation, the exponential with oscillating convergence, the nonergodic process, and the long-time tail decay. Moreover, the initial value theorem $[h(0) \equiv 1]$ must hold. Then, from the relation $s\hat{h}(s) = \int_0^\infty h(t)\exp(-st)sdt = h(0) + \int_0^\infty \dot{h}(t)\exp(-st)dt$, we have $\lim_{s\to\infty} s\hat{h}(s) = \lim_{s\to\infty} s/(s + \hat{\gamma}(s)) = 1$ and thus $\lim_{s\to\infty}\hat{\gamma}(s) =$ finite is required.

In addition, one might meet difficulty when one performs the Laplace transform and its inverse [10], for which we have to find an alternative approach to express the resolvent $h(t)$. To determine the VAF at time t related to the initial velocity obeying a Gaussian distribution with the second moment $\{v^2(0)\}$, we multiply Eq. (4) by $v(0)$ and take into account the double averages for the equation; we then have

$$\begin{aligned} \{\langle v(t)v(0)\rangle\} = \{v^2(0)\}h(t) + \frac{1}{m}\int_0^t h(t-t')[F\{v(0)\} \\ + \{\langle \varepsilon(t')v(0)\rangle\}]dt'. \end{aligned} \tag{14}$$

Assuming that $\{v(0)\} = 0$ and $\{\langle\varepsilon(t)v(0)\rangle\} = 0$, we write the relaxation function $h(t)$ using the VAF as

$$h(t) = \frac{1}{\{v^2(0)\}}\{\langle v(t)v(0)\rangle\}. \tag{15}$$

In this situation, knowing $\{\langle v(t)v(0)\rangle\}$ from numerical calculation, one obtain $h(t)$ and then $H(t) = \int_0^t h(t')dt'$, so that all average quantities of linear GLE will be evaluated fully.

III. ANOMALOUS RELAXATION

A. Condition for long-tail decay

In common practice, the nonexponential decay of VAF is often taken as explicit evidence for disorder. However, there are no studies detailing how nonexponential decay and long-time tail arise. Here, we show that even without disorder, nonexponential relaxation might arise from the long-time decaying memory function. Expressing the last two integrals in Eq. (13) along the contours L_1 and L_2 (Fig. 1), we obtain

$$-\frac{1}{2\pi i}\left(\int_{L_1}+\int_{L_2}\right)\hat{h}(s)\exp(st)ds = \frac{1}{2\pi i}\int_0^\infty\left[\frac{\exp(-rt)}{-r+\hat{\gamma}(re^{-\pi i})}-\frac{\exp(-rt)}{-r+\hat{\gamma}(re^{\pi i})}\right]dr, \quad (16)$$

where r is a real quantity. We now propose that the necessary condition for nonexponential decay of the VAF is

$$\hat{\gamma}(re^{\pi i})-\hat{\gamma}(re^{-\pi i})\neq 0. \quad (17)$$

This condition for the long-time tail appearing in the VAF is more generic than the previous results, i.e., either $\hat{\gamma}(s)$ has a pole at $s=0$ [23] or small-s behavior [24]. In this situation, however, we find that $b=0$, therefore, the GER is valid.

As an application, in classical hydrodynamic theory, the Stokes-Boussinesq formula [25] provides time-dependent corrections to the simpler Stokes formula for viscous drag on a sphere in uniform motion. The Fourier transform of the memory function reads

$$\tilde{\gamma}(\omega)=6\pi\eta R_0\left[1+R_0(-i\omega/\nu)^{1/2}-i\omega R_0^2/(9\nu)\right], \quad (18)$$

in which η is the viscosity of the fluid, R_0 the radius of the sphere, and ν the kinematic viscosity of the fluid. Then $\hat{\gamma}(-i\omega=s)=6\pi\eta R_0[1+R_0(s/\nu)^{1/2}+sR_0^2/(9\nu)]$ and $\hat{\gamma}(re^{\pi i})-\hat{\gamma}(re^{-\pi i})=6\pi\eta\nu^{-1/2}R_0^2r^{1/2}(2i)\neq 0$, so that condition (17) is obeyed. Using Eq. (18), we determine the maximum contribution coming from r around zero; hence, $h(t)\sim\frac{2}{3\eta\sqrt{\nu}}(4\pi t)^{-3/2}$, as $t\to\infty$. This is in agreement with Fox's result [25]. The existence of a tail indicates that a random force varies slowly and persists driving the particle in the same direction.

B. Conditions for ergodicity breakdown

Two-time correlated dynamics such the VAF of a force-free particle, as a probe of estimating ergodicity of the system, is given by

$$\{\langle v(t)v(t')\rangle\}_0=\frac{k_BT}{m}h(|t-t'|) + \left(\{v^2(0)\}-\frac{k_BT}{m}\right)h(t)h(t'). \quad (19)$$

According to the Khinchin theorem [16], if $\lim_{|t-t'|\to\infty}\langle v(t)v(t')\rangle\neq 0$, ergodicity is broken.

This plays a unique role in nonequilibrium statistical and chemical physics [15,26,27]. Let us now try to find alternative conditions for ergodicity breaking using spectral analysis. The memory function and its Laplace transform are determined from the noise spectral density (NSD) $\rho(\omega)$, i.e.,

$$\gamma(t)=\frac{2}{\pi}\int_0^\infty\rho(\omega)\cos(\omega t)d\omega \quad (20)$$

and

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

First, we assume that $s+\hat{\gamma}(s)=0$, finding the poles of $\hat{h}(s)$ to possess a zero root $s=0$, the residue at this point being equal to a non-vanishing constant. This requires that

$$\hat{\gamma}(0)=0 \text{ and } \hat{\gamma}'(0)=\frac{2}{\pi}\int_0^\infty\frac{\rho(\omega)}{\omega^2}d\omega<\infty. \quad (22)$$

It follows from Eq. (19) that the VAF decays to a finite value: $\{v^2(0)\}h(t\to\infty)=\{v^2(0)\}/(1+\hat{\gamma}'(0))$, which behaves as the first type of nonergodicity [28]. If the two conditions in Eq. (22) are fulfilled, diffusion of a force-free particle is classified as ballistic [12]. Naturally, the motion of a self-propelled artificial micro-swimmer is often modeled as ballistic Brownian motion [29].

Second, if $s+\hat{\gamma}(s)=0$ have a pair of pure imaginary roots $s_\pm=\pm ia$ (a real), then the VAF becomes non-stationary. Hence, the second type of nonergodicity arises although this situation is not included in Eq. (13). The reasoning is as follows. We propose other condition for ergodicity breaking,

$$\frac{2}{\pi}\int_0^\infty\frac{\rho(\omega)\Theta(\omega-\omega_d)}{\omega^2-a^2}d\omega+1=0, \quad (23)$$

where $\Theta(\omega-\omega_d)$ is a step function and ω_d denotes the cutoff frequency, namely, $\Theta(\omega-\omega_d)=1$ when $\omega\leqslant\omega_d$ and $\Theta(\omega-\omega_d)=0$ when $\omega>\omega_d$. Obviously, Eq. (23) requires $|a|>\omega_d$, because the NSD is always non-negative. A lack of scattering high frequencies leads yet to similar result in the microcosmical GLE case [15,30].

The conclusion is, for a non-stationary VAF oscillating around zero process where ergodicity is broken, $R(t)$ varies with time before the transition, and then approaches unity in the long-time limit. This is because the time-increasing term exceeds the oscillating part in the AD and MSD of the biased particle.

IV. APPLICATION AND COMPARISON

A. Evolution equation of VAF

One of the key features of the GLE is the fact that it contains an aftereffect function, termed a memory function. Although the memory function in the present study induces modification of the GER, it satisfies all the conditions shown in Sec. II. The inverse Laplace transformation of Eq. (11) is not easy analytically or numerically [10,31–34]. In order to observe the behavior of the VAF as a function of time in more detail and confirm the validity of the present theoretical findings, we employ a more simply approach. By multiplying both sides of Eq. (2) with $U(x)=0$ by $v(0)$ and performing the ensemble average, we obtain time evolution of the normalized VAF [i.e., $h(t)$ in Eq. (15)],

$$\dot{C}_v(t)=-\int_0^t\gamma(t-t')C_v(t')dt', \quad (24)$$

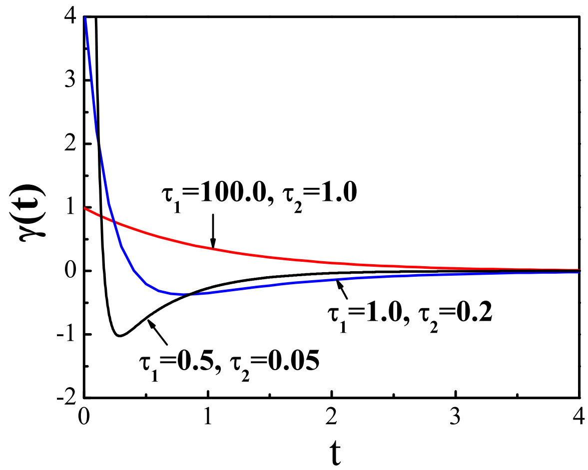

FIG. 2. The memory kernel function $\gamma(t)$ for various τ_1 and τ_2 at fixed $\gamma_0 = 1.0$.

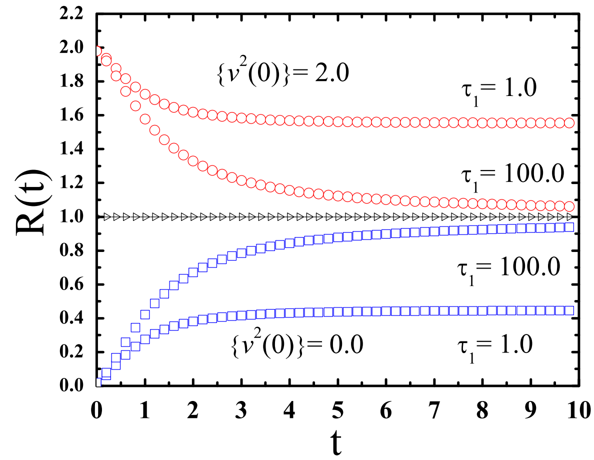

FIG. 3. Time variation of the dimensionless factor $R(t)$ for various τ_1 and $\{v^2(0)\}$ at fixed $\tau_2 = 0.2$. The parameter settings used are $T = 1.0$ and $\gamma_0 = 1.0$.

where $C_v(0) = 1$. Numerically solving this equation is a straightforward task. The VAF exhibits nonergodic behavior of two kinds based on the Khinchin theorem [16]. Once knowing the VAF, the AD and MSD of the diffusing particle can be evaluated.

In Sec. III, based on the Khinchin theorem, we have demonstrated that the VAF exhibits nonergodic behavior of two types. In order to evaluate the consequences [Eqs. (9), (10), and (19)] by using the memory kernel on the final result, we shall consider two situations in this section. Also, a comparison of the represent results with those obtainable through the reasonable memory kernel should be advisable.

B. The practical examples

As a realizable case of $R(t)$ being not equal to unity in the long-time limit, we employ a driven-noise from the difference between two Ornstein-Uhlenbeck (OU) noise sources induced by the identical white noise. The thermal noise of this type has been used to investigate the ballistic diffusion in the previous works [12,35–37]. It is associated with the following memory kernel:

$$\gamma(t) = A\left[\frac{1}{\tau_2}\exp\left(-\frac{t}{\tau_2}\right) - \frac{1}{\tau_1}\exp\left(-\frac{t}{\tau_1}\right)\right] \quad (25)$$

with $A = \gamma_0\tau_1^2/(\tau_1^2 - \tau_2^2)$, where τ_1 and τ_2 are two correlation times, γ_0 denotes the friction coefficient. The corresponding noise obeys the Kubo's requirements [2], which allows a coverage from "red" noise (τ_2 finite and $\tau_1 \to \infty$) to "green" noise ($\tau_2 \to 0$ and τ_1 finite). The case of $\tau_2 = 0$ and $\tau_1 \to \infty$ reduces into the white noise. Observably, the memory kernel (25) satisfies the condition (22) as long as the value τ_1 is finite.

In Fig. 2, we plot the memory kernel function (25) for various parameters τ_1 and τ_2. All quantities depicted therein, and in the forthcoming, are dimensionless (i.e., $k_B = 1$ and $m = 1$). In sharp contrast to usual OU colored noise, the present memory function corresponds to the thermal band-passing noise, which starts out positive, crosses zero towards negative values, and assumes in the asymptotic long time limit zero from below. Thus the effective Markovian friction vanishes $\int_0^\infty \gamma(t')dt' = 0$ when $\tau_1 \neq \tau_2$, however, through the FDT, the corresponding memory function of the OU noise ($\tau_1 \to \infty$), $\int_0^\infty \gamma(t')dt' = \gamma_0$.

Figure 3 shows $R(t)$ calculated by using Eqs. (24) and (25). We also compare the present result with the more usual exponentially decaying memory kernel. If the NSD has a zero-weight at low frequencies and rich high frequencies, for instance, Eq. (25), the condition (22) holds with the result that the VAF approaches a constant in the long-time limit. The factor b in Eq. (10) is given by

$$b = \left(1 + \frac{\gamma_0\tau_1^2}{\tau_1 + \tau_2}\right)^{-1}. \quad (26)$$

Consequently, in Fig. 3, the long-time value of $R(t)$ is not equal to unity but increases with increasing $\{v^2(0)\}$, namely, $R(t) > 1$ when $\{v^2(0)\} > k_BT/m$, $R(t) < 1$ when $\{v^2(0)\} < k_BT/m$, and $R(t) = 1$ when $\{v^2(0)\} = k_BT/m$. This is in agreement with our theoretical expression [Eq. (10)].

To emerge explicitly the origin of non-stationary VAF, we now consider the famous Debye model as the second example. Zwanzig [18,38], Adelman [39], and Millonas [40] had put the model into the GLE and the relaxation kinetics and they did not restrict themselves to the lattice dynamics. Then, they treated the frequency distribution as semicontinuous with a frequency density of the Debye type. Here, we employ the memory kernel function expressed by Zwanzig in Ref. [18], i.e.,

$$\gamma(t) = \left(3\gamma_0^2/\omega_d^2\right)\sin(\omega_d t)/t, \quad (27)$$

where ω_d is a cutoff frequency and γ_0 constant. As expected, $\gamma(t)$ vanishes in the long-time limit. If the system velocity aries sufficiently slowly over times of the order of $1/\omega_d$, then a δ-function approximation may be used for $\varepsilon(t)$, i.e., $\gamma(t) \simeq 2\tilde{\gamma}_0\delta(t)$; $\tilde{\gamma}_0 = 3\pi\gamma_0^2/(2\omega_d^2)$ [18]. This leads to the Markovian approximation.

Figure 4 shows the time-dependence VAF of a force-free particle calculated from Eqs. (24) and (27). It is seen that the VAF exhibits nonergodic behavior of the second types, namely, which continues oscillating with time if ω_d is finite. Moreover, it asymptotically vanishes when $\omega_d \to \infty$.

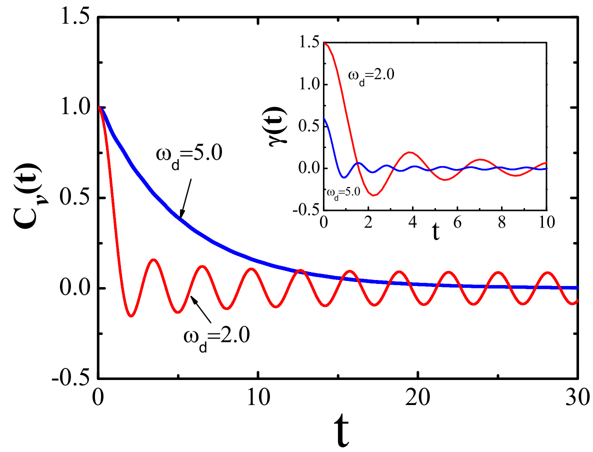

FIG. 4. The VAF of the force-free particle driven by a Debye-type noise for two cases of ω_d at fixed $\gamma_0 = 1.0$.

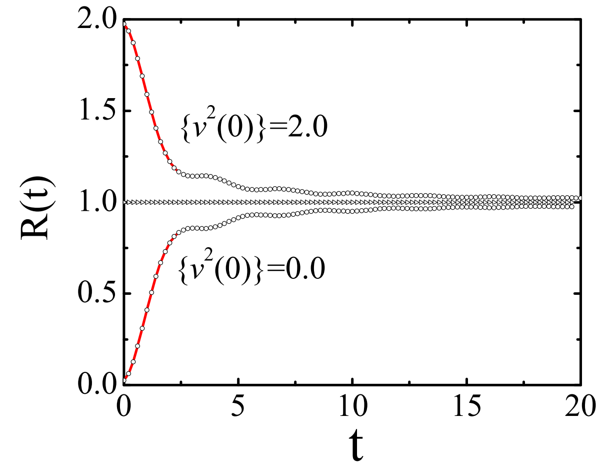

FIG. 5. Time variation of the dimensionless factor $R(t)$ for various initial velocity variances. The parameter settings used are: $T = 1.0$, $\gamma_0 = 1.0$, and $\omega_d = 2.0$.

Notably, for the second type of nonergodicity, we observe that the VAF exhibits non-stationary behavior that oscillates with time.

In Fig. 5, we plot the time-dependent $R(t)$ for two initial preparations. As the driving noise with zero-weight hight frequencies obeys the condition (23), such noise induces a non-stationary VAF result, which has been regarded as non-ergodicity of the second-type. Nevertheless, the leading terms in both the AD of the biased particle and the MSD of the force-free particle are identical, and they exceed the oscillation parts in the time domain. It is observed form Fig. 5 that the GER fails for the transition process but $R(t)$ approaches unity at long times. Based on the results of Fig. 4 in combination with Fig. 5, we conclude that the GER holding is not a full condition for the system being close to equilibrium.

V. SUMMARY

An integrated analysis of the mobility and diffusion processes using the GER has provided an interesting route in understanding the influence of ergodicity breaking of two types on transport. The first two moments are expressed using the residue theorem of the inverse Laplace transform or the VAF approach. They show a different dependence on the initial preparation. The conditions for the non-vanishing forms of the VAF derived in this context have a clear interpretation by means of spectral analysis, specifically, zero weights occur in either low frequency or high frequency.

To account for the non-vanishing results of the VAF and related quantities systematically, we considered exponential band-passing and Debye-type Gaussian noise sources. We revealed two types of nonergodicity: (i) the VAF decays asymptotically to a constant; (ii) the VAF oscillates forever with time. We have found that the GER fails for the nonergodic process of the first type because the ratio of MSD to AD depends on the initial velocity preparation of the particle. Moreover, for the second type of nonergodicity, the VAF oscillates around the zero value, the GER is asymptotically valid, however, the system is not close to equilibrium, because the VAF does not vanishing in the long-time limit. We believe that the present study has relevance to anomalous transport in which mobility and diffusion compete.

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[1] A. Einstein, Über die von der molekularkinetischen theorie der wärme geforderte bewegung von in ruhenden flüssigkeiten suspendierten teilchen, Ann. Phys. (Leipzig) **322**, 549 (1905).
[2] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II, Nonequilibrium Statistical Mechanics*, 2nd ed. (Springer-Verlag, Berlin, 1991).
[3] J.-P. Bouchaud and A. Georges, Anomalous diffusion in disordered media: Statistic mechanisms, models and physical applications, Phys. Rep. **195**, 127 (1990).
[4] R. Metzler, E. Barkai, and J. Klafter, Anomalous Diffusion and Relaxation Close to Thermal Equilibrium: A Fractional Fokker-Planck Equation Approach, Phys. Rev. Lett. **82**, 3563 (1999).
[5] F. Amblard, A. C. Maggs, B. Yurke, A. N. Pargellis, and S. Leibler, Subdiffusion and Anomalous Local Viscoelasticity in Actin Networks, Phys. Rev. Lett. **77**, 4470 (1996).
[6] E. Barkai and J. Klafter, Comment on 'Subdiffusion and Anomalous Local Viscoelasticity in Actin Networks', Phys. Rev. Lett. **81**, 1134 (1998).
[7] E. Lutz, Fractional Langevin equation, Phys. Rev. E **64**, 051106 (2001).
[8] T. Sandev, R. Metzler, and Ž. Tomovski, Correlation functions for the fractional generalized Langevin equation in the presence of internal and external noise, J. Math. Phys. **55**, 023301 (2014).

[9] D. Froemberg and E. Barkai, Time averaged Einstein relation and fluctuating diffusivities for the Lévy walk, Phys. Rev. E **87**, 030104(R) (2013).

[10] H. K. Shin, B. Choi, P. Talkner, and E. K. Lee, Normal versus anomalous self-diffusion in two-dimensional fluids: Memory function approach and generalized asymptotic Einstein relation, J. Chem. Phys. **141**, 214112 (2014).

[11] E. Barkai and V. N. Fleurov, Generalized Einstein relation: A stochastic modeling approach, Phys. Rev. E **58**, 1296 (1998).

[12] J. D. Bao and Y. Z. Zhuo, Ballistic Diffusion Induced by a Thermal Broadband Noise, Phys. Rev. Lett. **91**, 138104 (2003).

[13] L. Ferrari, Test particles in a gas: Markovian and non-Markovian Langevin dynamics, Chem. Phys. **523**, 42 (2019).

[14] G. W. Ford, J. T. Lewis, and R. F. O'Connell, Quantum Langevin equation, Phys. Rev. A **37**, 4419 (1988).

[15] F. Ishikawa and S. Todo, Localized mode and nonergodicity of a harmonic oscillator chain, Phys. Rev. E **98**, 062140 (2018).

[16] L. C. Lapas, R. Morgado, M. H. Vainstein, J. M. Rubi, and F. A. Oliveira, Khinchin Theorem and Anomalous Diffusion, Phys. Rev. Lett. **101**, 230602 (2008).

[17] H. Mori, A continued-fraction representation of time-correlation functions, Prog. Theor. Phys. **34**, 399 (1965).

[18] R. Zwanzig, Nonlinear generalized Langevin equation, J. Stat. Phys. **9**, 215 (1973).

[19] A. V. Plyukhin, Nonergodic solution of the generalized Langevin equation, Phys. Rev. E **83**, 062102 (2011).

[20] S. A. Adelman, Fokker-Planck equations for simple non-Markovian systems, J. Chem. Phys. **64**, 124 (1976).

[21] L. Ferrari, Particles dispersed in a dilute gas. II. From the Langevin equation to a more general kinetic approach, Chem. Phys. **428**, 144 (2014).

[22] R. Muralidhar, D. J. Jacobs, D. Ramkrishna, and H. Nakanishi, Diffusion on two-dimensional percolation clusters: Influence of cluster anisotropy, Phys. Rev. A **43**, 6503 (1991).

[23] J. Kim and I. Sawada, Dynamics of a harmonic oscillator on the Bethe lattices, Phys. Rev. E **61**, R2172 (2000).

[24] S. Stachura and G. R. Kneller, Communication: Probing anomalous diffusion in frequency space, J. Chem. Phys. **143**, 191103 (2015).

[25] R. F. Fox, Long-time tails and diffusion, Phys. Rev. A **27**, 3216 (1983).

[26] K. Julian and D. Frenkel, Communication: Evidence for non-ergodicity in quiescent states of periodically sheared suspensions, J. Chem. Phys. **143**, 241103 (2015).

[27] F. A. Oliverira, R. M. S. Ferreira, L. C. Lapas, and M. H. Vainstein, Anomalous diffusion: A basic mechanism for the evolution of inhomogeneous systems, Front. Phys. **7**, 1 (2019).

[28] J. D. Bao, P. Hänggi, and Y. Z. Zhuo, Non-Markovian Brownian dynamics and nonergodicity, Phys. Rev. E **72**, 061107 (2005).

[29] P. K. Ghosh, Y. Y. Li, G. Marchegiani, and F. Marchesoni, Communication: Memory effects and active Brownian diffusion, J. Chem. Phys. **143**, 211101 (2015).

[30] A. Dhar and W. Wagh, Equilibrium problem for the generalized Langevin equation, Europhys. Lett. **79**, 60003 (2007).

[31] T. Srokowski, Stochastic process with finite correlation time: Modeling and application to the generalized Langevin equation, Phys. Rev. E **64**, 031102 (2001).

[32] M. H. Vainstein, I. V. L. Costa, R. Morgado, and F. A. Oliveira, Non-exponential relaxation for anomalous diffusion, Europhys. Lett. **73**, 726 (2006).

[33] R. M. S. Ferreira, M. V. S. Santos, C. C. Donato, J. S. Andrade, Jr., and F. A. Oliveira, Analytical results for long-time behavior in anomalous diffusion, Phys. Rev. E **86**, 021121 (2012).

[34] I. V. L. Costa, R. Morgado, M. V. B. Lima, and F. A. Oliveira, The fluctuation-dissipation theorem fails for fast superdiffusion, Europhys. Lett. **63**, 173 (2003).

[35] J. D. Bao, Y. Z. Zhuo, F. A. Oliveira, and P. Hänggi, Intermediate dynamics between Newton and Langevin, Phys. Rev. E **74**, 061111 (2006).

[36] P. Siegle, I. Goychuk, and P. Hänggi, Origin of Hyperdiffusion in Generalized Brownina Motion, Phys. Rev. Lett. **105**, 100602 (2010).

[37] P. Siegle, I. Goychuk, P. Talkner, and P. Hänggi, Markovian embedding of non-Markovian superdiffusion, Phys. Rev. E **81**, 011136 (2010).

[38] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2001).

[39] S. A. Adelman, Generalized Langevin equation approach for atom/solid-surface scattering: General formulation for classical scattering off harmonic solids, J. Chem Phys. **64**, 2375 (1976).

[40] M. M. Millonas and C. Ray, Relaxation Kinetics of Nonlinear Systems Coupled to a Nonequilibrium Bath, Phys. Rev. Lett. **75**, 1110 (1995).