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Microarticle

Generalized Langevin equation and the fluctuation-dissipation theorem for particle-bath systems in a harmonic field

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ABSTRACT

The generalized Langevin equation (GLE) is extended to the case when not only the tagged particle but also the surrounding bath particles respond to the external harmonic potential $K(x)$. The second fluctuation-dissipation theorem is derived omitting the Kubo's assumption $K = 0$. Within a modified Caldeira-Legget particle-bath model a new form of the GLE and an explicit expression for the memory function depending on the strength of the external field are obtained.

Introduction

The generalized Langevin equation (GLE) [1,2],

$$m\dot{v}(t) + \int_0^t dt'\Gamma(t-t')v(t') - K(x) = f(t), \ t > 0 \tag{1}$$

is a natural extension of the equation designed by Langevin [3] for the description of the Brownian motion (BM) of particles. As discussed by Kubo [2], the mass m of the particle is not necessarily much larger than that of the surrounding particles so that the time scale of the molecular motion is no longer very much shorter than that of the motion of the observed particle. The random force $f(t)$ is no more white and the Stokes force $-\xi v(t)$ with the friction coefficient ξ is replaced by the convolution of the memory function $\Gamma(t)$ with the particle velocity $v(t) = \dot{x}(t)$. Kubo [2] derived from (1) the relation $\langle f(0)f(t)\rangle = k_B T\Gamma(t)$, called by him the second fluctuation–dissipation theorem (FDT). He assumed that the random force averages to zero, $\langle f(t)\rangle = 0$, it is not correlated with the velocity $v(0)$ (causality), the particle is in equilibrium with the surroundings (due to which the process $v(t)$ is stationary, i.e., for the time correlation functions like the velocity autocorrelation function (VAF), we have $C_{vv}(t) = \langle v(t_0)v(t_0+t)\rangle = \langle v(0)v(t)\rangle$), and that $f(t)$ does not depend on the external force $K(x)$. The FDT was thus derived by Kubo with the assumption $K = 0$.

Below we show for the case of the harmonic external field that in the derivation of the FDT this assumption is unnecessary and for the first time derive the FDT for the GLE of the full form (1). The other Kubo's assumptions remain the same. As a result, $\Gamma(t)$ and $f(t)$ now can depend on the elasticity constant κ of the force $K(x) = -\kappa x(t)$, with $x(t) = x(0) + \int_0^t v(t')dt'$ being the distance from the minimum of the harmonic potential. Moreover, in the next section we derive a modified GLE and obtain a κ-dependent $\Gamma(t)$ for the BM of a tagged particle in a bath of harmonic oscillators, when both the particle and the oscillators are affected by the external force. The presented paper is closely related to two recent remarkable works [4] and [5]. In the first one it has been shown, by computer simulations, that if the dynamics of a single methane molecule solvated in water and subjected to a harmonic potential is modeled by the GLE (1), the memory function is necessarily κ-dependent. In Ref. [5], devoted to the study of the influence of external oscillating electric fields on the particle-bath systems, it is discussed that so far all versions of the GLE and of the associated FDT are limited to either systems in the absence of such forces or, if they are present, their action is restricted to the tagged Brownian particle, leaving the bath particles unaffected by the external field. It has been clearly demonstrated in [5] that such approach is not realistic. There are a number of important physical problems, where not only the tagged particle is subjected to the ac field, but also the particles that constitute the heat bath are subjected to it. The account for this leads to an important modification of the FDT [5]. Our opinion is that not only the effect of the ac electric field on the bath must be taken into account, but the influence of external mechanical forces should be considered as well. This will be done here within a simple modification of the so called Caldeira-Legget model [6].

Second fluctuation-dissipation theorem in the presence of an external harmonic field

The solution of Eq. (1) in the form of relevant time correlation functions can be easily obtained by the method presented, e.g., in [7,8].

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So, the VAF of the particle reads, in the Laplace transform (LT),

$$\widetilde{C}_{vv}(s) = \int_0^\infty dt e^{-st} C_{vv}(t) = k_B T\, [ms + \widetilde{\Gamma}(s) + \kappa s^{-1}]^{-1} \tag{2}$$

Due to the equipartition theorem $C_{vv}(0) = k_B T/m$. Other correlation functions of interest are the positional autocorrelation function $C_{xx}(t) = \langle x(0)x(t)\rangle$, the mean square displacement $X(t) = 2[C_{xx}(0) - C_{xx}(t)]$, and the time-dependent diffusion coefficient $D(t) = \dot{X}(t)/2$. All these functions are thus connected to $C_{vv}(t) = \dot{D}(t)$. In the LT, $\widetilde{X}(s) = 2\widetilde{D}(s)/s = 2\widetilde{C}_{vv}(s)/s^2$.

If there is no external force acting on the studied system, the FDT is easily obtainable from the GLE [2]. For the case when $K \neq 0$, to our knowledge, the corresponding explicit calculation is not present in the literature. This relation can be obtained in the following way. Let us multiply Eq. (1) by $f(0) = m\dot{v}(0) + \kappa x(0)$ and statistically average, obtaining in the right hand side $C_{ff}(t) = \langle f(0)f(t)\rangle$. The correlation functions that appear at the left are $\langle \dot{v}(0)\dot{v}(t)\rangle = -\ddot{C}_{vv}(t)$, (these expressions follow from the assumption of stationarity [2]), $C_{xx}(t) = k_B T/\kappa - X(t)/2$ and its derivatives, with $\langle \dot{v}(0)x(0)\rangle = -\ddot{X}(0)/2 = -k_B T/m$ [7]. All these terms can be expressed through $C_{vv}(t)$ (2). Taking into account the connection between these functions in the time domain and the initial conditions $X(0) = \dot{X}(0) = 0$, we arrive at $\widetilde{C}_{ff}(s) = k_B T\widetilde{\Gamma}(s)$, which proves the (second) FDT also in the case when the external elastic force is present in the GLE.

Generalized Langevin equation within a modified Caldeira-Legget model

It follows from the above derivation of the FDT that possible memory kernels in (1) are not limited to those that do not depend on the external field. A question thus arises how to model a κ-dependent $\Gamma(t)$. Here we show that this can be done coming from a simple modification of the Caldeira-Legget theory [6], in which the bath is represented by a set of noninteracting harmonic oscillators. The tagged particle is linearly coupled to the oscillators. The system is in thermal equilibrium. As distinct from [6], let both the particle and oscillators respond to a harmonic external field. For the motion along the axis x, the Hamiltonians for the particle and the bath are

$$H_P = \frac{p^2}{2m} + \frac{1}{2}\kappa x^2,\ H_B = \frac{1}{2}\sum_{i=1}^{N}\left[\frac{p_i^2}{m_i} + m_i\omega_i^2\left(x_i - \frac{c_i x}{\omega_i^2}\right)^2 + \kappa x_i^2\right] \tag{3}$$

Here c_i are strengths of coupling between the tagged particle and the oscillators with eigen frequencies ω_i, p and p_i stay for the particle and oscillator momenta. From (3) the equations of motion are constructed in the standard way. By solving the equations for the bath particles, $\ddot{x}_i = -\gamma_i^2 x_i + c_i x$, where $\gamma_i^2 = \omega_i^2 + \kappa/m_i$, and substituting $x_i(t)$ into the equation for $p(t)$, one comes to the GLE,

$$m\dot{v}(t) = -\kappa' x(t) - \int_0^t ds\, v(s)\Gamma(t-s) + f(t) \tag{4}$$

with $\kappa'/\kappa = 1 + \sum_i c_i^2/\omega_i^2\gamma_i^2$, $\Gamma(t) = \sum_i m_i c_i^2 \gamma_i^{-2}\cos(\gamma_i t)$ as the memory function, and $f(t) = \sum_i m_i c_i \{[x_i(0) - c_i\gamma_i^{-2}x(0)]\cos(\gamma_i t) + p_i(0)(m_i\gamma_i)^{-1}\sin(\gamma_i t)\}$ as the stochastic force, defined in terms of random initial positions and momenta. When $\kappa' \to \kappa$ and $\gamma_i \to \omega_i$ in $\Gamma(t)$ and $f(t)$, we return to the GLE first derived for a particle-bath model by Zwanzig (for details see [9]). By choosing the spectrum $\{\omega_i\}$ and coupling constants c_i for concrete systems, $\Gamma(t)$ can be given very different forms, similarly as in the models where it does not depend on κ [6,9,10]. For example, if the spectrum is continuous, $\sum_i \to \int d\omega$ and $m_i = \mu$, the often used memory function $\Gamma(t) = (\xi/\tau)\exp(-t/\tau)$ [10] is obtained by replacing c_i^2 with $g^2(\omega) = (2\xi\omega^2/\pi\mu\tau^2)(\omega^2 + \tau^{-2})^{-1}$. Now, with the same spectral function, $\Gamma(t) = \mu\int_0^\infty d\omega\, g^2(\omega)\gamma^{-2}(\omega)\cos[\gamma(\omega)t]$, where $\gamma(\omega) = (\omega^2 + \kappa/\mu)^{1/2}$. This integral is easily evaluated in terms of the LT $\widetilde{\Gamma}(t)$. The solution of the GLE (4) is given by Eq. (2) with $\kappa \to \kappa'$ in [...]. The correlation functions of interest are calculated as described in the second section, the simplest one being $\langle x^2\rangle = k_B T/\kappa'$.

Conclusion

In conclusion, we have derived the second FDT for the Brownian motion in a harmonic confinement potential. In experiments, this situation can be realized by optical traps [11]. As distinct from the Kubo's derivation, we have abandoned the assumption that the external force $-\kappa x$ does not affect the random force $f(t)$ and can be skipped from the GLE. The correlation function $\langle f(0)f(t)\rangle$ and the memory function $\Gamma(t)$ can thus, in principle, depend on the elastic constant κ. We have also, within a Caldeira-Legget model modified so that both the tagged particle and the bath oscillators respond to the external force, derived the GLE in which $\Gamma(t)$ explicitly depends on κ. These results could be important for a number of new studies and interpretation of experiments on different systems and processes whose description is related to the theory of the stochastic motion of trapped particles [4,5,11].

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