NON-EQUILIBRIUM FLUCTUATION-DISSIPATION THEOREM FOR STATIONARY ANOMALOUS DIFFUSION

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We derive a Fluctuation-Dissipation Theorem (FDT) from the generalized Langevin equation for both the equilibrium and far-from-equilibrium states. The equilibrium FDT is obtained under the assumption of energy balance and stationarity condition. We derive a non-equilibrium relation of the FDT, which can be applied in slow relaxation processes and non-ergodic systems whenever the second law of thermodynamics is brought to bear. We obtain also a relationship between stationary and non-ergodic behaviour based on the non-equilibrium FDT. Emphasis is placed on ballistic diffusion, which goes to local equilibrium.

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1. Introduction

The Fluctuation-Dissipation Theorem (FDT) plays a particularly important role by providing a general relationship between the correlation fluctuations and the kinetic coefficients (or susceptibilities), given by the response of a system to an external and internal perturbation [1–3]. Within a large class of proposal and problems in complex systems, FDT is of crucial importance for understanding anomalous relaxation phenomena [4].

Most diffusive systems are driven to an equilibrium state or steady state due to a relaxation process. However, a non-equilibrium state can arise from internal inhomogeneities resulting in the appearance of thermal perturbations. Since thermal fluctuations can preserve the initial condition through a slow relaxation process, the standard FDT does not hold [5–7]. Some examples can be found in some studies in anomalous diffusion [8–10] and aging process in spin-glass [11, 12].

More recently, it has been shown that Khinchin Theorem [13] as well as skewness and the non-Gaussian factor [6] for the probability distribution function for all ranges of normal and anomalous diffusion, despite of linear response description is possible. Costa *et al.* [9] have proved that FDT does not hold for ballistic diffusion. Although it evolves towards a state of maximum entropy, ballistic regime fails to achieve a global equilibrium, increasing the entropy less than the maximum feasible and a non-Gaussian behaviour occurs [6]. In other words, it reaches a local equilibrium in which the effective friction disappears. In the absence of dissipation of energy, the system goes to a local maximum entropy steady state, such that its temperature can be different from the thermal bath.

In this work, we will be focused on the ballistic diffusion, for which the dissipation (effective friction) is null and the system retains memory of the initial conditions even after long times. We derive an expression of the FDT for anomalous diffusion, which holds for both ergodic and non-ergodic systems. The outline of this paper is as follows. In Section 2, we present a general description of the Brownian dynamic concepts. In Section 3, we derive the FDT from energy balance conditions taking into account systems in the thermal equilibrium. In Section 4, we extend our approach to out-of-equilibrium systems. In Section 5, we derive a relationship between non-ergodic behaviour and stationary process based on the non-equilibrium FDT. In Section 6, we show numerical results and finally, in Section 7, we emphasize our main conclusions.

2. Brownian dynamics

Since the celebrated work of Einstein [14], diffusion processes have been understood as microscopic phenomena having their origin associated with the Brownian motion. The Brownian motion was further developed by Langevin [15] without making explicit reference to the interactions between the systems that are kept in contact. For some physical systems, it is quite complicated to perform a time scale separation from the classical form of the Langevin equation. In these cases, a more detailed description of certain aspects of particle dynamics is crucial, including also intermediate time scales. The resulting equation is known as the Generalized Langevin Equation (GLE) [16, 17], which is written here in terms of the momentum operator $p(t)$

$$\frac{dp}{dt} = -\int_0^t \mathit{\Gamma}\left(t-t'\right) p\left(t'\right) dt' + \eta(t)\,, \tag{1}$$

where $\mathit{\Gamma}(t)$ is the memory function, acting as a generalized friction. Obviously if $\mathit{\Gamma}(t) = 2\gamma\delta(t)$, the GLE reduces to the classical Langevin equation, representing the well-known Ohmic limit [18]. Here, $\eta(t)$ is a generalized stochastic process, with a Gaussian probability distribution, with independent and stationary increments, such that the statistical characteristics of its increments of some fixed order do not vary with time. The quantity $\langle \eta(t)\eta(t')\rangle$ depends only on the difference $t - t'$. Averaging here $\langle \ldots \rangle$ is over an ensemble, *i.e.*, an averaging over the probabilities of all possible values of the quantity $\eta(t)$ at times t and t'. In accordance with the ergodic hypothesis, this statistical average is equal to a time average, whereas the mechanical system goes to equilibrium. In this case, the noise $\eta(t)$ has a correlation given by the FDT of first kind [1, 2]

$$\left\langle \eta(t)\eta\left(t'\right)\right\rangle = \left\langle p^2\right\rangle_{\mathrm{eq}} \mathit{\Gamma}\left(t-t'\right)\,, \tag{2}$$

where $\left\langle p^2\right\rangle_{\mathrm{eq}} = mk_{\mathrm{B}}T$ is related to the equilibrium energy with the thermal bath at temperature T, with k_{B} being Boltzmann's constant. The above expression establishes the relationship between the dissipative term, removing energy from the system, and the stochastic noise, which supplies one. Furthermore, it is important to stand out that the noise is not a stochastic process in the usual sense, it is the generalized derivative of another process $w = \int \eta(t)dt$, which is a stochastic process in the usual sense as a Wiener process. Generally, $\eta(t)$ must be understood as a continuous linear mapping of the space of infinitely-differentiable functions into the space of random variables defined in some probability space [19].

We recognize a variety of diffusive systems which do not obey the classical Einstein diffusion theory; the so-called normal diffusion. This anomalous diffusion is characterized by a non-linear behaviour in the time stemmed from square position average $\left\langle x^2\right\rangle$, where $x = 1/m\int p(t')dt'$ is the position of the particles in the system, in contrast to the linear behaviour observed from the normal diffusion. We can write $\left\langle x^2\right\rangle \sim t^\alpha$, such that the system is regarded as subdiffusive for $0 < \alpha < 1$, normal for $\alpha = 1$, and superdiffusive for $1 < \alpha \leq 2$; the ballistic diffusion occurs for $\alpha = 2$. In these cases, one verifies that there is a general relationship between the memory function and the diffusion exponent in Laplace space [20, 21]

$$\lim_{z\to 0} \widetilde{\mathit{\Gamma}}(z) \propto z^{\alpha-1}\,, \tag{3}$$

where $\widetilde{\Gamma}(z)$ is the Laplace transform of the memory function $\Gamma(t)$. The above expression is also equivalent to the relationship of effective friction, $\gamma = \int_0^\infty \Gamma(t)dt$, which is null for all superdiffusive motions $1 < \alpha \leq 2$. Note that for superdiffusion $\alpha > 1$, the effective friction $\gamma = \lim_{z\to 0} \widetilde{\Gamma}(z)$ is null.

3. Equilibrium Fluctuation-Dissipation Theorem

If an isolated physical system is initially in a non-equilibrium state afterwards it should evolve towards equilibrium. On the other hand, if this system is initially in a thermal equilibrium, it is necessary to impose an appropriated condition on the stochastic noise $\eta(t)$ such that the system remains in equilibrium. In observing the macroscopic properties of this system over a sufficiently long time, all physical quantities should be practically constant with equal average values. Then, the total mean energy is a constant and it can be represented by the stationary condition from $\langle p^2 \rangle$, such that

$$\left\langle p^2(t)\right\rangle = \left\langle p^2(0)\right\rangle = \left\langle p^2\right\rangle_{\mathrm{eq}} . \tag{4}$$

This can be clear for most of diffusion regimes. However, for superdiffusive and ballistic diffusion, where the effective function $\tilde{\Gamma}(z) \to 0$ is null, it needs special attention [6, 9, 13]. This condition can be also formulated by requiring that

$$\frac{d\left\langle p^2(t)\right\rangle}{dt} = 0 \quad \text{with} \quad t \geq 0 . \tag{5}$$

By using Laplace transform, one can solve Eq. (1),

$$p(t) = p(0)R(t) + \int_0^t R\left(t - t'\right) dw\left(t'\right) , \tag{6}$$

where w, or more accurately $dw(t) = \eta(t)dt$, is a correlated stochastic process with stationary increments. In addition, R is the normalized correlation function [9], *i.e.*, $R(t) = \langle p(t)p(0)\rangle / \left\langle p^2(0)\right\rangle$, given by the Volterra equation

$$\frac{dR(t)}{dt} = -\int_0^t R\left(t'\right) \Gamma\left(t - t'\right) dt' . \tag{7}$$

We have obtained this expression by using the hypothesis that the noise is not correlated with the initial momentum, *i.e.*, $\langle p(0)dw(t)\rangle = 0$. From Eq. (6), one obtains

$$\left\langle p^2(t)\right\rangle = \left\langle p^2(0)\right\rangle R^2(t) + g(t) , \tag{8}$$

where

$$g(t) = \int_0^t \int_0^t R\left(t'\right) R\left(t''\right) \left\langle dw\left(t'\right) dw\left(t''\right)\right\rangle . \tag{9}$$

One obtains the latter expression using

$$\int_0^t R\left(t-t'\right) dw\left(t'\right) = \int_0^t R\left(t'\right) dw\left(t-t'\right) = \int_0^t R\left(t'\right) dw\left(t'\right) \tag{10}$$

with dw being stationary increments, enabling us to write $dw(t-t') = dw(t')$, where the equality covers for distribution of probability. Owing to this stationarity, we assume that the correlation of this process is a function only of the time differences, given by

$$\left\langle dw\left(t'\right) dw\left(t''\right)\right\rangle = \phi\left(t'-t''\right) dt'dt'' , \tag{11}$$

where $\phi(t)$ is an even function. Inserting the latter equation into Eq. (9) and using the time translation symmetry of $\phi(t)$, we obtain

$$g(t) = 2\int_0^t R\left(t'\right) \int_0^{t'} R\left(t''\right) \phi\left(t'-t''\right) dt''dt' . \tag{12}$$

Then, taking the derivative of Eq. (8), with $g(t)$ given by Eq. (12), and using the condition in Eq. (5), we obtain

$$\left\langle p^2\right\rangle_{\mathrm{eq}} R(t)\frac{dR(t)}{dt} + R(t)\int_0^t R\left(t'\right) \phi\left(t-t'\right) dt' = 0 . \tag{13}$$

From Eq. (7), we can replace the term $dR(t)/dt$ in the above expression by the integral term, which results

$$R(t)\int_0^t R\left(t'\right) \left[\phi\left(t-t'\right) - \left\langle p^2\right\rangle_{\mathrm{eq}} \mathit{\Gamma}\left(t-t'\right)\right] dt' = 0 . \tag{14}$$

Notice that the latter equation is well-defined for all t and $R(t)$. It implies that

$$\phi(t) = \left\langle p^2\right\rangle_{\mathrm{eq}} \mathit{\Gamma}(t) . \tag{15}$$

Using the function $\phi(t)$ obtained above, finally, we can write the end form of the FDT as

$$\left\langle dw\left(t'\right) dw\left(t''\right)\right\rangle = \left\langle p^2\right\rangle_{\mathrm{eq}} \mathit{\Gamma}\left(t'-t''\right) dt'dt'' . \tag{16}$$

This equation shows that the equilibrium FDT is based on equilibrium mean value operator $\left\langle p^2\right\rangle_{\mathrm{eq}}$. Indeed, the condition on the noise correlation is quite important for the balance of energy for the systems in thermal equilibrium.

4. Non-equilibrium Fluctuation-Dissipation Theorem

In order to derive a fluctuation-dissipation relation far from equilibrium, we will assume that the system evolves to a stationary state after a long enough time, longer than the relaxation one, on the assumption that

$$\lim_{t\to\infty} \left\langle p^2(t)\right\rangle = \left\langle p^2\right\rangle_{\mathrm{st}} , \tag{17}$$

where $\left\langle p^2\right\rangle_{\mathrm{st}}$ is the stationary value. For ergodic systems, since they have a Gaussian probability distribution function for $p(t)$ (PDF) [6], one has $\left\langle p^2\right\rangle_{\mathrm{st}} = \left\langle p^2\right\rangle_{\mathrm{eq}} = mk_{\mathrm{B}}T$. In the non-ergodic case, since the system is kept in an out-of-equilibrium state [22], we cannot state that $\left\langle p^2\right\rangle_{\mathrm{st}} = \left\langle p^2\right\rangle_{\mathrm{eq}}$. In addition, since the PDF in a non-ergodic system is not necessarily a Gaussian [6, 7], we cannot say that in this case $\left\langle p^2\right\rangle_{\mathrm{st}} = mk_{\mathrm{B}}T$.

Since the stochastic noise as well as the dissipative term of the GLE has the same physical origin (intermolecular collisions), as in the case of an isolated system in thermal equilibrium, a relationship between the stochastic noise and dissipative term can be represented by Eq. (2). From the hypothesis stationary increments, the noise correlation must be a function only of the time difference. Thus, we propose that

$$\left\langle dw\left(t'\right) dw\left(t''\right)\right\rangle = Q\mathit{\Gamma}\left(t'-t''\right) dt'dt'' . \tag{18}$$

Here, Q is a constant to be determined via the condition (17). Substituting Eqs. (9) and (18) into Eq. (8), we obtain

$$\left\langle p^2(t)\right\rangle = \left\langle p^2(0)\right\rangle R^2(t) + Q\left(1-R^2(t)\right) . \tag{19}$$

From the latter expression, we can analyse both the ergodic and non-ergodic cases [23]. Since the system is ergodic the irreversibility condition must be satisfied [13], *i.e.*, $\lim_{t\to\infty} R(t) = 0$, and one gets

$$\lim_{t\to\infty} \left\langle p^2(t)\right\rangle = Q = \left\langle p^2\right\rangle_{\mathrm{eq}} \Rightarrow Q = \left\langle p^2\right\rangle_{\mathrm{eq}} \tag{20}$$

recovering the equilibrium form of the FDT, Eq. (16). This ergodic condition means, in practice, that the experimental time is longer than relaxation one, in such a way that the effects of the initial state of the system vanish.

In non-ergodic systems, we will consider a local equilibrium where $\lim_{t\to\infty} R(t) = \kappa$, such that it must satisfy the second law of thermodynamics [6, 7] with $0 \leq \kappa^2 < 1$. Thus, we have

$$\lim_{t\to\infty} \left\langle p^2(t) \right\rangle = \left\langle p^2(0) \right\rangle \kappa^2 + Q \left(1 - \kappa^2\right) = \left\langle p^2 \right\rangle_{\rm st} \tag{21}$$

or equivalently

$$Q = \frac{\left\langle p^2 \right\rangle_{\rm st} - \left\langle p^2(0) \right\rangle \kappa^2}{1 - \kappa^2}\,, \tag{22}$$

where κ is given by [9]

$$\kappa = \lim_{t\to\infty} R(t) = \left[1 + \left.\frac{\partial \widetilde{\Gamma}(z)}{\partial z}\right|_{z=0} \right]^{-1}. \tag{23}$$

We can now generalize the equilibrium FDT for an out-of-equilibrium FDT, such that

$$\left\langle dw\left(t'\right) dw\left(t''\right) \right\rangle = \left[\frac{\left\langle p^2 \right\rangle_{\rm st} - \left\langle p^2(0) \right\rangle \kappa^2}{1 - \kappa^2} \right] \Gamma\left(t' - t''\right) dt' dt''\,. \tag{24}$$

The above expression is a remarkable result, which shows that the noise correlation depends intrinsically on the initial condition and the stationary state of the system. For all irreversible processes driven by GLE, the coefficient κ is null. In this sense, the relaxation dynamics lead the system from the initial stationary state to another as a consequence of the change of the external contributions or parameters. Since we are dealing with an irreversible process, the system goes to a stationary state, which can be different from the equilibrium state. This suggests that the particles can be trapped in a rough energy landscape, common to a great variety of complex systems such as glasses [5, 24] and proteins [25, 26], just to mention some examples. When $\left\langle p^2(0) \right\rangle = \left\langle p^2 \right\rangle_{\rm st}$, *i.e.*, the system is initially at a stationary state, it assumes a local equilibrium FDT for any value of κ setting up the equilibrium since $\left\langle p^2 \right\rangle_{\rm st} = \left\langle p^2 \right\rangle_{\rm eq}$.

5. Stationary condition

In order to deal with the stationary effect for the non-equilibrium FDT, we recall condition (5). Using Eq. (14) and taking the limit $t \to \infty$, we have that for ergodic systems ($\kappa = 0$) the condition (5) is fulfilled, independently of the function $\phi(t)$. For non-ergodic systems with κ^2 in the interval $[0, 1)$, and Q assuming a stationary state, from Eqs. (5), (7) and (19), we obtain

$$\lim_{t\to\infty} \frac{d\left\langle p^2(t)\right\rangle}{dt} = 2\kappa\left[Q - \left\langle p^2(0)\right\rangle\right] \lim_{z\to 0} z\widetilde{R}(z)\widetilde{\Gamma}(z)\,, \tag{25}$$

where we have used the final-value theorem of Laplace transform. Note that $\lim_{z\to 0} z\widetilde{R}(z) = \kappa$ and by using Eq. (3) for all kinds of diffusion, including ballistic regime ($\alpha = 2$), one obtains that Eq. (25) is null. In other words, all regimes described by GLE should be stationary. This is another remarkable result, since it establishes that these systems go to a stationary state only through the non-equilibrium FDT, Eq. (24).

In addition, Lapas *et al.* have demonstrated [6] that the evolution of all diffusive systems depends powerfully on the momentum correlation and the initial states. They also predict that a local stationary equilibrium distribution will be established in the ballistic system as long as the noise distribution assumes a stationary state due to its Gaussian nature.

6. Numerical results

In order to clarify our main results, we developed a numerical simulation of Eq. (1) with a memory given by

$$\Gamma(t) = \int_0^\infty \rho\left(k\right)\cos\left(kt\right)dk\,, \tag{26}$$

where

$$\rho\left(k\right) = \begin{cases} \gamma & k_1 \le k \le k_s \\ 0 & \text{otherwise} \end{cases} \tag{27}$$

with $k_1 \geq 0$. This memory is expected to result in ballistic behaviour if $k_1 \neq 0$ [9]. In Fig. 1, we show $\left\langle p^2\left(t\right)\right\rangle$ as a function of time t for the ballistic memory defined above, fitting the results for the non-equilibrium FDT, Eq. (24). In the inset, we show the results with the original FDT, Eq. (2).

Note that the main inconsistency with the original FDT [9], *i.e.*, $\lim_{t\to\infty}\left\langle p^2(t)\right\rangle \neq \left\langle p^2\right\rangle_{\rm st}$, has been removed.

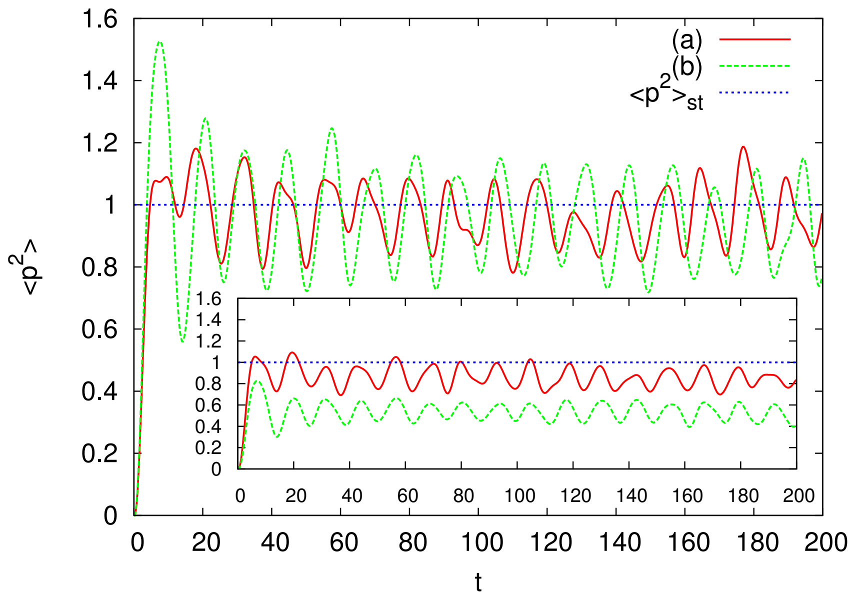

Fig. 1. $\langle p^2(t) \rangle$ as a function of time t for the memory given in Eq. (27), with $\gamma = 0.25$ and $k_s = 0.5$. In (a) (solid/red line) $k_1 = 0.1$, while in (b) (dashed/green line) $k_1 = 0.25$. We have shown the results of the non-equilibrium FDT, Eq. (24). In the inset, we have shown the results with the traditional FDT, Eq. (2). In all those cases, we have chosen $\langle p^2 \rangle_{\rm st} = 1$ (dotted/black line) and $\langle p^2(0) \rangle = 0$.

7. Conclusions

In this article, we have obtained both the equilibrium and the non-equilibrium FDT from generalized Langevin equation in the absence of external field. We have further analysed the relationship between ergodicity and the energy balance to deal with all stationary diffusive regime. The only requirements are: the noise with stationary increments (which implies $\phi(t,t') = \phi(t-t')$) and the momentum with stationary distribution. This result may have deep consequences in many areas [27–30]. For an ergodic system ($\kappa = 0$), we conclude that the equilibrium FDT is always obeyed and the system reaches thermal equilibrium with the bath. In slow relaxation processes, however, the system can be lead up to an activated regime, having only a permanent local equilibrium [22], such that the response of the thermal bath to the diffusive system vanishes. For these systems, when the second law of thermodynamics holds, we have proposed a non-equilibrium FDT taking into account the local equilibrium effects by using the linear response theory.

We verify that the non-ergodic system (*e.g.*, ballistic diffusion) depends strongly on its initial condition and the bath's stationarity. Despite the ballistic diffusion being a reversible process, it reaches a maximum local of entropy, moving from a state of equilibrium to another, achieving the local equilibrium with a temperature different from the bath's temperature [6]. For non-stationary systems, the linear response theory cannot predict about FDT as well as temperature relation. The presence of non-stationarity leads to a hierarchy of relaxation times responsible for the ageing phenomena, where one can obtain an effective temperature [31].

In order to make further progress, one must relax the condition of a noise with stationary increments. This introduces, however, many other complications like, *e.g.*, ageing regime [5]. As well non-equilibrium situation such as those appearing in growth dynamics [32–34] deserves quite a lot of attention.

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