Generalized dynamics and fluctuation-dissipation theorem for a parabolic potential

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This article revisits the fluctuation-dissipation relationship of a generalized Brownian particle constrained in a harmonic potential and immersed in a thermal bath whose degrees of freedom also interact with the external field. The generalized Langevin equation put forth herein keeps its original form. The different terms now depend on a compound strength related to those of the field and bath oscillators. The resulting theorem keeps Kubo's original form with the memory kernel depending on the frequency of the field. It has the consequence that friction is not a constant but is a function of the field frequency as predicted by molecular dynamics simulations. The position particle distribution and the Fokker-Planck equation associated with the generalized Langevin equation are also derived.

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I. INTRODUCTION

Relevant investigations have been carried out on the theory of Brownian motion of a particle in contact with a thermal bath and subjected to external potentials. The results inevitably lead to a reformulation of Kubo's fluctuation-dissipation theorem (FDT) [1], mainly because its derivation must include the effect of the external field on the dynamics of the thermal reservoir. The most relevant work involves molecular dynamics (MD) simulations. Thus, Daldrop *et al.* [2] showed that for methane in a Lennard-Jones (LJ) water bath subjected to a harmonic potential, the kernel depends on both time and field strength because the friction is not a constant but is a function of the latter.

Therefore, from a theoretical point of view, it is essential to include the interaction between the field and the degrees of freedom of the reservoir. It has been deduced mainly for the harmonic potential. Effectively, in a short article, Lisý and Tóthová [3] found an expression for the kernel. It is not formally calculated but expressed as an integral over the frequency of the bath oscillators.

It is also worth mentioning the work of Olivares-Rivas and the present author [4], where it was shown that for a constant field, the noise correlation depends on its squared strength, and that of Costa *et al.* [5], where it is even inconsistent in the linear regime of superdiffusive processes. Seifert and Speck [6] even discovered that the dynamics of Markov processes driven into nonequilibrium steady states lead to writing the FDT as the equilibrium process and an additive correction.

Tóthová and Lisý [7] expanded their previous work [3] using a modified version of the Zwanzig-Caldeira-Leggett particle-bath Hamiltonian model.[1] They obtained a modified generalized Langevin equation (GLE) in which the FDT was the same as in their previous work [3]. The kernel decreased and oscillated with time for various arbitrary combinations of the system parameters. The authors did not provide any information about the frequency-dependent friction coefficient.

Generalization to time-dependent fields was performed by Cui and Zaccone [8] for a charged particle-bath system subjected to a combination of a general external electric force acting on the dynamics of the particle and the thermal bath. The FDT is Kubo's relation plus an additional contribution proportional to the electric-field intensity squared as found in Ref. [4] for a constant field. They found that the mean of the stochastic force is not zero but directly proportional to the static friction and the electric field, so the process is skewed where excursions away from the initial position at any $t > 0$ occur with different probabilities [9]. Likewise, the authors also wrote at the beginning of the Introduction an extensive review of the historical evolution of the FDT and its importance in Brownian dynamics. An extension of this work to determine the velocity correlation function of the particle was performed by Tóthová *et al.* [10].

Recently, Vroylandt and Monmarché [11] extended the theory to the nonlinear case. They applied the Zwanzig-Mori formalism [12] to derive the GLE in terms of a nonlinear effective mean force and friction linear in the velocity if the kernel is allowed to depend on the position. The MD simulation of two Lennard-Jones dimers confirms the prediction. Previously, Straub *et al.* [13] had shown that the memory kernel is position dependent for a pair of particles in a simple liquid using MD. Thus, for a parabolic potential, MD results dictate that the bath Hamiltonian must have a term describing the interaction of the field with the reservoir degrees of freedom to obtain a more realistic physical description of the phenomenon.

This article aims to present an algebraic derivation of the FDT to account for the above consideration. It is inspired by the methodology of the work by Adelman on the Fokker-Planck equation (FPE) for non-Markovian systems [14]. The method used here has not explicitly appeared in the literature as it does not appeal to linear response theory [15,16].

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[1]For more information, see the references cited in [7].

The theorem, given by Eq. (30), is identical in structure to Kubo's original but now the friction coefficient depends on the frequency. The main results of this proposal are the analytic kernels given by either Eq. (38) or (40), which are quite simpler than those of Refs. [3,7] in which the kernels were given in terms of the bath parameters in addition to Drude's spectral density being invoked in the calculation. Furthermore, in [3] no calculations were provided and the same kernel was used in [7] despite the authors starting their derivation from a different Hamiltonian. They only present results for the kernels without any mention of the dependence of the friction on the field frequency. We show instead in this paper that our kernel is always positive because it requires the redefinition of the lower limit of its frequency integration. It allows for determining the friction coefficient as a frequency-dependent function. When the bath-field interaction is off, our FDT reduces to Kubo's original theorem. It will be shown that the kernel and friction share some general attributes with those determined by MD simulations.

The paper is organized as follows. Sections II and III cover the derivation of the GLE and the corresponding FDT, respectively, where the total Hamiltonian includes the interaction of the bath particles with the field. The calculation of the effective strength experienced by the particle and an analysis of the new dissipation kernel and friction follows in Sec. IV. Section V deals with deriving the particle distribution function (PDF) to subsequently get its FPE. We show that the diffusion term is a function of the FDT. We summarize in Sec. VI and conclude with some general observations.

II. THE GLE

The system is composed of a tagged particle of mass M immersed in a bath of N harmonic oscillators (HOs) held at temperature T. The whole system is subjected to the parabolic potential $V(q) = M\omega^2 q^2/2$.

The Hamiltonians for the particle $\mathcal{H}_S$ and for the bath $\mathcal{H}_B$ are given as in the classical literature [17,18] with the difference that the latter includes the interaction with the field. They read

$$\mathcal{H}_S = \frac{p^2}{2M} + V(q), \tag{1}$$

$$\mathcal{H}_B = \frac{1}{2}\sum_{j=1}^{N}\left[\frac{p_j^2}{m_j} + m_j\omega_j^2\left(q_j - \frac{\lambda_j q}{m_j\omega_j^2}\right)^2 + M\omega^2 q_j^2\right], \tag{2}$$

where λ_j is the intensity of the bilinear coupling between the particle and each of the HOs in the bath. The last term in $\mathcal{H}_B$ is the aforementioned field-bath interaction.

The equations of motion for the particle read

$$\dot{q} = \frac{p}{M}, \tag{3}$$

$$\dot{p} = -M\omega^2 q + \sum_{j=1}^{N}\lambda_j\left(q_j - \frac{\lambda_j}{m_j\omega_j^2}q\right), \tag{4}$$

and for the thermal bath degrees of freedom (BDF)

$$\dot{q}_j = \frac{p_j}{m_j}, \tag{5}$$

$$\dot{p}_j = -A_j q_j + \lambda_j q, \tag{6}$$

where $A_j = m_j\omega_j^2 + M\omega^2$. Solving the BDF set of equations gives [19]

$$q_j = q_j(0)\cos(\alpha_j t) + \frac{p_j(0)}{\beta_j}\sin(\alpha_j t) + \frac{\lambda_j}{\beta_j}\int_0^t dy\, q(y)\sin[\alpha_j(t-y)], \tag{7}$$

with compound parameters $\alpha_j = (A_j/m_j)^{1/2}$ and $\beta_j = (A_j m_j)^{1/2}$. The integral on the right-hand side of Eq. (7) can be written as

$$\int_0^t dy\, q(y)\sin[\alpha_j(t-y)] = -\frac{1}{\alpha_j}\int_0^t dy\, q(y)\frac{\partial}{\partial y}\cos[\alpha_j(t-y)], \tag{8}$$

which can be integrated by parts. Substituting the resulting expression in Eq. (7) to later be used in Eq. (4) gives the GLE in terms of velocity $v(t)$. It reads

$$\dot{v}(t) = -\Omega q(t) - \int_0^t dy\, v(y)\Gamma_\Omega(t-y) + R_\Omega(t), \tag{9}$$

where Ω is the effective strength experienced by the particle due to the field corrected by that coming from the bath oscillators. This is given by

$$\Omega = \omega^2\left[1 + \frac{1}{M\omega^2}\sum_{j=1}^{N}\lambda_j^2\left(\frac{1}{m_j\omega_j^2} - \frac{1}{\alpha_j\beta_j}\right)\right] \tag{10}$$

$$= \omega^2\left(1 + \sum_{j=1}^{N}\frac{\lambda_j^2}{A_j m_j\omega_j^2}\right). \tag{11}$$

The memory kernel $\Gamma_\Omega(t-y)$ and colored noise $R_\Omega(t)$ are defined as

$$\Gamma_\Omega(t-y) = \frac{1}{M}\sum_{j=1}^{N}\frac{\lambda_j^2}{\alpha_j\beta_j}\cos[\alpha_j(t-y)], \tag{12}$$

$$R_\Omega(t) = \frac{1}{M}\sum_{j=1}^{N}\lambda_j\left[\left(q_j(0) - \frac{\lambda_j}{\beta_j\alpha_j}q(0)\right)\cos(\alpha_j t) + \frac{p_j(0)}{\beta_j}\sin(\alpha_j t)\right], \tag{13}$$

where the subscript Ω emphasizes the dependence on the frequencies of the external field and bath oscillators.

Without the field-bath interaction term, $\beta_i = m_j\omega_j$. Thus, the second term on the right-hand side of Eq. (10) vanishes and along with the kernel and noise functions properly reduced, the GLE agrees with the standard expression [14,17,19]. Since $q(t) = q_0 + \int_0^t dy\, v(y)$ and defining $\Theta_\Omega(t-s) = \Gamma_\Omega(t-s) + \Omega$, the GLE can be rewritten as

$$\dot{v}(t) = -\Omega q_0 - \int_0^t dy\, v(y)\Theta_\Omega(t-y) + R_\Omega(t), \tag{14}$$

whose solution is obtained through its Laplace transform (LT), it reads

$$v(t) = v_0\chi(t) - \Omega q_0 \int_0^t dy\, \chi(y) + \varphi_{\rm v}(t), \tag{15}$$

$$\chi(t) = \mathcal{L}^{-1}\left\{\frac{1}{k + \hat{\Theta}_\Omega(k)}\right\}, \tag{16}$$

$$\varphi_{\rm v}(t) = \int_0^t dy\, \chi(t-y) R_\Omega(y), \tag{17}$$

where $\hat{\Theta}_\Omega(k)$ is the LT of $\Theta_\Omega(t)$.

A complete statistical description of the noise requires knowing its equilibrium distribution conditioned on the particle's initial position is its actual position. It is given by [19]

$$\rho_{\rm B}(\{p_j, q_j\} \mid q(0) = q) = \frac{1}{Z}\exp\left(-\frac{\mathcal{H}_{\rm B}(p_j, q_j, q)}{k_{\rm B}T}\right), \tag{18}$$

where Z is the partition function and $k_{\rm B}$ is Boltzmann's constant. Therefore, the noise is Gaussian, so its first moment $\langle R_\Omega(t)\rangle = 0$. The correlation is of Kubo's kind since the our GLE has the same structure as the original GLE [17] with the difference that all terms now depend on Ω. Nonetheless, we present its derivation in the next section without appealing to the average over the bath distribution $\rho_{\rm B}(\cdot)$.

III. THE FDT

Before proceeding to derive the FDT, we need some useful expressions evaluated at equilibrium, such as $\langle v_0\rangle = \langle q_0\rangle = 0$, $\langle v_0^2\rangle = k_{\rm B}T/M$, and

$$\langle q_0^2\rangle = \frac{k_{\rm B}T}{M\Omega}, \tag{19}$$

according to the equipartition theorem [20]. Thus, from Eq. (15) we get

$$\langle v(t)v_0\rangle = \frac{k_{\rm B}T}{M}\chi(t), \tag{20}$$

$$\langle v(t)q_0\rangle = -\frac{k_{\rm B}T}{M}\int_0^t dy\, \chi(y). \tag{21}$$

Likewise, from Eq. (14) and using Eq. (20) we get

$$\langle \dot{v}(t)v_0\rangle = -\frac{k_{\rm B}T}{M}\int_0^t dy\, \Theta_\Omega(t-y)\chi(y), \tag{22}$$

and from Eq. (20) and using Eq. (22),

$$\dot{\chi}(t) = -\int_0^t dy\, \Theta_\Omega(t-y)\chi(y), \tag{23}$$

where the averaging is performed over the noise distribution and $R_\Omega(t)$ is uncorrelated with $v(t)$. These relations will be used in the derivation of the FDT that follows.

Let us define

$$Q(t) = \left\langle\left(v(t) - v_0\chi(t) + \Omega q_0\int_0^t dy\, \chi(y)\right)^2\right\rangle. \tag{24}$$

Expanding the term in large parentheses and making the above substitutions gives

$$Q(t) = \frac{k_{\rm B}T}{M}\left[1 - \chi^2(t) - \Omega\left(\int_0^t dy\, \chi(y)\right)^2\right]. \tag{25}$$

Thus, the time derivative of $Q(t)$ renders

$$\dot{Q}(t) = 2\frac{k_{\rm B}T}{M}\chi(t)\int_0^t dy\, \Gamma_\Omega(t-y)\chi(y), \tag{26}$$

where Eqs. (22) and (23) are used along with the definition of $\Theta_\Omega(t)$.

Once $\dot{Q}(t)$ is identified with an integral of the kernel, we proceed to find an equivalent expression in terms of the colored noise correlation. This is achieved by setting $Q(t)$ in Eq. (24) equal to the last term on the right-hand side of Eq. (15) using the definition of $\varphi_{\rm v}(t)$ given by Eq. (17), that is,

$$Q(t) = \int_0^t dy\, \chi(t-y)\int_0^t dz\, \chi(t-z)\langle R_\Omega(y)R_\Omega(z)\rangle, \tag{27}$$

which after changing the limits of integration gives

$$Q(t) = 2\int_0^t dy\, \chi(y)\int_0^y dz\, \chi(z)\langle R_\Omega(y-z)R_\Omega(0)\rangle. \tag{28}$$

Then, taking its time derivative and switching $z \mapsto y$, we get

$$\dot{Q}(t) = 2\chi(t)\int_0^t dy\, \chi(y)\langle R_\Omega(t-y)R_\Omega(0)\rangle. \tag{29}$$

Finally, setting this equation equal to Eq. (26), we get for the noise correlation function

$$\langle R_\Omega(t-s)R_\Omega(0)\rangle = \frac{k_{\rm B}T}{M}\Gamma_\Omega(t-s). \tag{30}$$

Equation (30) is the required FDT for the GLE completing the statistics of the Gaussian colored noise.

IV. CALCULATION OF EFFECTIVE STRENGTH, MEMORY KERNEL, AND FRICTION

The strength Ω, memory kernel, and friction depend on the parameters defining the reservoir. We can dispense of them by switching the discrete description to an integral by considering the bath containing an infinite number of oscillators [21].

To begin with, we use Eq. (12) as a prototype to exemplify the derivation. It can be written as

$$\Gamma_\Omega(t) = \frac{1}{M}\sum_{j=1}^N \frac{\lambda_j^2}{m_j\tilde{\omega}_j^2}\cos(\tilde{\omega}_j t), \tag{31}$$

with $\tilde{\omega}_j = (\omega_j^2 + \kappa\omega^2)^{1/2}$ and $\kappa = M/\mu$, where each of the oscillators has a mass $\mu = m_j$. Furthermore, the equation is equivalent to

$$\Gamma_\Omega(t) = \frac{1}{M}\int_{-\sqrt{\kappa}\omega}^\infty d\tilde{\omega}\sum_{j=1}^N \frac{\lambda_j^2}{m_j\tilde{\omega}_j}\frac{\cos(\tilde{\omega}t)}{\tilde{\omega}}\delta(\tilde{\omega} - \tilde{\omega}_j). \tag{32}$$

Choosing the lower bound to be zero gives the same result as $-\sqrt{\kappa}\omega$. However, choosing $-\sqrt{\kappa}\omega$ makes the kernel more physically significant than choosing zero. Next we will explain this issue in more detail.

Because of the shift, the choice of the negative bound $-\sqrt{\kappa}\omega$ can be justified in the following way. The frequency of the oscillators is upshifted by the amount of $\sqrt{\kappa}\omega$ as seen in the definition of $\tilde{\omega}_j$. For the system to resonate in phase with the external field and to get meaningful physical feedback, we have to choose the negative value of the upshifting as the lower bound to increase the signal-to-noise ratio of the oscillator and achieve a low interference in the response. Otherwise, if the lower bound is equal to or greater than zero, the overall effect is similar to if the frequencies of the field and of the bath are out of phase and therefore generating a function out of bounds with a nonphysical meaning. Additionally, the concept of negative frequency has a mathematical basis. It is defined by the phasor $e^{-i\omega t}$ rotating clockwise in the complex plane. Thus, according to Euler's equation, $\cos(\omega t)$ is equal to $(e^{i\omega t}+e^{-i\omega t})/2$ or, equivalently, to two phasors rotating in different directions.

From Eq. (32) we define the spectral density (SD) $J(\tilde{\omega})$ as [21,22]

$$J(\tilde{\omega}) = \frac{\pi}{2}\sum_{j=1}^{N}\frac{\lambda_j^2}{m_j\tilde{\omega}_j}\delta(\tilde{\omega}-\tilde{\omega}_j). \tag{33}$$

Then the kernel in terms of the bath parameters reduces to

$$\Gamma_\omega(t) = \frac{2}{\pi M}\int_{-\sqrt{\kappa}\omega}^{\infty} d\tilde{\omega}\frac{J(\tilde{\omega})}{\tilde{\omega}}\cos(\tilde{\omega}t), \tag{34}$$

where the subscript Ω is switched to the more specific ω.

We use Drude's SD for the coupling with the environment [21]

$$J(\tilde{\omega}) = M\gamma_0\tilde{\omega}\frac{\tau^{-2}}{\tilde{\omega}^2+\tau^{-2}}, \tag{35}$$

where γ_0 is the static value of the friction coefficient and τ^{-1} is a cutoff frequency, that is, frequencies above the order of τ^{-1} are suppressed. This choice of SD makes it unnecessary to specify the bath parameters $\{m_j, \omega_j, \lambda_j\}$ in the calculation of the kernel.

This procedure can be adapted to any calculation involving the discrete description of the thermal bath. As the first illustration, we can get a closed expression for the effective strength Ω in which the summation renders

$$\begin{aligned}\sum_{j=1}^{N}\frac{\lambda_j^2}{A_j m_j\omega_j^2} &= \sum_{j=1}^{N}\frac{\lambda_j^2}{m_j^2\omega_j^2(\omega_j^2+\kappa\omega^2)}\\ &= \mathrm{P}\frac{2}{\pi\mu}\int_{-\sqrt{\kappa}\omega}^{\infty} d\tilde{\omega}\frac{J(\tilde{\omega})}{\tilde{\omega}}\frac{1}{(\tilde{\omega}^2+\kappa\omega^2)}\\ &= -\frac{\gamma_0}{2\omega(\kappa\tau^2\omega^2-1)}\\ &\quad\times\left[3\sqrt{\kappa}-2\kappa\tau\omega\left(1+\frac{2}{\pi}\arctan(\sqrt{\kappa}\tau\omega)\right)\right],\end{aligned} \tag{36}$$

where P denotes the Cauchy principal value and $J(\tilde{\omega})$ is replaced by Eq. (35). The resulting effective strength experienced by the tagged particle and given by Eq. (11) is shown in Fig. 1 for the parameters described in the caption. Thus, Eq. (36) allows us to write the GLE as a closed expression of the system parameters and field frequency.

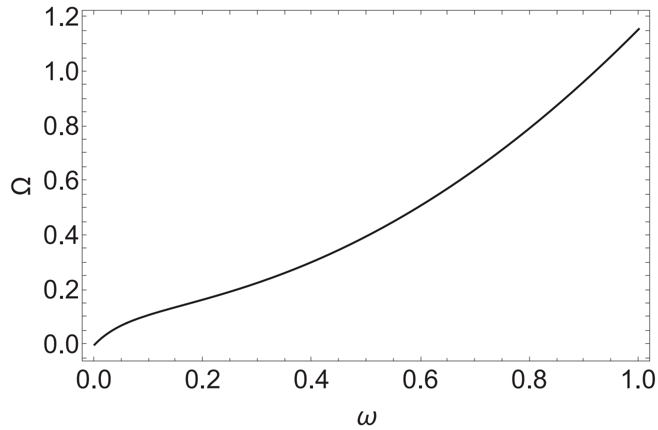

FIG. 1. Strength Ω as a function of the field frequency for $\gamma_0 = 1$ and $\{\kappa, \tau\} = \{2, 12\}$.

Continuing with the analysis, the integral (34) gives $\Gamma(t) = (t/\tau)\exp(-t/\tau)$ for $\omega = 0$ corresponding to the free particle with a symmetrical Fourier transform. For finite positive values of ω, the substitution of Drude's SD in Eq. (34) gives

$$\Gamma_\omega(t) = \frac{2\gamma_0\tau^{-2}}{\pi}\int_{-\sqrt{\kappa}\omega}^{\infty} d\tilde{\omega}\frac{\cos(\tilde{\omega}t)}{\tilde{\omega}^2+\tau^{-2}}, \tag{37}$$

whose solution is instead[2]

$$\begin{aligned}\Gamma_\omega(t) = \frac{\gamma_0}{\tau}\Bigg\{&e^{-t/\tau}-\frac{1}{\pi}\sinh\left(\frac{t}{\tau}\right)\left[\mathrm{Si}\left(H_-\frac{t}{\tau}\right)\right.\\ &\left.+\mathrm{Si}\left(H_+\frac{t}{\tau}\right)\right]+\frac{i}{\pi}\cosh\left(\frac{t}{\tau}\right)\left[\mathrm{Ci}\left(-i\frac{t}{\tau}\right)\right.\\ &\left.-\mathrm{Ci}\left(i\frac{t}{\tau}\right)-\mathrm{Ci}\left(H_-\frac{t}{\tau}\right)+\mathrm{Ci}\left(H_+\frac{t}{\tau}\right)\right]\Bigg\},\end{aligned} \tag{38}$$

$$H_\pm = \kappa\tau\omega \pm i, \tag{39}$$

or, equivalently, using Euler's identity,

$$\begin{aligned}\Gamma_\omega(t) = \frac{\gamma_0}{\tau}e^{-t/\tau}\Bigg(&1+e^{2t/\tau}+\frac{i}{2\pi}\Bigg\{\mathrm{Ei}\left(G_-\frac{t}{\tau}\right)\\ &-\mathrm{Ei}\left(G_+\frac{t}{\tau}\right)+e^{2t/\tau}\left[\mathrm{Ei}\left(-G_-\frac{t}{\tau}\right)\right.\\ &\left.-\mathrm{Ei}\left(-G_+\frac{t}{\tau}\right)\right]\Bigg\}\Bigg),\end{aligned} \tag{40}$$

$$G_\pm = 1 \pm i\sqrt{\kappa}\tau\omega, \tag{41}$$

where $\mathrm{Si}(\cdot)$, $\mathrm{Ci}(\cdot)$, and $\mathrm{Ei}(\cdot)$ are the sine, cosine, and exponential integral functions of the argument, respectively [23]. Either of the kernels is an elaborate function whose complexity lies in the intertwined dependence on ω and t. In particular, they present high fluctuations at a given field strength with no physical justification for times outside the experimental interest, which will be defined below. This circumstance forces

[2]Because of the complexity of the integrand of this equation, we use the computer package *Mathematica* [23] to execute the integration.

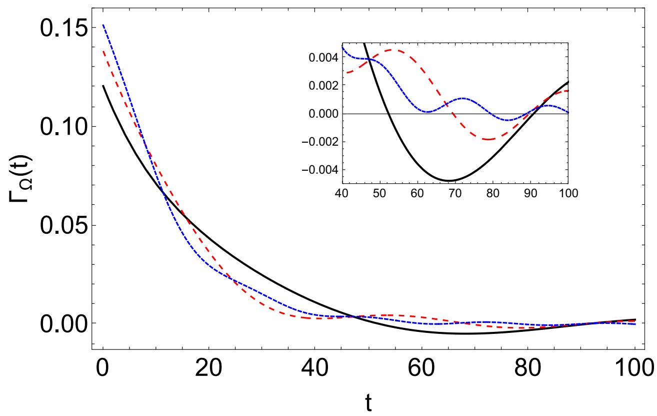

FIG. 2. Memory kernel for ω of 0.05 (black solid line), 0.1 (red dashed line), and 0.2 (blue dotted line) as a function of time. The parameters are $\{\gamma, \tau, \kappa\} = \{1, 12, 2\}$.

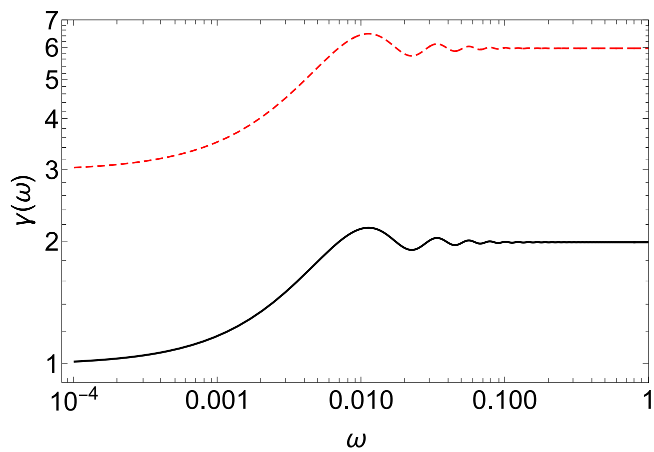

FIG. 3. Friction as a function of the field frequency and $\kappa = 2$ for the kernels of Fig. 1. The dashed red line is for $\gamma = 3$ and $\tau = 20$.

us to truncate it to get acceptable vanishing values. Note that the kernels are in units of the inverse of time squared and depend only on four parameters: the field ω and cutoff $1/\tau$ frequencies, the static friction constant γ_0, and the mass ratio κ. All of the above equations are the principal results of this investigation.

Regarding this observation, the calculations will include a final time t_f of 200, which is sufficiently large for calculation purposes, and arbitrary system parameters, such as $\gamma_0 = 1$, $\tau = 12$, $\kappa = 2$, and field frequencies of 0.05, 0.1, and 0.2. For higher frequencies, there are no major changes in the figure. Figure 2 shows the result with either of the solutions given by Eq. (38) or (40) up to $t = 100$, so the figure can show the relevant dependence on time. The frequencies are identified by the black solid, red dashed, and blue dotted curves, respectively. The kernels are nonexponentially decaying, exhibiting relatively small shoulders at specific times and presenting small negative values, as seen in the inset. They could be categorized as spurious numerical data since their contribution to the total area is too small to be considered important in the numerical calculation. The spurious area decreases further for higher frequencies.

In general, the friction coefficient is given by an integral of the equilibrium autocorrelation function of the instantaneous microscopic force experienced by the Brownian particle [24]. The equation for a free particle reduces to Einstein's relationship, which in turn is related to the mean-square displacement [25–27]. Daldrop *et al.* in their MD simulation [2] corroborate the former for the parabolic potential and the latter for a vanishing field frequency. Because in our case the kernel is a function of time and frequency, friction is given as the time integral of the kernel for nonvanishing field frequencies [2], providing as a consequence a function depending on ω.

It is a well-defined real expression, equal to γ_0 plus a long term, not displayed for presentation purposes, depending on the original integral functions and the hyperbolic Shi and Chi, as well as the natural logarithm. Their arguments are complex numbers involving combinations of $\{\sqrt{\kappa}, \tau, t_f, \omega\}$ [23]. The result is displayed in Fig. 3 for $\kappa = 2$, where the black solid curve is for $\gamma_0 = 1$ and $\tau = 12$ and the red dashed curve is for 3 and 20, respectively. Surprisingly, it is a saturation curve with small fluctuations after the maximum due to the invoked approximation on the final time. Their origin is due to the small oscillations in the memory kernel. The result makes sense because the greater the ω, the greater the confinement, and the friction will increase to reach a maximum value. As mentioned in the Introduction, Daldrop *et al.* [2] simulated with MD a methane molecule in a parabolic potential surrounded by a fixed number of LJ water molecules in the simulation box. Their memory kernel is an intricate decaying function of time where unexpected prominent shoulders appear for intermediate field strengths, similar to the results for the diatomic kernel spectrum in LJ fluids [28]. Likewise, they found that friction as a function of field strength is a sigmoidlike curve. At very low field intensity, the friction is equal to its static value.

Next we contrast our approach with that of MD simulation. The parameters are those from Ref. [2], setting the mass of the tagged particle to $M = 1$ Kg. Therefore, the friction $\gamma_0 = 2.2$ ps^{-1}, the mass ratio $\kappa = 0.89$, and the relaxation time $\tau = 0.4$ ps, corresponding approximately to the middle value between of the two timescales of the confinement limit. Frequencies of $\{1, 2, 3\}$ ps^{-1} will be identified by black solid, red long-dashed, and blue short-dashed curves, respectively. The $\omega = 0$ case will be used as a reference and displayed as the black dash-dotted curve. The calculation of the memory kernel is up to $t_f = 6$ ps, being an order of magnitude higher than τ, to get a meaningful value. Figure 4 displays the prediction, where we note that the kernels do not converge to a unique value at $t = 0$ and friction at a frequency sufficiently big is double that of γ_0. They share behavior similarities with those calculated with arbitrary parameters.

Therefore, with the proper definition of the lower limit in Eq. (34) and companion approximations, we can conclude that our frequency-dependent kernel is an acceptable approximation having some of the attributes of the MD simulation concerning its temporal dependence. Regarding friction, we

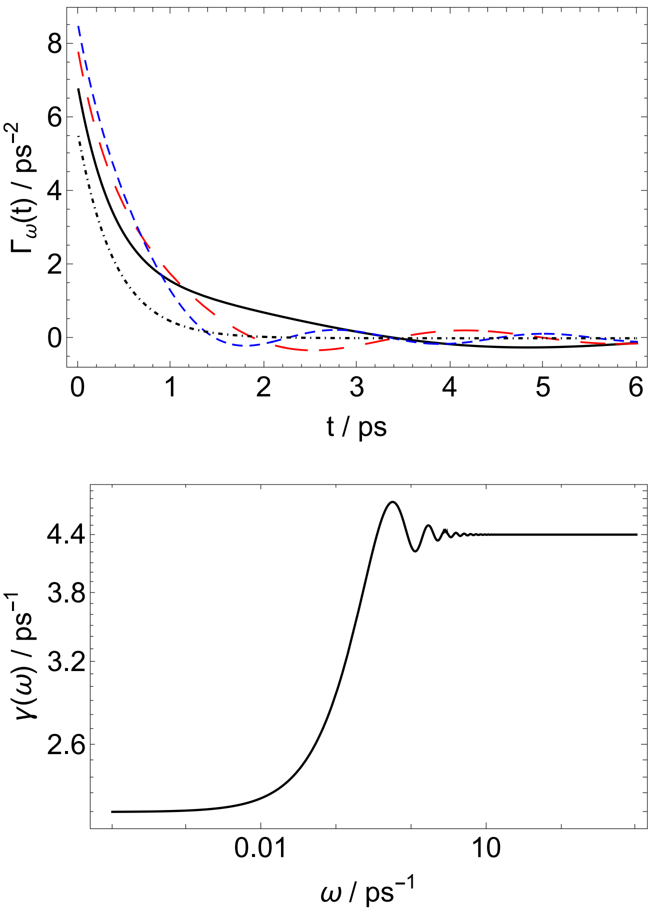

FIG. 4. Memory kernel and friction using the MD data of Daldrop *et al.* for methane in water [2]. See the text for details.

found a similar topology for its dependence on the field frequency. For purposes of comparison, the friction function for a system without an external field shows a decay with the natural system frequency [29,30].

V. PARTICLE PDF AND FPE

In Brownian dynamics, the diffusion coefficient no longer satisfies the Stokes-Einstein relation of stationary motion [30]. It is a time-dependent function correctly predicted in the FPE formalism. Its calculation requires first knowing the PDF for the position of the Brownian particle described in Sec. 3.1 of Ref. [4]. Adapting it to our problem, as shown in the Appendix, gives a normal distribution with mean and variance

$$\overline{q}(t) = q_0\left(1 - \Omega\int_0^t dy\, y\,\chi(t-y)\right), \tag{42}$$

$$\sigma^2(t) = 2\int_0^t dy\int_0^y dz\langle\varphi_v(y)\varphi_v(z)\rangle + \frac{k_B T}{M}\left(\int_0^t dy\,\chi(y)\right)^2, \tag{43}$$

respectively. The noise correlation in Eq. (43), according to the definition of $\varphi_v(t)$, is written as

$$\langle\varphi_v(y)\varphi_v(z)\rangle = \int_0^y dy'\int_0^z dz'\chi(y-y')\chi(z-z') \times \langle R_\Omega(y'-z')R_\Omega(0)\rangle, \tag{44}$$

which depends on the FDT. Since the Gaussian is a well-defined function in terms of the model parameters, some thermodynamic properties such as heat, work, and entropy, to name a few, can be determined.

The next step is to devise an inverse process consisting of deriving the FPE whose solution is the PDF mentioned above. It is achieved by the general method originally designed by Adelman and Garrison [20] and shown in detail in Ref. [31]. It renders

$$\frac{\partial p(q,t)}{\partial t} = -\Phi(t)\frac{\partial}{\partial q}qp(q,t) + \frac{1}{2}D(t)\frac{\partial^2 p(q,t)}{\partial q^2}, \tag{45}$$

$$\Phi(t) = \frac{d\ln\overline{q}(t)}{dt}, \tag{46}$$

$$D(t) = \dot{\sigma}^2(t) - 2\sigma^2(t)\Phi(t), \tag{47}$$

where $D(t)$ is the time-dependent diffusion. The structure of the FPE for the GLE when the field-bath interaction is off remains the same as Eq. (45) with the corresponding mean position and standard deviation, respectively.

VI. CONCLUSION

We have presented in this article the derivation of the fluctuation-dissipation relationship for the parabolic potential. It is a well-defined expression that involves a frequency-dependent memory kernel. When the field-reservoir interaction is off, the FDT is Kubo's. So far, the literature appearing on this topic has always supposed the FDT is equal to Kubo's relationship even in the presence of the parabolic potential except for those of Refs. [3,7] and the subject of this investigation. For the cases where the system is under the influence of an external electric field, the FDT is Kubo's plus a correction [8,10].

We based our calculations on recognizing the resonance between the field and the system as a fundamental factor because the oscillators and the external field vibrate at different frequencies. It requires changing the lower bound of the integral defining the kernel to include this effect.

In this circumstance, the memory kernel and friction depending on time and the field frequency, respectively, resemble, in a general way, the topology of MD simulation's curves. However, the theory needs some adjustments to improve the prediction for the final time proposed in the calculations. The oscillations of the kernel appearing at long times could be prevented by numerically smoothing them to get a positive lower value.

The noninertial or overdamped limit must be carefully analyzed as demonstrated by Nascimento and Morgado [32]. By setting the inertial term to zero, they proved that the PDF does not reach the stationary Gibbs-Boltzmann distribution. The resulting dynamics underestimates the fast collisions of the oscillators with the particle, leaving the memory effect of the friction kernel leading the dynamics. They proposed adding extra white noise to the overdamped expression with an intensity exceeding the memory effect to recover the correct stationary dynamics.

An alternative equation can be obtained to describe the dynamics from the derived FPE. We rely on Itô's formula to derive a stochastic differential equation (SDE) knowing the associated FPE [33] given by Eq. (47). Thus, according to this rule, the dynamics can also be described by the first-order SDE

$$\dot{q}(t) = \Phi(t)q(t) + \sqrt{D(t)}\xi(t), \tag{48}$$

mathematically equivalent to the GLE given by Eq. (9). It describes the generalized diffusion of the particle as a time-dependent Ornstein-Uhlenbeck process defined by a drift $\Phi(t)q(t)$ and a diffusion $D(t)$ driven by the zero-mean Gaussian white noise $\xi(t)$.

The physical application of the our findings for systems already analyzed in previous works is straightforward. It allows a more formal investigation of several thermodynamical properties such as heat, mechanical work, optimal protocols, and entropy.

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APPENDIX: PROBABILITY DENSITY FOR THE POSITION

For a given realization of $\varphi_v(t)$, the temporal evolution for the density of the flow in q space described by Eq. (15) is given by the stochastic Liouville equation [34], that is,

$$\frac{\partial f(q[\varphi_v],t)}{\partial t} = -\frac{\partial}{\partial q}\left[f(q[\varphi_v],t)\frac{dq[\varphi_v]}{dt}\right]. \tag{A1}$$

As was pointed out by van Kampen [35,36], averaging this flow over all realizations of the noise then results in $\langle f(q[\varphi_v],t)\rangle = P(q,t,v_0,q_0)$. Therefore, replacing Eq. (15), we find

$$\frac{\partial P(q,t,q_0,v_0)}{\partial t} = -\overline{v}(t)\frac{\partial p(q,t,q_0,v_0)}{\partial q} - \frac{\partial}{\partial q}\langle f(q[\varphi_v],t)\varphi_v(t)\rangle_{\varphi_v}, \tag{A2}$$

$$\overline{v}(t) = v_0\chi(t) - \Omega q_0\int_0^t dy\,\chi(y), \tag{A3}$$

where the subindex φ_v is a reminder that the PDF of the colored noise has to be employed in the calculation of the average. It can be determined by the formula of differentiation derived independently by Furutzu [37], Novikov [38], and Donsker [39] for Gaussian noises. It reads

$$\langle f(q[\varphi_v],t)\varphi_v(t)\rangle_{\varphi_v} = \int_0^t dy\langle\varphi_v(t)\varphi_v(y)\rangle \times\left\langle\frac{\partial f(q[\varphi_v],t)}{\partial q[\varphi_v]}\frac{\delta q[\varphi_v]}{\delta\varphi_v(t)}\right\rangle_{\varphi_v} \tag{A4}$$

$$= -\frac{1}{2}D_q(t)\frac{\partial P(q,t,q_0,v_0)}{\partial q}, \tag{A5}$$

$$D_q(t) = 2\int_0^t dy\langle\varphi_v(t)\varphi_v(y)\rangle. \tag{A6}$$

The functional derivative inside the average is obtained by integrating first Eq. (15),

$$q(t) = \overline{q}(t) + v_0\int_0^t dy\,\chi(y) + \int_0^t dy\,\varphi_v(y), \tag{A7}$$

$$\overline{q}(t) = q_0\left(1 - \Omega\int_0^t dy\,y\,\chi(t-y)\right), \tag{A8}$$

where from Eq. (A7) it is equal to 1. The average of the partial derivative of the flow is just the variation of the PDF with the position according to van Kampen's definition. Equation (A8) is just the average position appearing in Eq. (42).

Then, carrying out the proper substitutions, we get the FPE

$$\frac{\partial P(q,t,q_0,v_0)}{\partial t} = -\overline{v}(t)\frac{\partial p(q,t,q_0,v_0)}{\partial q} + \frac{1}{2}D_q(t)\frac{\partial^2 P(q,t,q_0,v_0)}{\partial q^2}. \tag{A9}$$

Setting $s = q - \int_0^t dy\,\overline{v}(y)$ and $r = \int_0^t dy\,D_q(y)$, the FPE reduces to a diffusionlike equation [40]

$$\frac{\partial P(s,r,q_0,v_0)}{\partial r} = \frac{1}{2}\frac{\partial^2 P(s,r,q_0,v_0)}{\partial s^2}. \tag{A10}$$

Its solution for the initial condition $\delta(s-s_0)$ is a Gaussian centered at $s=0$, which in the original variables is given by

$$P(q,t|q_0,v_0) = \frac{1}{\sqrt{2\pi\sigma_q^2(t)}}\exp\left(-\frac{[q-\tilde{q}(t)]^2}{2\sigma_q^2(t)}\right), \tag{A11}$$

$$\tilde{q}(t) = \overline{q}(t) + v_0\int_0^t dy\,\chi(y), \tag{A12}$$

$$\sigma_q^2(t) = \int_0^t dy\,D_q(y). \tag{A13}$$

Averaging this equation over the initial velocity Maxwell distribution renders the PDF for the position of the particle, that is,

$$P(q,t|q_0) = \frac{1}{\sqrt{2\pi\sigma^2(t)}}\exp\left(-\frac{[q-\overline{q}(t)]^2}{2\sigma^2(t)}\right), \tag{A14}$$

$$\sigma^2(t) = \sigma_q^2(t) + \frac{k_B T}{M}\left(\int_0^t dy\,\chi(y)\right)^2. \tag{A15}$$

Substituting $\sigma_q^2(t)$ in terms of $\varphi_v(t)$ gives the standard deviation described by Eq. (43).

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