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The Entropy of a Brownian Particle in a Thermal Bath Interacting Both with a Parabolic Potential

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Abstract: In a recent article, the author derived a new generalized Langevin equation (NGLE) and its associated Fokker-Planck equation (FPE) of a Brownian particle in a parabolic potential where the thermal bath, consisting of N harmonic oscillators, interacts bilinearly with the external field. The time needed for the system to reach a steady state is longer than that for the classical version (CGLE). We found a completely different scenario for the entropy than when the interaction of the field with the heat bath is off. The new findings for the entropy and its rate physically improve the thermodynamics description of the system.

Keywords: Stochastic processes; Brownian motion; Fokker-Planck equation

1. Introduction

There have been numerous applications of the CGLE to describe simple and complex systems. Most of the descriptions are based on Zwanzig's model where the interaction of the external field affects only the particle dynamics. Thus, the fluctuation-dissipation theorem (FDT) is linear with the static friction coefficient of the bath fluid [1]. Nieuwenhuizen and Allahverdyan [2] worked out the CGLE in the configuration space including an extra term due to the interactions among the bath particles and the Zwanzig's overdamped limit by Jiménez and Velazco [3]. Paredes, Medina, and Colmenares [4] applied the CGLE in the whole phase space. However, afterward, Daldrop, Kowalik, and Netz [5] applied molecular dynamic simulations to a particle in a thermal bath interacting with a parabolic potential, finding the memory kernel and friction depending on the field frequency. In a previous author's work [6] the description was modeled by deriving an NGLE to include a specific field interaction with the bath. The FDT is Kubo's type with the above frequency dependency. Acceptable results were obtained for the kernel and the friction function.

The present work aims to extend the description of the NGLE to the realm of thermodynamics. In this respect, the objective is to determine the entropy and its rate and compare them with the results obtained from the CGLE.

We begin with a *resumé* of the general equations already derived followed by an analysis of the results. The article ends with a general conclusion.

2. Basic equations

The system is a particle of mass M immersed in a bath of N harmonic oscillators held at temperature T where both subsystems interact with a parabolic potential $V(q) = M\omega^2 q^2/2$. The NGLE was derived in [6] and given by:

$$\dot{v}(t) \quad = \quad -\Omega\, q_0 - \int_0^t dy\, v(y)\, \Theta_\Omega(|\,t-y\,|) + R_\omega(t), \tag{1}$$

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where the dot over a variable denotes its time derivative. Its solution reads,

$$v(t) = v_0\chi(t) - \Omega\, q_0 \int_0^t dy\, \chi(y) + \varphi_v(t), \tag{2}$$

$$\chi(t) = \mathcal{L}^{-1}\left\{\frac{1}{k+\widehat{\Theta}_\Omega(k)}\right\}, \tag{3}$$

$$\varphi_v(t) = \int_0^t dy\, \chi(t-y)\, R_\omega(y), \tag{4}$$

$$\Omega = \omega^2\left\{1 - \frac{\gamma_0}{2\,\omega\,(\kappa\,\tau^2\,\omega^2-1)}\left[3\sqrt{\kappa} - 2\,\kappa\,\tau\,\omega\left(1+\frac{2}{\pi}\arctan(\sqrt{\kappa}\,\tau\,\omega)\right)\right]\right\}, \tag{5}$$

where $\chi(t)$ is the susceptibility of the system, parameter τ is the Drude's spectral density cutoff frequency of the bath harmonic oscillators, κ is the mass ratio of the tag particle to a single bath one, γ_0 is the static friction coefficient, and $\{q_0, \Omega\}$ are the initial position and the effective frequency felt by the particle, respectively. Function $\Theta_\Omega(|t-s|) = \Gamma_\omega(|t-s|) + \Omega$ where the memory kernel $\Gamma_\omega(t)$ is a composite function involving cosine and sine integral functions of the complex field frequency H. It reads,

$$\Gamma_\omega(t) = \frac{\gamma_0}{\tau}\left\{e^{-t/\tau} - \frac{1}{\pi}\sinh\left(\frac{t}{\tau}\right)\left[\mathrm{Si}\left(H_-\frac{t}{\tau}\right) + \mathrm{Si}\left(H_+\frac{t}{\tau}\right)\right] + \frac{i}{\pi}\cosh\left(\frac{t}{\tau}\right)\left[\mathrm{Ci}\left(-i\,\frac{t}{\tau}\right) - \mathrm{Ci}\left(i\,\frac{t}{\tau}\right) - \mathrm{Ci}\left(H_-\frac{t}{\tau}\right) + \mathrm{Ci}\left(H_+\frac{t}{\tau}\right)\right]\right\}, \tag{6}$$

$$H_\pm = \kappa\,\tau\,\omega \pm i. \tag{7}$$

The noise $R_\omega(t)$ is Gaussian and colored with zero mean and a correlation obeying an FDT of Kubo's type $\langle R_\omega(t-s)R_\omega(0)\rangle = T\,\Gamma_\omega(|t-s|)$. The friction function $\gamma(\omega)$ is the integral of $\Gamma_\omega(t)$ over the frequency ω. It is a function too large to display containing Si, Ci, Ei, and the natural log functions of different complex terms of the field frequency. From now on, Boltzmann constant and M are set to 1.

We use the associated reduced position FPE for the probability density function associated with Eq. (2) instead of the bi-variate general one involving velocity and position. It was already obtained in [7] in a different context, reading,

$$\frac{\partial P(q,t)}{\partial t} = -\frac{\partial J(q,t)}{\partial q}, \tag{8}$$

$$J(q,t) = \left[\Phi(t)\,q - \frac{1}{2}D(t)\frac{\partial}{\partial q}\right]P(q,t), \tag{9}$$

$$\Phi(t) = \frac{d\ln\langle q(t)\rangle}{dt}, \tag{10}$$

$$D(t) = \dot{\sigma}^2(t) - 2\,\sigma^2(t)\,\Phi(t), \tag{11}$$

with a solution given by the Gaussian

$$P(q,t|q_0) = \frac{1}{\sqrt{2\,\pi\,\sigma^2(t)}}\exp\left[-\frac{(q-\langle q(t)\rangle)^2}{2\,\sigma^2(t)}\right], \tag{12}$$

$$\langle q(t)\rangle = q_0\left(1 - \Omega\int_0^t dy\, y\,\chi(t-y)\right), \tag{13}$$

$$\sigma^2(t) = 2\int_0^t dy\int_0^y dz\,\langle\varphi_v(y)\,\varphi_v(z)\rangle + T\left(\int_0^t dy\,\chi(y)\right)^2. \tag{14}$$

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The steady-state $P^{ss}(q,t)$ is obtained from Eq. (8). It renders the Gaussian

$$P^{ss}(q,t) = \frac{1}{\sqrt{\pi\,\zeta(t)^{-1}}} e^{-\zeta(t)\,q^2} \left(1 - \mathrm{Erf}\left[i\,\zeta(t)\,q\right]\right), \tag{15}$$

where $\zeta(t) = |\Phi(t)/D(t)|$.

According to [8–10], the mean heat $\langle Q \rangle$ evolves with time as

$$\frac{d\,\langle Q(t)\rangle}{dt} = \int_0^t dq\, J(q,y)\, \frac{dE}{dq}, \tag{16}$$

where $E = (p^2 + \omega^2\, q^2)/2$. After making the substitutions, we find

$$\frac{d\,\langle Q(t)\rangle}{dt} = \omega^2 \left[\Phi(t) \left(\sigma^2(t) + \langle q(t)\rangle^2\right) + \frac{1}{2} D(t)\right], \tag{17}$$

The irreversible Gibbs entropy of the Brownian particle, equivalent to Shannon's, and the entropy rate $\dot{S}(t)$ are

$$S(t) = -\int_{-\infty}^{\infty} dq\, P(q,t)\, \ln P(q,t), \tag{18}$$

$$\dot{S}(t) = -\int_{-\infty}^{\infty} dq\, \dot{P}(q,t)\, \ln P(q,t). \tag{19}$$

In a system at equilibrium, the response function is the correlation of the fluctuations subjected to disturbances of the external field. For stationary systems, the detailed balance relation is broken if it is out of equilibrium. Therefore, there is a continuous degradation of energy to the thermal reservoir. This behavior occurs along the trajectory, where the correlation of the fluctuations reduces to the conventional FDT if the velocity fluctuations are written in terms of the local mean velocity [11].

In the detailed balance restoration, Van den Broeck and Esposito [12] integrate by part $\dot{S}(t)$ giving two contributions compiling a non-adiabatic part $\dot{S}_{na}(t)$ due to the presence of driving, the external field, and an adiabatic one because of a non-equilibrium constrain, the temperature in our case. They, however, introduce the so-called excess $-\dot{S}_{ex}(t)$ representing the dissipation due to the presence of the reservoir. The latter is the systematic entropy generated by the bath degrees of freedom [13]. They propose then an equivalent entropy balance equation for the total entropy production as,

$$\dot{S}_{tot}(t) = \dot{S}_{na}(t) - \dot{S}_{ex}(t), \tag{20}$$

$$\dot{S}_{na}(t) = -\int_{-\infty}^{\infty} dq\, P(q,t)\, \ln\left[\frac{P(q,t)}{P^{ss}(q,t)}\right], \tag{21}$$

$$\dot{S}_{ex}(t) = \int_{-\infty}^{\infty} dq\, J(q,t)\, \partial_q P^{ss}(q,t). \tag{22}$$

Similar equations hold for the Zwanzig's CGLE [14–16] replacing Ω by ω^2 and the memory kernel substituted by the well-known exponential decay $\Gamma(t) = \alpha\gamma_0\, e^{-\alpha t}$ obeying the original Kubo's FDT $\langle R(t-s)R(0)\rangle = T\,\Gamma(|t-s|)$ [1].

We will compare the results obtained by the two versions of the generalized Langevin equation NGLE and CGLE.

3. Discussion of numerical results

Because the external potential is time-independent, no work is produced. The interchange of heat between the particles and the bath is needed for the whole system to be kept isothermal and steady.

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All calculations [17] were made for the parameter set of Ref. [6], namely, $\{\gamma_0, \kappa, q_0\} = \{1, 2, 0.1\}$. We choose $\omega = 0.0045$ representing the approximated midpoint between the branches of $\gamma(\omega)$ displayed in Figure 3 of [6]. Black curves identify the set $\{T, \tau\} = \{1, 12\}$ while the red ones are for $T = 10$ and an arbitrary $\tau = 20$. Blue curves designate the NGLE at a frequency as low as $\omega = 0.0001$ and $\{T, \tau\} = \{1, 12\}$. The procedure to compare NGLE with the CGLE must suit the memory kernel, Equation (6), to the new initial conditions of the system. Noticing from Figure 3 of [6] that at very low ω the frequency-dependent friction is equal to its static value γ_0, we evaluate $\Gamma_\omega(t)$ at such a frequency which can be fitted as $\alpha\, \gamma_0 \exp(-\alpha\, t)$. It gives $\alpha = 0.083$ which together with the substitution $\Omega = \omega^2$ and $\{\gamma_0, T\} = \{1, 1\}$ defines fully the CGLE. They are displayed as dashed blue plots.

The numerical calculations then require first the determination of the memory kernel given by Eq. (6). Before the calculation, it is smoothed to suppress the spurious data at log times [6] to find next the susceptibility $\chi(t)$ through the inversion of Equation (3). Using a method designed by Fox for the CGLE [18], the noise correlation $\langle \varphi_v(t)\, \varphi_v(s)\rangle$ becomes analytical which for our problem renders

$$\begin{aligned}\langle \varphi_v(t)\varphi_v(s)\rangle &= T\Big[\chi(|t-s|) - \chi(t)\,\chi(s) \\ &- \Omega \int_0^t ds_1\, \chi(s_1) \int_0^s ds_2\, \chi(s_2)\Big], \end{aligned} \tag{23}$$

Once these quantities are calculated then the standard deviation $\sigma^2(t)$ and $\langle q(t)\rangle$ follow and all functions are fully specified.

The effect of the external field is to heat up the tagged and reservoir particles in different proportions, so on average, some heat is absorbed by the tagged particles to keep a steady temperature. Figure 1 displays this effect as the mean heat. The dissipation of the average heat in the system increases to keep it isothermal; it is smaller for $T = 1$ (black curve). Curves for NGLE at low ω ($\{T, \tau\} = \{1, 12\}$, blue) and the CGLE (dashed blue) have significantly low magnitude and are almost identical, which is not a surprise because both descriptions are for the same static friction coefficient. Oscillations increase with the temperature.

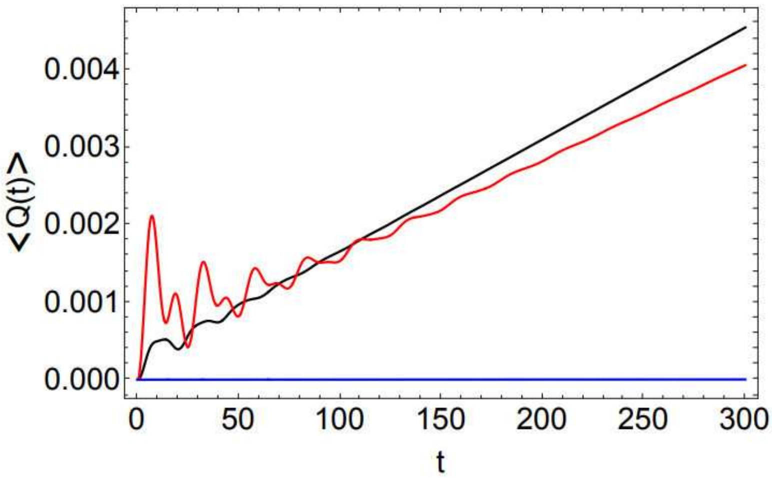

Figure 1. Mean heat. See text for details.

Figure 2 shows the entropy of the whole system, where a smoothed behavior for $t \geq 50$ appears, which is also an indication of reaching a steady state. It is positive because the system is isolated. The omission of the physical field-bath interaction (blue) overestimates the total entropy by a little compared to NGLE (black). The difference is irrelevant but will become significant in discussing the entropy production. All curves display a small oscillation at the beginning. Previous works have found that when the interaction field-bath is off, and a classical underdamped Markovian Langevin

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describes the dynamics, $S(t)$ monotonically increases and saturates to a constant value instead [19]. The same behavior occurs with a single oscillation at the beginning when the bath particle interactions are included [2].

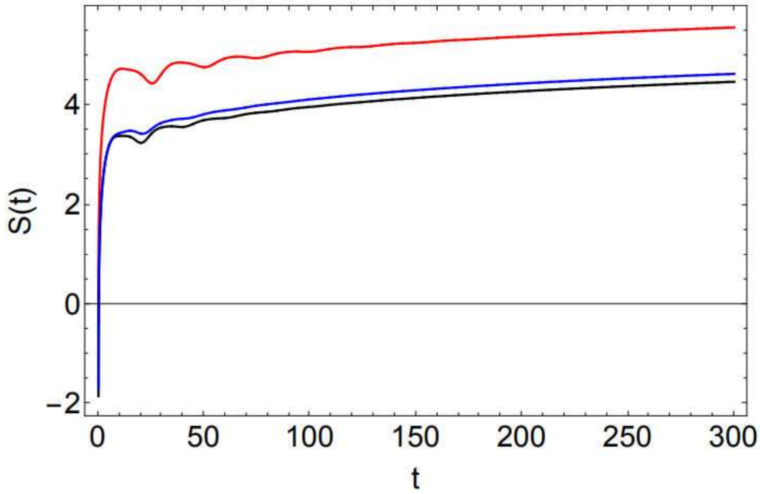

Figure 2. Entropy of tag particles as a function of t.

The processes responsible for the appearance of the initial oscillations might be due to the heat bath. One approximate way to explain it is by calculating the entropy production as we will show next.

The entropy production rate $\dot{S}_{na}(t)$ due to the field is depicted in Figure 3. It is positive as should be [12]. All curves collapse to a single plot to indicate that no matter the parameters defining the system, the field effects seem to generate almost the same rate of entropy production. Any minor difference disappears because of the scale. It goes to zero as the PDF relaxes to the uniform equilibrium distribution. This production rate doesn't provide information about the oscillations of $S(t)$.

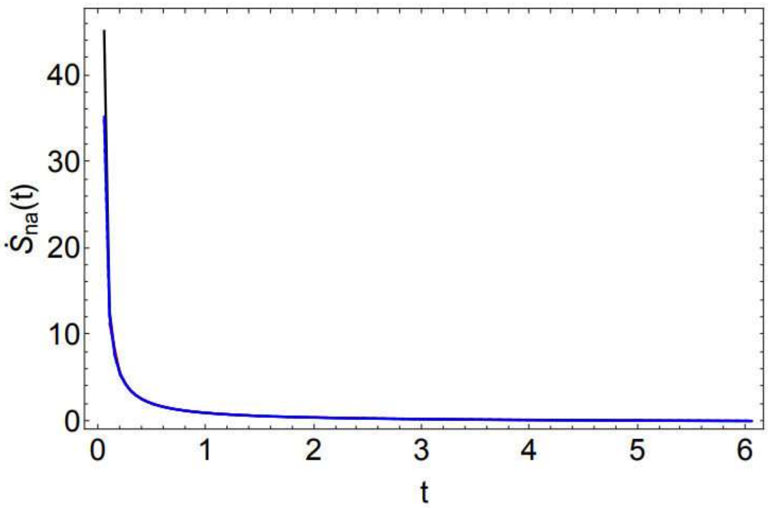

Figure 3. Non-adiabatic entropy production as a function of t. The curve for $T = 10$ superimposes the solid black curve.

However, the monotonic behavior of $\dot{S}_{na}(t)$ changes dramatically by examining $\dot{S}_{ex}(t)$, that is, the net effect of the heat transfer by/from the bath. Figure 4 displays this property where the oscillations appear. They are due to the irreversible heat transfer process, which tends to vanish as time evolves. An increasing steady heat flux from the reservoir, different from zero, is kept in the system to ensure the system's steady state.

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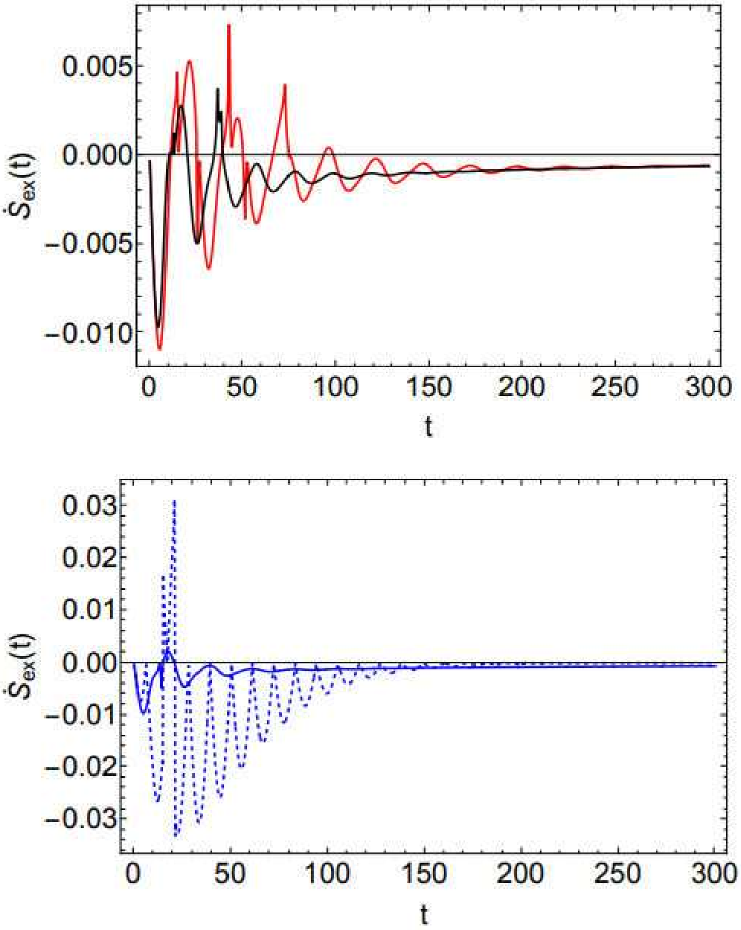

Figure 4. Systematic entropy rate of the reservoir as a function of t.

Because of the low magnitude of $\dot{S}_{ex}(t)$, the major contribution to $\dot{S}_{tot}(t)$ comes from $\dot{S}_{na}(t)$. The entropy production obtained from Equation (18) (not shown) is just $\dot{S}_{tot}(t)$ complying with the second law.

Unlike the simple system of a Brownian motion on a circle worked in [12] where the adiabatic and non-adiabatic contributions are positively satisfying Jensen inequality [20], $\dot{S}_{ex}(t)$ is not a convex function as required by Jensen [21] but a fulctuating one. There is no contradiction with the second law because the definition (20) involves two separate interacting subsystems where the bath is not isolated, delivering heat to the particles to be returned afterward [22]. What is important is that $\dot{S}_{tot}(t) > 0$ agrees with the second law and mathematically is a convex function obeying Jensen's inequality.

4. Conclussion

Since the results obtained from the NGLE, Eq. (1), acceptably describe the MD calculations of Daldrop, Kowalitz, and Netz [5] for the same system, should be taken into consideration to observe the effect of the field-bath interaction in the already calculation of other properties as free energies and work with time-dependent external protocols. These should include, to cite a few, the previous works on the classical Langevin equation in the versions with an exponential memory kernel [4] and both Markovians, overdamped [23,24] and inertial [25].

The effect of the field-bath interaction when the kernel is an exponential decay is just NGLE determined at frequencies too small. It allows a direct comparison with the CGLE [4].

For Markovian systems, we make the substitution $\Theta_\Omega(|t-s|) = \gamma_0\,\delta(t-s) + \Omega$ in Eq. (1) and use the effective parabolic potential $V(q,t) = \Omega(q-\lambda(t))^2/2$ to get

$$\dot{v}(t) = -\gamma_0\, v(t) - \Omega\,(q(t) - \lambda(t)) + \xi(t), \tag{24}$$

$$\langle \xi(t-s)\,\xi(0)\rangle = T\,\delta(t-s), \tag{25}$$

where $\lambda(t)$ is an external protocol of free choice. The objective of these works, however, is the determination of the optimal one, which optimizes the mechanical work done by/on the particle for the initial conditions set. To derive it, the Euler-Lagrange formalism [26] is applied to the function defining the mechanical work. Therefore, the overdamped system [23,24] and inertial [25] of the ordinary Langevin equation can be compared with the theory of this research.

Unlike the previous versions where the interaction field bath is off, the protocol, work, entropy, and the FPE now depend on the characteristics of the bath through the effective frequency Ω, which in turn is itself a function of the field frequency ω.

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Abbreviations

The following abbreviations are used in this manuscript:

FPE	Fokker-Planck equation
CGLE	Classical generalized Langevin equation
NGLE	New generalized Langevin equation
FDT	Fluctuation-dissipation theorem

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