Nonergodic Brownian Dynamics and the Fluctuation-Dissipation Theorem

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The phenomenon of Brownian motion has assumed a fundamental and influential role in the development of thermodynamical and statistical theories and continues to do so as an inspiring source for active research in various fields of natural sciences [1]. The Brownian dynamics can conveniently be described by a generalized Langevin equation (GLE), reading: $m\ddot{v}(t) + m\int_0^t \gamma(t, t')v(t')dt' + \partial_x U(x, t) = \xi(t)$. The thermal random force $\xi(t)$ is assumed to be uncorrelated with the initial velocity. The memory friction $\gamma(t, t')$ is typically related to the correlation of the random forces [2, 3]. Kubo [2] has addressed the common behavior of a classical equilibrium bath by setting (i) $\langle \xi(t)\xi(t') \rangle = mk_BT\gamma(t, t')$ with (ii) $\gamma(t, t') = \gamma(|t - t'|)$ being time-homogeneous. The one-sided Fourier transform consequently then obeys $Re[\gamma(\omega)] \geq 0$, for real-valued $\omega$. Here $k_B$ is the Boltzmann constant and $T$ denotes the bath temperature. The validity of the GLE is thus restricted to the case of a stationary thermal noise obeying the above two conditions; e.g. see in Refs. [2, 3, 4]. The complex-valued mobility $\mu(\omega)$ and the memory-friction $\gamma(\omega)$, respectively, are given in terms of the Fourier-Laplace transforms of the time-homogeneous correlations of the particle velocity $v(t)$ and the environmental noise $\xi(t)$, respectively, as

$$\mu(\omega) = \frac{1}{k_BT} \int_0^\infty dt \exp(-i\omega t) \langle v(t_0)v(t_0 + t) \rangle,$$  \hspace{1cm} (1)

$$m\gamma(\omega) = \frac{1}{k_BT} \int_0^\infty dt \exp(-i\omega t) \langle \xi(t_0)\xi(t_0 + t) \rangle.$$  \hspace{1cm} (2)

To differentiate between these two relations (1) and (2), one refers to the first relation as the FDT of the first kind and the second one as the FDT of the second kind, respectively [2, 3]. The former characterizes the relaxation of the average particle velocity, while the latter yields the generalized susceptibility, describing the response of the bath degrees of freedom.

These two FDT relations play a central role in the theory of thermal Brownian motion; its validation and generalization presents a timely subject that is presently hotly debated, both within theory and experiment.

With this work we aim at demonstrating that Kubo’s conditions for the equilibrium bath are generally not complete within the framework of linear response theory. This is so, because the existence of anomalous diffusion has not been considered in the original treatment by Kubo and others. We thus not only seek to complete set of conditions for general Brownian motion to obey an ergodic behavior but, more importantly, we like to dwell on rich behavior that emerges if ergodicity does not hold. Throughout the following we use the nomenclature of ergodicity in the context of the theory of stochastic processes, i.e. for open systems that are subjected to noise: Then the process is ergodic if the temporal long-time average of a state function equals its stationary ensemble average [5]. Thus, we work beyond the well-known case of isolated systems obeying an area preserving, Hamiltonian dynamics [6, 7]. Put differently, our main objective is to extend the theory of classical Brownian motion by focussing on the intricacies of a possible non-ergodic, non-Markovian dynamics [8, 9, 10, 11, 12]. In particular, the asymptotic long-time statistical probability density will be termed ergodic if it approaches a stationary state that is independent of the choice of the initial preparation.

Noisy dynamics exhibiting nonergodic behavior. As we shall show below, systems possessing via the FDT of the second kind no finite friction at zero frequency typically exhibit an non-ergodic behavior. Thus, there is an abundance of open system dynamics for which ergodicity is not granted. The thermal fluctuations result typically from a coupling to environmental degrees of freedom. In the cases of bi-linear system-bath coupling these are characterized by a corresponding spectral density of bath modes, $J(\omega)$, obeying $Re[\gamma(\omega)] = J(\omega)/m\omega$ [13, 14, 15, 16]. Thus, if the coupling to low frequency modes is weak, as it is the case with optical-like phonons [6, 12], or broadband colored noise [17], or also for the...
celebrated case with a blackbody radiation field of the Rayleigh-Jeans type, the static friction vanishes at zero frequency \( \omega = 0 \). Then, no efficient mechanism necessary for the compliance of the ergodic behavior is at work. Other situations that come to mind involve the vortex diffusion in magnetic fields, or diverse other open dynamics with an inherent velocity-dependent system-bath coupling. Note also that a typical solid state Drude bath spectrum is proportional to \( \omega^2 \), thus yielding as well a vanishing, zero-frequency friction.

Conditions for the validity of the FDT. The GLE was originally derived by Mori by use of the Gram-Schmidt procedure; it was re-obtained by Lee using the recurrence relations method. Starting out from the well-known system-plus-oscillator-reservoir model detailed in Ref. 23, the equations of motions directly yield the GLE with a stationary, correlated thermal noise \( \epsilon(t) \). The initial coordinate and velocity of each oscillator are assumed to be distributed according to thermal equilibrium. We now add two additional mixing conditions to the above given, well-known relations (i) and (ii). These read: (iii) \( \lim_{s \to 0} [s \gamma(s)] = \infty \) and (iv) \( \lim_{s \to 0} [s^2 \gamma(s)] = 0 \), where \( \gamma(s) \) is the Laplace transform of the memory friction kernel that enters the GLE. Our terminology will be as follows: If one of the above given four conditions (i)-(iv) is not satisfied we term the bath – in the specified order (i) – (iv): (i) a nonequilibrium bath, (ii) a relaxing (or ageing) one, (iii) a ballistic one, or (iv) a nonergodic-bath, respectively. The notion embracing the latter two cases (iii-iv) will also be referred to as weak nonequilibrium heat baths.

For the force-free GLE, i.e. with \( U(x) = 0 \), the two-time velocity correlation function (VCF) reads,

\[
C_{vv}(t_1, t_2) = \{v^2(0)\} b^2 + \frac{k_BT}{m} \left[ \frac{S(\tau)}{k_BT/m} + b - b^2 \right] + \left( \{v^2(0)\} - \frac{k_BT}{m} \right) A(t_1, t_2),
\]

where \( \tau = |t_1 - t_2| \) and the explicit forms of the two relaxation functions \( A \) and \( S \) are detailed in Ref. 24. Note that depending on the choice of initial preparation this correlation generally is not time-homogeneous. Herein, we indicate by \( \{ \cdots \} \) the average with respect to the initial preparation of the state variables. The relevant, generally non-vanishing quantity \( b \) is given by:

\[
b = [1 + \lim_{s \to 0} (\gamma(s)/s)]^{-1}.
\]

The non-equilibrium, time-inhomogeneous relaxation part \( A(t_1, t_2) \) obeys \( A(t_1 \to \infty, t_2 \to \infty) = 0 \). The asymptotic equal-time dynamics is found to read 24:

\[
\{v^2(0)\}_{st} = \{v^2(0)\} b^2 + k_BT m^{-1}(1 - b^2).
\]

Moreover, the asymptotic velocity correlation function emerges as \( C_{vv, st} = b k_BT/m \) for the case that we set the initial velocity variance in accordance with the thermal equilibrium value \( \{v^2(0)\} = k_BT/m \). These results follow for \( b \neq 0 \), thus implying that the condition (iii) is not satisfied (case with a ballistic bath). This in turn requires that \( \gamma(0) = \int_0^\infty \gamma(t) dt = 0 \), meaning a vanishing effective friction at zero frequency, or equivalently a vanishing of the spectral density of the noise \( \epsilon(t) \) at \( \omega = 0 \), see in (2) 8 17. This causes a breakdown of the FDT of the first kind because of the preparation-dependent, i.e. \( v(0) \)-dependent asymptotic result. This is so although the FDT of the second kind in (2) is valid.

Next, we discuss the situation with a nonergodic bath with \( \lim_{s \to 0} [s \gamma(s)] \neq 0 \). Towards this goal, we consider the solution \( v(t) \) of the GLE for a case where \( b \neq 0 \) constitutes a stationary noise source that drives the force-free Brownian GLE-dynamics. Put differently, we set for the acting thermal (tailed) noise source

\[
\varepsilon_1(t) \equiv c v(t) = c \left[ \{v(0)\} R(t) + \frac{1}{m} \int_0^t R(t - t') \epsilon(t') dt' \right],
\]

where the parameter \( c \) denotes a coupling strength. The response function is \( R(t) = b + \sum_j \text{res}[R(s_j)] \exp(s_j t) \), with its Laplace transform reading \( R(s) = (s + \gamma(s))^{-1} \). The set \( \{s_j\} \) denote the nonzero roots of the equation \( s + \gamma(s) = 0 \), and the probability density for \( v(0) \) is chosen as a Gaussian with zero-mean and variance \( \{v^2(0)\} = k_BT/m \). In this case, the resulting memory-friction kernel corresponding to the effective thermal noise \( \varepsilon_1(t) \) is given by \( \gamma_1(t) = c^2 \{(v(t)v(0))\}/(k_BT) \), yielding \( \gamma_1(t) \to \infty \), but \( \lim_{s \to 0} [s \gamma_1(s)] = c^2 b \to \infty \). This finding implies that the Brownian particle with \( b \neq 0 \) is immersed in a nonergodic bath.

Substituting (5) into the GLE, we obtain an additional quadratic potential with the frequency \( c^2 b \) and a friction kernel given by \( \gamma_1(t) = \gamma(t) - c^2 b \). This leads to \( \gamma_1(0) \to \infty \) so that \( \mu(0) = 0 \). Therefore, the diffusion constant vanishes, meaning that the motion of a force-free particle remains bounded. This phenomenon of localization at finite temperature may occur for a particle dynamics that is coupled to a set of frozen environmental oscillators corresponding to the sub-Ohmic bath density \( J(\omega) \), being proportional to \( \omega^\delta \) in the limit of \( \delta = 0 \) 14. A realization provides a harmonic chain on a Bethe lattice possessing no diffusion thus acting as a frozen bath in this context 20.

The case with an inherent ballistic bath. We will concentrate on nonergodic Brownian motion where the Kubo FDT of the second kind is assumed to be satisfied, the condition (iii), however, is not met. A colored noise that induces ballistic diffusion is harmonic velocity noise (HVN) \( \epsilon(t) \). The HVN obeys the Langevin equations: \( \dot{y} = \varepsilon, \dot{\varepsilon} = -\Gamma \varepsilon - \Omega^2 y + \xi(t) \), where \( \xi(t) \) is Gaussian white noise of vanishing mean with \( \langle \xi(t)\xi(t') \rangle = 2mT^2 k_BT \delta(t - t') \), \( \eta \) is the damping coefficient, \( \Gamma \) and \( \Omega \) denote the damping and frequency parameters. The second moments of \( y(0) \) and \( \varepsilon(0) \) obey \( \langle y^2(0) \rangle = \eta T \gamma^{-2} k_BT \) and \( \langle \varepsilon^2(0) \rangle = \eta \Gamma k_BT \). The Laplace and Fourier transformations of the damping kernel function read \( \gamma(s) = \eta \Gamma s/(s^2 + \Gamma s + \Omega^2) \) and
Re[\gamma(\omega)] = \eta\Gamma^2\omega^2/[(\Omega^2 - \omega^2)^2 + \Gamma^2\omega^2], respectively. The latter corresponds to the spectrum of HVN which now vanishes at zero-frequency. In presence of the FDT of the second kind with the conditions (i) and (ii) satisfied, the complex-valued mobility now emerges as

$$\tilde{\mu}(\omega) = \frac{b}{m} \tilde{\delta}(\omega) + \frac{\eta\Gamma}{m(\Omega^2 + \eta\Gamma)} \frac{\Gamma(\Omega^2 + \eta\Gamma) + i\omega(\Omega^2 + \eta\Gamma - \Gamma^2 - \omega^2)}{(\Omega^2 + \eta\Gamma - \omega^2)^2 + \Gamma^2\omega^2},$$

where $b = (1 + \eta\Gamma)^{-1}$ and $\tilde{\delta}(\omega) = \lim_{t \to -\infty} (1 - \exp(-i\omega t))/(i\omega)$. Therefore, $\tilde{\mu}(0) \to \infty$, yielding a diverging diffusion constant $D = \tilde{\mu}(0)k_BT \to \infty$.

This free non-Markovian Brownian motion can also be recast as an embedded, higher-dimensional Markovian process. The Fokker-Planck equation (FPE) for the probability density $P(x, v, w, u, y, z, t)$ corresponding to the set of Markovian LEs via introducing the appropriate set of auxiliary-variables $(w, u, y, z)$ obeys $\partial_t P - L_{FP}P = 0$, where $L_{FP}$ denotes the associated FPE operator:

$$L_{FP} = -v \frac{\partial}{\partial x} - m^{-1} w \frac{\partial}{\partial v} + (\Gamma w + \eta \Gamma v + \Omega^2 y + w) \frac{\partial}{\partial w} - \Omega^2 (w - \varepsilon) \frac{\partial}{\partial w} + (\Gamma\varepsilon + \Omega^2 y) \frac{\partial}{\partial y} + \eta \Gamma^2 k_BT \frac{\partial^2}{\partial w^2} + \eta \Gamma^2 k_BT \frac{\partial^2}{\partial z^2}. \tag{7}$$

The mean total energy of the thermal HVN-driven force-free particle reads $\{E(t)\} = \frac{1}{t} m \{\langle v^2(t) \rangle\} = \frac{1}{m} \{\langle \langle v(t) \rangle^2 \rangle + \{\{\langle v(t) \rangle - \langle v(t) \rangle^2 \} \} \}$. Their stationary values are given by first two terms in the r.h.s of Eq. (3). In particular, the first part describes the remnant initial kinetic energy of the particle, which is dissipated partly by the present bath because of $\{\langle v(t \to \infty) \rangle = bv(0)$. This part vanishes for the common case with $b = 0$. The second part denotes the energy provided from the heat bath and is independent of the initial particle velocity; it does not relax, however, towards equilibrium. The absorbed power of the particle is $P_{abs} = \eta k_BT[1 + \eta/(2\Gamma) + 2\Omega^2/(\eta\Gamma)]^{-1}$, being smaller than the equilibrium value $\eta k_BT$. This implies that the Brownian particle is hindered in re-gaining the energy from a thermal noise that lacks a finite, zero-frequency spectral weight. Our numerical results are depicted in the figure 1, which are obtained from simulating a set of Markovian LEs equivalent to the FPE of (7). The numerics fully corroborate our theoretical findings.

**Non-steady transport in ratchet potential.** A most intriguing situation refers to Brownian motors when driven by non-ergodic Brownian motion. Take the case of thermal HVN driving a Brownian particle in a rocking ratchet potential: $U(x, t) = U_0 [\sin(2\pi x) + c_1 \sin(4\pi x) + c_2 \sin(6\pi x)] + A(t)x$ with $U_0 = 0.461, c_1 = 0.245, \text{ and } c_2 = 0.042$. Here $A(t)$ is a square-wave periodic driving force that switches forth and back between $A(t) = A_0$ when $2nt_p \leq t < (2n + 1)t_p$ and $A(t) = -A_0$ when $(2n + 1)t_p \leq t < 2(n + 1)t_p$. We next study whether a stationary non-equilibrium current results that can be put to a constructive use in order to direct, separate or shuttle particles efficiently. We thus research the resulting, time- and ensemble-averaged current with the condition (iii) not obeyed.

**Figure 2** depicts the time-dependent, accelerated mean velocity $\{\langle v(t) \rangle \} = (2\eta^2)^{-1} \int_0^{t+1} \int_0^{2\pi} dt' \{\langle v'(t') \rangle \}$ for various strengths of the driving force as obtained via the simulation of the Markovian LEs corresponding to the FPE of (7), being supplemented by the ratchet forcing $-U'(x, t)$. A startling finding is that the averaged velocity increases linearly with time. This directed acceleration is presented by the slope (see dashed lines in Fig. 2) of the average velocity. For a weak rocking (small $A_0$) the phenomenon of directed motion involves the surmounting of barriers. In contrast, for strong rocking the averaged displacement is related to the mean square displacement through the modified Einstein relation, i.e.,

$$\kappa_2/\mu_2(0) = k_BT_{eff}. \tag{8}$$

The ballistic diffusion coefficient is $k_BT_{eff} = b^2(\Gamma^2)^{-1}$, the linear mobility $\mu_2(0) = 0$ follows from the nonlinear mobility $\mu_2(A_0) = \mu_{\text{eff}} \langle x(t) \rangle / \langle A(t)^2 \rangle$, and the effective temperature is $T_{eff} := T + b^2(\mu(\langle v^2(0) \rangle)/k_BT)$. The dissipative acceleration of a particle of mass $m$ subjected to a constant
force $F$ yields $a = F b / m$, with $0 < b < 1$. This finding is therefore intermediate between a purely Newton dynamics (with $b = 1$) and an ordinary Langevin dynamics (with $b = 0$). Note also that the acceleration assumes a non-monotonic function vs. temperature.

Resume. We have studied the nonergodic Brownian motion occurring in so termed weak nonequilibrium baths, where the fluctuation-dissipation theorem of the second kind still holds. The nonequilibrium results are directly related to the ergodicity breaking theorem of the first kind. The nonergodic behavior is either due to a vanishing or a divergent zero-frequency spectral density of the thermal noise. Our theory produces two limits of abnormal diffusions, namely ballistic diffusion and a localized behavior. For ballistic diffusion the effective friction vanishes at zero frequency while it assumes infinity for localization. In order to assure the ergodic behavior of an equilibrium bath the usual conditions (i) and (ii) must be completed by two additional conditions: (iii) $\lim_{s \to 0} [s^{-1} \hat{\gamma}(s)] \to \infty$ and (iv) $\lim_{s \to 0} [s \hat{\gamma}(s)] = 0$, where $\hat{\gamma}(s)$ is the Laplace transform of the memory friction kernel. Yet another riveting result is that the corresponding Brownian dynamics for a rocking Brownian motor exhibits a distinct, accelerated, nonstationary velocity, rather than the constant drift which typifies the situation with normal, Ohmic dissipation.

We are also confident that our present results will crucially impact other quantities of thermodynamic and quantum origin. Thus, this field is open for future studies that in turn may reveal further surprising findings.

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