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Fluctuation theorems for harmonic oscillators

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Abstract. We study experimentally the thermal fluctuations of energy input and dissipation in a harmonic oscillator driven out of equilibrium, and search for fluctuation relations. Both the transient evolution from the equilibrium state, and non-equilibrium steady states are analyzed. Fluctuation relations are obtained experimentally for both the work and the heat, for the stationary and transient evolutions. A stationary state fluctuation theorem is verified for various time dependences of the imposed external torque. The transient fluctuation theorem is satisfied for the work given to the system but not for the heat dissipated by the system in the case of linear forcing. Experimental observations on the statistical and dynamical properties of the position fluctuations of the torsion pendulum allow us to derive analytical expressions for the probability density functions of the work and the heat. We obtain for the first time an analytic expression for the probability density function of the heat. The agreement between experiments and our predictions is excellent.

Keywords: fluctuations (theory), fluctuations (experiment), stochastic processes (theory), stochastic processes (experiment)

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1. Introduction

Nanotechnology, like biology, biophysics and chemistry, is using or studying set-ups and objects which are smaller and smaller. In these systems, one is usually interested in mean values, but thermal fluctuations play an important role because their amplitudes are often comparable with the mean values. This is for example the case for quantities such as the energy injected into the system or the energy dissipated by the system. These fluctuations can lead to unexpected and undesired effects: for instance, the instantaneous energy transfer can be reversed by a large fluctuation, leading energy to flow from a cold source to a hot one. These events, although rare, are quantitatively studied using the recent fluctuation relations (FRs) that quantify the probabilities of these rare events in systems which can be arbitrarily far from equilibrium. FRs have been demonstrated in both deterministic systems [1, 2] and stochastic dynamics [3]–[9]. Furthermore van Zon and Cohen proved that there is an important difference between the FRs for the injected power and those for the dissipated power [7, 8]. It is important to notice that the fluctuations of the work done by the external forces to drive the system between two equilibrium states A and B allows one to compute, in some cases, the free energy difference ΔF between A and B, using the Jarzynski equality [10, 11] and the Crooks relation (CR) [12] which are in some way related to the FRs. Indeed using the JE and CR one takes advantage of these work fluctuations and relates ΔF to the probability distribution function (PDF) of the work performed on the system to drive it from A to B along any path (either reversible or irreversible) in the system parameter space. Hatano and Sasa produced a relation of the same kind [13] and an interesting extension of the JE has been proposed in [14]. The JE and CR are beginning to be widely used to measure the free energy in various biological [16]–[18], chemical [19] and physical systems [20, 14].

To safely apply FRs in practical cases, it is useful and important to check in very controlled experiments the hypothesis on which these theorems are based. These experiments will also allow a test of the accuracy with which the predicted effects are observable and the limits of FRs in general applications. From this point of view, it is of paramount importance to take into account that FRs and the JE and CR may use different definitions of work which, if not correctly used, may lead to misleading results (see [15] for a discussion of this point).

Experiments searching for FRs have been performed on dynamical systems [21]–[23], but interpretations are very difficult because a quantitative comparison with theoretical prediction is impossible. Other experiments have been performed on stochastic systems described by a first-order Langevin equation: a Brownian particle in a moving optical trap [24] and an out-of-equilibrium electrical circuit [25] in which existing theoretical predictions [7, 8] were verified. Other experimental tests for FRs have been performed on driven two-level systems [20] and in colloids [26]. The limits of the applicability of the JE and CR in a second-order Langevin system have been studied experimentally in [27]. Other interesting comments on the Langevin equation can be found in [28].

In a recent letter [29] we presented experimental and theoretical results for the fluctuations of the work done by an external time dependent force on a harmonic oscillator either in the stationary or in the transient state, which are described by a second-order Langevin equation. In the present paper, we describe the results on the work in more detail and we extend the study to the heat dissipated by the system. We also present

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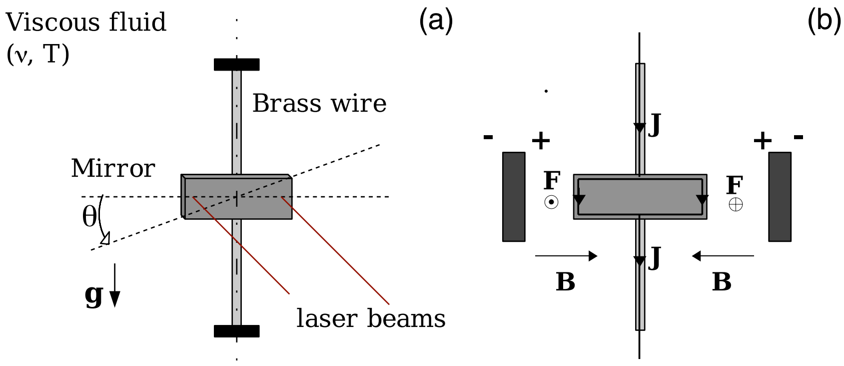

Figure 1. (a) The torsion pendulum. (b) The magnetostatic forcing.

detailed analytical derivations of FRs based on experimental observations. As we will see, there are important differences between the first-order and second-order Langevin equations which are induced by the presence of the kinetic energy especially as regards heat fluctuations. For this reason it is important to study the two cases separately.

This paper is organized as follows. In section 2, we present the experimental system, and write its energy balance to define the work given to the system together with the heat dissipated. We then introduce the fluctuation relations (FRs). In sections 3–5, we present experimental results on the fluctuations of first the work and then the heat. A short discussion on experimental results is given in section 6. Then, in sections 7 and 8, we present some analytical derivations of FRs based on a hypothesis inspired by experimental observations. We compare these analytical predictions to the experimental observations and finally conclude in section 9.

2. System description

2.1. The harmonic oscillator

Our system is a harmonic oscillator and we measure the non-equilibrium fluctuations of its position degree of freedom. The oscillator is damped due to the viscosity of a surrounding fluid that acts as a thermal bath at temperature T. Our oscillator, depicted in figure 1(a), is a torsion pendulum composed of a brass wire (length 10 mm, width 0.5 mm, thickness 50 μm) and a glass mirror glued in the middle of this wire (length 2 mm, width 8 mm, thickness 1 mm). The elastic torsional stiffness of the wire is $C = 4.65 \times 10^{-4}$ N m rad^{-1}. It is enclosed in a cell filled by a water–glycerol mixture at 60% concentration. The system is a harmonic oscillator with resonant frequency $f_0 = \sqrt{C/I_{\text{eff}}}/(2\pi) = \omega_0/(2\pi) = 217$ Hz and a relaxation time $\tau_\alpha = 2I_{\text{eff}}/\nu = 1/\alpha = 9.5$ ms. I_{eff} is the total moment of inertia of the displaced masses (i.e. the mirror and the mass of displaced fluid) [30]. The damping has two contributions: the viscous damping ν of the surrounding fluid and the viscoelasticity of the brass wire which can be neglected here.

The angular displacement of the pendulum θ is measured by a differential interferometer [27, 29, 31]. The measurement noise is two orders of magnitude smaller than the thermal fluctuations of the pendulum. $\theta(t)$ is acquired with a resolution of 24 bits at a sampling rate of 8192 Hz, which is about 40 times f_0. We drive the system out of equilibrium by forcing it with an external torque M by means of a small electric current J flowing in a coil glued behind the mirror (figure 1(b)). The coil is inside a static magnetic field. The displacements of the coil and therefore the angular displacements of the mirror are much smaller than the spatial scale of inhomogeneity of the magnetic field. So the torque is proportional to the injected current: $M = A \cdot J$; the slope A depends on the geometry of the system.

The angular displacement θ of this harmonic oscillator is very well described by a second-order Langevin equation:

$$I_{\rm eff}\frac{{\rm d}^2\theta}{{\rm d}t^2} + \nu\frac{{\rm d}\theta}{{\rm d}t} + C\theta = M + \sqrt{2k_{\rm B}T\nu}\eta, \tag{1}$$

where η is the thermal noise, delta correlated in time of variance 1, and $k_{\rm B}$ the Boltzmann constant and T the temperature of the system which is that of the surrounding fluid. The fluctuation dissipation theorem (FDT) gives a relation between the amplitude of the thermal angular fluctuations of the oscillator at equilibrium and its response function. For a harmonic oscillator, the equilibrium thermal fluctuation power spectral density (psd) is

$$\langle|\hat{\theta}|^2\rangle = \frac{4k_{\rm B}T}{\omega}\,{\rm Im}\,\hat{\chi} = \frac{4k_{\rm B}T\nu}{(-I_{\rm eff}\omega^2 + C)^2 + (\omega\nu)^2}, \tag{2}$$

where $\hat{\chi} = \hat{M}/\hat{\theta} = A(\hat{J}/\hat{\theta})$. Using FDT (equation (2)), we measure the coefficient A and test the calibration accuracy of the apparatus which is better than 3%. More details on the set-up can be found in [27, 31].

2.2. Energy balance

When the system is driven out of equilibrium using a deterministic torque, some work is done on it and a fraction of this energy is dissipated into the heat bath. Multiplying equation (1) by $\dot{\theta}$ and integrating between t_i and $t_i + \tau$, one obtains a formulation of the first law of thermodynamics between the two states at time t_i and $t_i + \tau$ (equation (3)). This formulation was first proposed in [32] and used in other theoretical and experimental works [13, 26]. The change in internal energy ΔU_τ of the oscillator over a time τ, starting at a time t_i, is written as

$$\Delta U_\tau = U(t_i + \tau) - U(t_i) = Q_\tau + W_\tau, \tag{3}$$

where W_τ is the work done on the system over a time τ:

$$W_\tau = \frac{1}{k_{\rm B}T}\int_{t_i}^{t_i+\tau} M(t')\frac{{\rm d}\theta}{{\rm d}t}(t')\,{\rm d}t', \tag{4}$$

and Q_τ is the heat given to the system. Equivalently, $(-Q_\tau)$ is the heat dissipated by the system. ΔU_τ, W_τ and Q_τ are defined as energy in $k_{\rm B}T$ units. The internal energy is the sum of the potential energy and the kinetic energy:

$$U(t) = \frac{1}{k_{\rm B}T}\left\{\frac{1}{2}I_{\rm eff}\left[\frac{{\rm d}\theta}{{\rm d}t}(t)\right]^2 + \frac{1}{2}C\theta(t)^2\right\}. \tag{5}$$

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The heat transfer Q_τ is deduced from equation (3); it has two contributions:

$$\begin{aligned} Q_\tau &= \Delta U_\tau - W_\tau \\ &= -\frac{1}{k_{\rm B}T}\int_{t_i}^{t_i+\tau} \nu \left[\frac{{\rm d}\theta}{{\rm d}t}(t')\right]^2 {\rm d}t' + \frac{\sqrt{2k_{\rm B}T\nu}}{k_{\rm B}T}\int_{t_i}^{t_i+\tau} \eta(t')\frac{{\rm d}\theta}{{\rm d}t}(t')\,{\rm d}t'. \end{aligned} \tag{6}$$

The first term corresponds to the opposite of viscous dissipation and is always negative, whereas the second term can be interpreted as the work of the thermal noise which has a fluctuating sign. The second law of thermodynamics imposes that $\langle -Q_\tau\rangle$ is positive. We rescale the work W_τ (the heat Q_τ) by the average work $\langle W_\tau\rangle$ (the average heat $\langle Q_\tau\rangle$) and define $w_\tau = W_\tau/\langle W_\tau\rangle$ ($q_\tau = Q_\tau/\langle Q_\tau\rangle$). The brackets are ensemble averages. In the present paper, x_τ (resp. X_τ) stands for either w_τ or q_τ (resp. W_τ or Q_τ).

It is worth saying that the definition of work in equation (4) is the classical one but it is not the one used in JE and CR. This may lead to different FRs and to some contradictions, as we have shown in [15].

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2.3. Fluctuation relations

There are two classes of FRs. The *stationary state fluctuation theorem* (SSFT) considers a non-equilibrium steady state. The *transient fluctuation theorem* (TFT) describes transient non-equilibrium states where τ measures the time since the system left the equilibrium state. A fluctuation relation (FR) examines the symmetry of the probability density function (PDF) $p(x_\tau)$ of a quantity x_τ around 0; x_τ is an average value over a time τ. It compares the probability of having a positive event ($x_\tau = +x$) versus the probability of having a negative event ($x_\tau = -x$). We quantify the FR using a function S (symmetry function):

$$S(x_\tau) = \frac{1}{\langle X_\tau\rangle}\ln\left(\frac{p(x_\tau = +x)}{p(x_\tau = -x)}\right). \tag{7}$$

The *transient fluctuation theorem* (TFT) states that the symmetry function is linear with x_τ for any values of the time integration τ and the proportionality coefficient is equal to 1 for any value of τ:

$$S(x_\tau) = x_\tau, \qquad \forall x_\tau, \qquad \forall\tau. \tag{8}$$

Contrary to the TFT, the *stationary state fluctuation theorem* (SSFT) holds only in the limit of infinite time (τ):

$$\lim_{\tau\to\infty} S(x_\tau) = x_\tau, \qquad \forall x_\tau. \tag{9}$$

The questions that we ask are whether fluctuation relations for $x_\tau = w_\tau$ or $x_\tau = q_\tau$ for finite time satisfy the two theorems and what the finite time corrections are. In a first time period, we test the correction to the proportionality between the symmetry function $S(x_\tau)$ and x_τ. In the region where the symmetry function is linear with x_τ, we define the

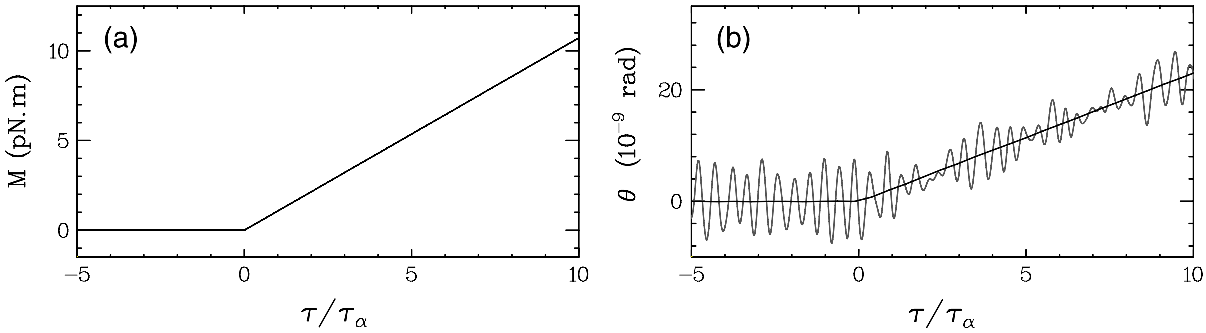

Figure 2. (a) Typical driving torque applied to the oscillator; (b) response of the oscillator to the external torque (gray line). The dark line represents the mean response $\bar{\theta}(t)$ to the applied torque $M(t)$.

slope $\Sigma_x(\tau) : S(x_\tau) = \Sigma_x(\tau)x_\tau$. In a second time period we measure finite time corrections to the value $\Sigma_x(\tau) = 1$ which is the asymptotic value expected from the two theorems.

3. Transient non-equilibrium state

For the transient fluctuation theorem, we choose the torque $M(t)$ depicted in figure 2(a). It is a linear function of time: $M(t) = M_0 t/\tau_r$ with $M_0 = 11.28$ pN m and $\tau_r = 0.1$ s $= 10.52\tau_\alpha$. The value of M_0 is chosen such that the mean response of the oscillator is of the order of the thermal noise, as can be seen in figure 2(b) where $\theta(t)$ is plotted during the same time interval as figure 2(a). The system is at equilibrium at $t_i = 0$ ($M(t_i = 0) = 0$ pN m and $M(t) = 0$ pN m $\forall t < t_i$). In this section the starting time t_i of integration of all quantities defined before (W_τ, ΔU_τ and Q_τ) is $t_i = 0$. So the work is

$$W_\tau = \frac{1}{k_{\rm B}T}\int_0^\tau M(t')\frac{\mathrm{d}\theta}{\mathrm{d}t}(t')\,\mathrm{d}t'. \tag{10}$$

3.1. Average value information

In figure 3(a), we represent the time average ($\langle\tau^{-1}W_\tau\rangle$) of the power injected into the system, the internal energy difference ($\langle\tau^{-1}\Delta U_\tau\rangle$) and the time average of the power dissipated by the system ($\langle\tau^{-1}Q_\tau\rangle$). $\langle\tau^{-1}W_\tau\rangle$ and $\langle\tau^{-1}\Delta U_\tau\rangle$ are linear in τ after some short relaxation time τ_α defined in the Langevin equation: for τ/τ_α smaller than 1, some oscillations around the linear behavior can be seen. The average value of the work $\langle W_\tau\rangle$ is therefore quadratic in τ and is equal to 33 $k_{\rm B}T$ for $\tau = \tau_r$. The difference between $\langle W_\tau\rangle$ and $\langle\Delta U_\tau\rangle$ corresponds to the mean value of dissipated heat $\langle -Q_\tau\rangle$ (equation (6)). As can be seen in figure 3(a), $\langle W_\tau\rangle$ is larger than $\langle\Delta U_\tau\rangle$ for all times τ. The average of the dissipated power ($\langle -\tau^{-1}Q_\tau\rangle$) is therefore positive for all times τ as expected from the second principle. For τ larger than several τ_α, the dissipated power is constant and equal to a few $k_{\rm B}T$ per second because $\langle\tau^{-1}W_\tau\rangle$ and $\langle\tau^{-1}\Delta U_\tau\rangle$ have the same slope after some τ_α. So we have the following behavior: the work done by the external work is used by the system to increase its internal energy but a small amount of energy is lost at a constant rate by viscous dissipation and exchange with the thermostat.

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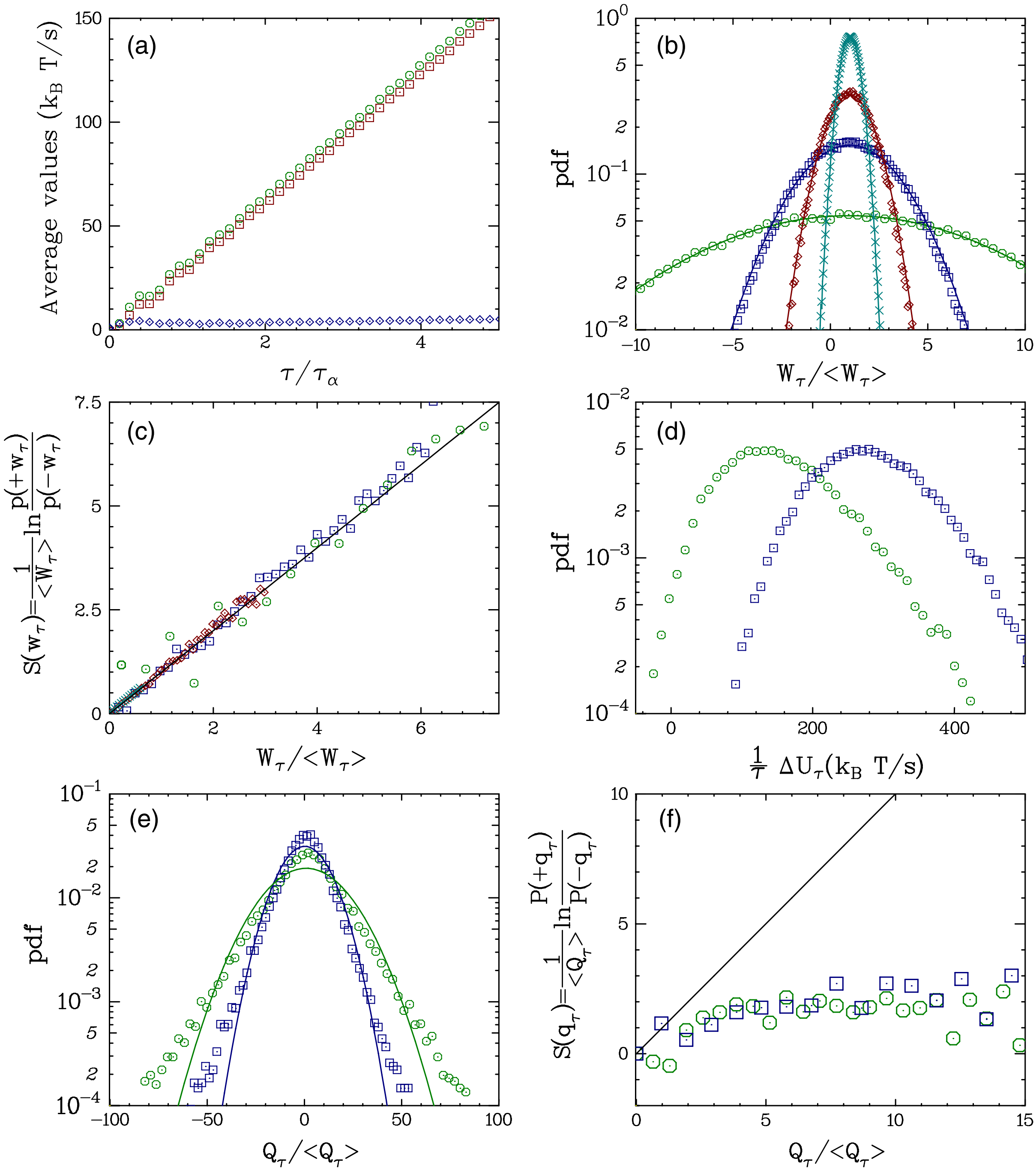

Figure 3. TFT. (a) Average values of $\tau^{-1}W_\tau$ (○), $\tau^{-1}\Delta U_\tau$ (□) and $\tau^{-1}Q_\tau$ (◊) plotted as functions of τ. (b) PDFs of w_τ for various τ/τ_α: 0.31 (○), 1.015 (□), 2.09 (◊) and 4.97 (×). Continuous lines are theoretical predictions with no adjustable parameters. (c) Corresponding functions $S(w_\tau)$. The straight continuous line is a line with slope 1. (d) PDFs of $\tau^{-1}\Delta U_\tau$ for two values of τ/τ_α: 4.97 (○) and 8.96 (□). (e) Corresponding PDFs of q_τ. Continuous lines are Gaussian fits. (f) Corresponding functions $S(q_\tau)$. The straight continuous line is a line with slope 1.

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3.2. Work fluctuations

The probability density functions (PDFs) $p(w_\tau)$ of w_τ are plotted in figure 3(b) for different values of τ/τ_α. Four typical values of τ are presented: the first is smaller than the relaxation time and the last equals five relaxation times; the results are the same for any value of τ. The PDFs of w_τ are Gaussian for any τ. In some way, this result could be expected because it has been proved that in the case of a first-order Langevin equation with a harmonic potential the work fluctuations are Gaussian for any kind of driving [33]. We observe that w_τ takes negative values as long as τ is not too large. The probability of having negative values of w_τ decreases when τ is increased. From the PDFs, we compute the symmetry functions. They are plotted in figure 3(c) as a function of w_τ. They all collapse on the same linear function of w_τ for any τ, which implies that they all have the same slope $\Sigma_w(\tau)$. The straight line in figure 3(c) has slope 1. Within experimental error bars, $\Sigma_w(\tau)$ is equal to 1 for all time τ. Therefore work fluctuations for a harmonic oscillator under a linear forcing satisfy the TFT. We checked that this property holds for other values of M_0 and τ_r.

3.3. Heat fluctuations

The PDFs of $\tau^{-1}\Delta U_\tau$ are plotted in figure 3(d) for two values of τ/τ_α: they are not symmetric and have exponential tails. The PDFs of q_τ can be seen in figure 3(e) for the same values of τ/τ_α. They are qualitatively different from those of the work. We have plotted in the same figure the Gaussian fit of the two PDFs of the dissipated heat. It is clear that the PDFs of q_τ are not Gaussian. Extreme events of q_τ are distributed on exponential tails. These tails can be interpreted noticing that $Q_\tau = \Delta U_\tau - W_\tau$ and ΔU_τ have exponential tails. The variance of the PDFs of q_τ is also much larger than the variance of the PDFs of w_τ.

We plot on figure 3(f) symmetry functions $S(q_\tau)$ for the same times τ/τ_α. Only the behavior of large events can be analyzed here because the variance is much larger than the mean $\sigma_{w_\tau} \gg 1$. As can be seen in figure 3(f), $S(q_\tau)$ is not proportional to q_τ; therefore TFT is not satisfied for finite time. Within experimental resolution, $S(q_\tau)$ is constant for extreme events and equal to 2. This behavior can be interpreted by writing for large q_τ, $p(q_\tau) = A_\pm \exp(-\alpha_\pm |q_\tau|)$ where α_+ and α_- are the rates of decrease on the exponential tails. Each coefficient depends on τ. There is a simple expression for $S(q_\tau)$ for large fluctuations:

$$S(Q_\tau) = (\alpha_+ - \alpha_-)Q_\tau + \frac{1}{\langle Q_\tau \rangle} \ln\left(\frac{A_+}{A_-}\right). \qquad (11)$$

In figure 3(c), we see that the PDFs of q_τ are symmetric around the mean value for the two values of τ. This is not the case for small τ/τ_α. Thus we can conclude that $\alpha_+ = \alpha_-$ and that the symmetry function is equal to a constant: $(\langle Q_\tau \rangle)^{-1}(\ln(A_+) - \ln(A_-))$.

As can be seen in figure 3(e), the PDFs become more and more Gaussian when τ tends to infinity. It is expected that for infinite time, the PDF of q_τ is a Gaussian. Thus, the TFT appears to be satisfied experimentally in the limit of infinite τ. Our interesting finding is that for Q_τ the TFT if not valid for any times.

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4. Steady state: linear forcing

4.1. Definition of the work done on the system

We call a steady state a state in which both the forcing and the response to the forcing do not depend on the initial time t_i, but only on τ. This implies that $\langle M(t_i+\tau)\rangle$ is independent of t_i; and so is $\langle\theta(t_i+\tau)\rangle$. If the torque drifts through time, the mean of $M(t_i+\tau)$ is linear with $t_i+\tau$. Thus we have to change the definition of the work done on the system to keep it in a steady state. This is equivalent to a Galilean change of reference frame. The work is now defined as

$$W_\tau = \frac{1}{k_{\mathrm{B}}T}\int_{t_i}^{t_i+\tau}[M(t)-M(t_i)]\frac{\mathrm{d}\theta}{\mathrm{d}t}(t')\,\mathrm{d}t'. \tag{12}$$

With this definition, the forcing is $\tilde{M}(t)=M(t)-M(t_i)$ and the response to the forcing $\tilde{\theta}(t)=\theta(t)-\theta(t_i)$. When we impose a forcing linear in time ($M(t)=M_0t/\tau_r$), the first condition ($\langle\tilde{M}(t_i+\tau)\rangle$ independent of t_i) is satisfied. The second ($\langle\tilde{\theta}(t_i+\tau)\rangle$ independent of t_i) is also satisfied if $t_i\geq 3\tau_\alpha$, i.e. after a transient state. Thus the system is in a steady state. We remark that, in the transient state, this definition of the work reduces to the usual one, because $M(t_i)=M(t=0)=0$ pN m.

4.2. Work fluctuations

The average of W_τ is quadratic in τ for any value of τ/τ_α. There are no oscillations in time for small τ/τ_α. The PDFs of w_τ are Gaussian for any value of τ/τ_α (figure 4(a)) [33]. The probability of negative values is high and decreases with τ, like in the transient case. The symmetry functions $S(w_\tau)$ are again proportional to w_τ (figure 4(b)) but the slope Σ_w is not equal to 1 for smaller τ and tends to 1 for $\tau\gg\tau_\alpha$ only, as can be seen in figure 4(c). Thus we obtain a fluctuation relation for the work done on the system in this steady state and this relation satisfies the SSFT. The slope at finite time is slightly oscillating at a frequency close to f_0.

4.3. Heat fluctuations

The heat dissipated during this linear forcing has a behavior very similar to the one observed in the transient case (section 3.3). We can hence repeat here all that we said in section 3.3.

5. Steady state: sinusoidal forcing

We now consider a periodic forcing $M(t)=M_0\sin(\omega_d t)$ which has been briefly described in [29]. This is a very common kind of forcing which has already been studied in the case of the first-order Langevin equation [26] and that of the two-level system [20] and in a different context for the second-order Langevin equation [34]. Using the Fourier transform, any periodic forcing can be decomposed as a sum of sinusoidal forcings. We explain here the behavior of a single mode. We choose $M_0=0.78$ pN m and $\omega_d/(2\pi)=64$ Hz. This torque is plotted in figure 5(a). The mean of the response to this torque is sinusoidal, with the same frequency, as can be seen in figure 5(b). We studied other frequencies ω_d.

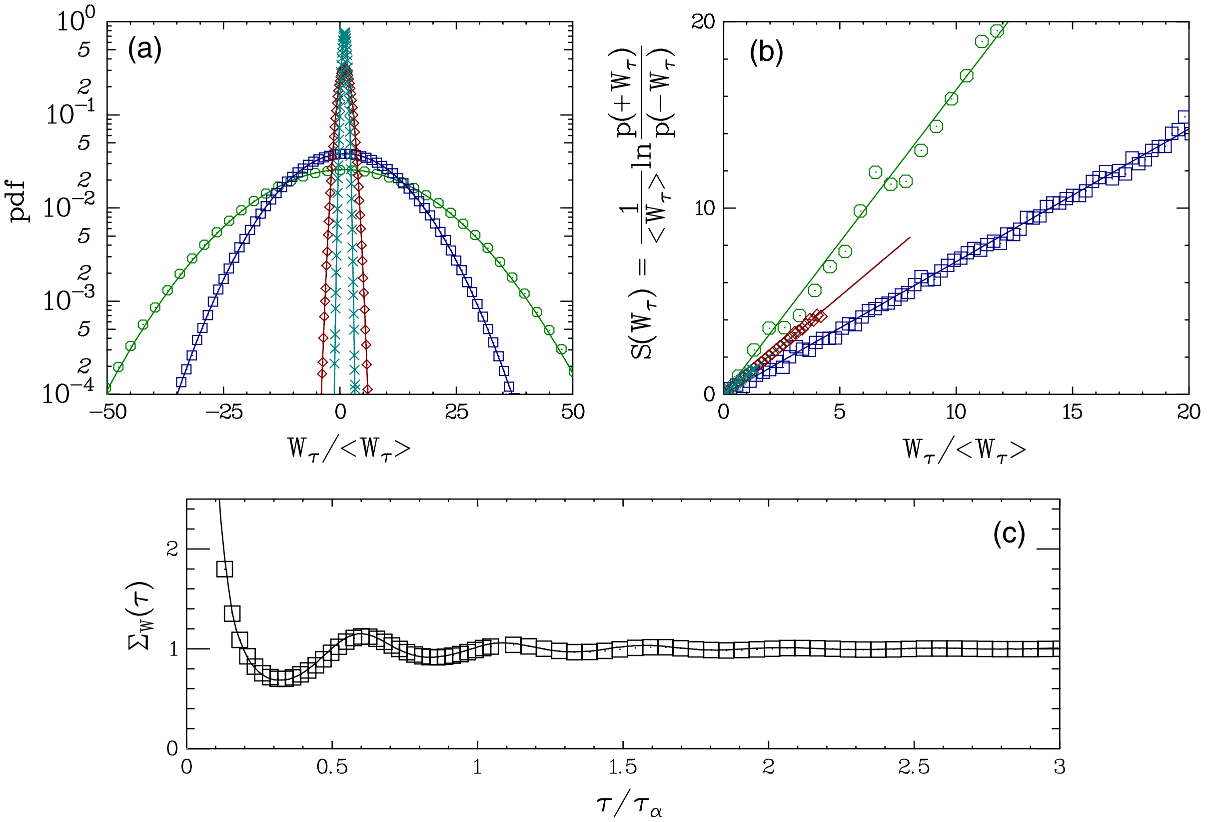

Figure 4. SSFT with a ramp forcing. (a) PDF of W_τ for various τ/τ_α: 0.019 (○), 0.31 (□), 2.09 (◊) and 4.97 (×). (b) Corresponding functions $S(W_\tau)$. (c) The slope $\Sigma_w(\tau)$ of $S(W_\tau)$ is plotted versus τ (□: experimental values; continuous line: theoretical prediction from equation (20) with no adjustable parameters).

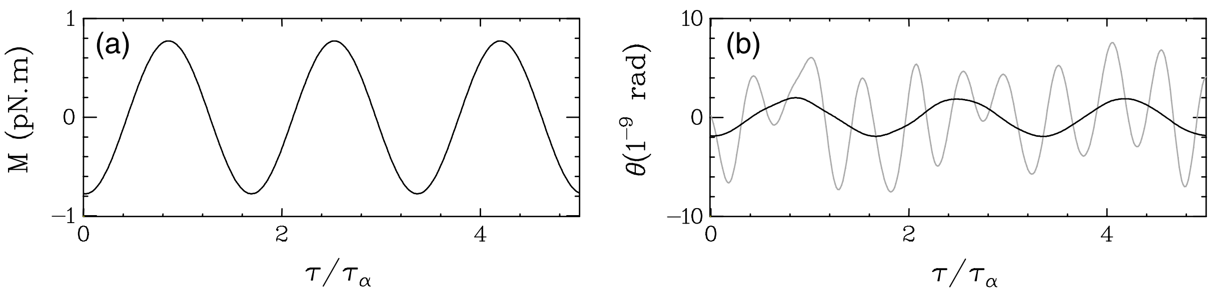

Figure 5. (a) Sinusoidal driving torque applied to the oscillator. (b) Response of the oscillator to this periodic forcing (gray line); the dark line represents the mean response $\langle\theta(t)\rangle$.

The system is clearly in a steady state. We choose the integration time τ to be a multiple of the period of the driving ($\tau = 2n\pi/\omega_d$ with n an integer). The starting phase $t_i\omega_d$ is averaged over all possible t_i in order to increase the statistics; in the remainder of this section, we drop the brackets $\langle\cdot\rangle_{t_i}$.

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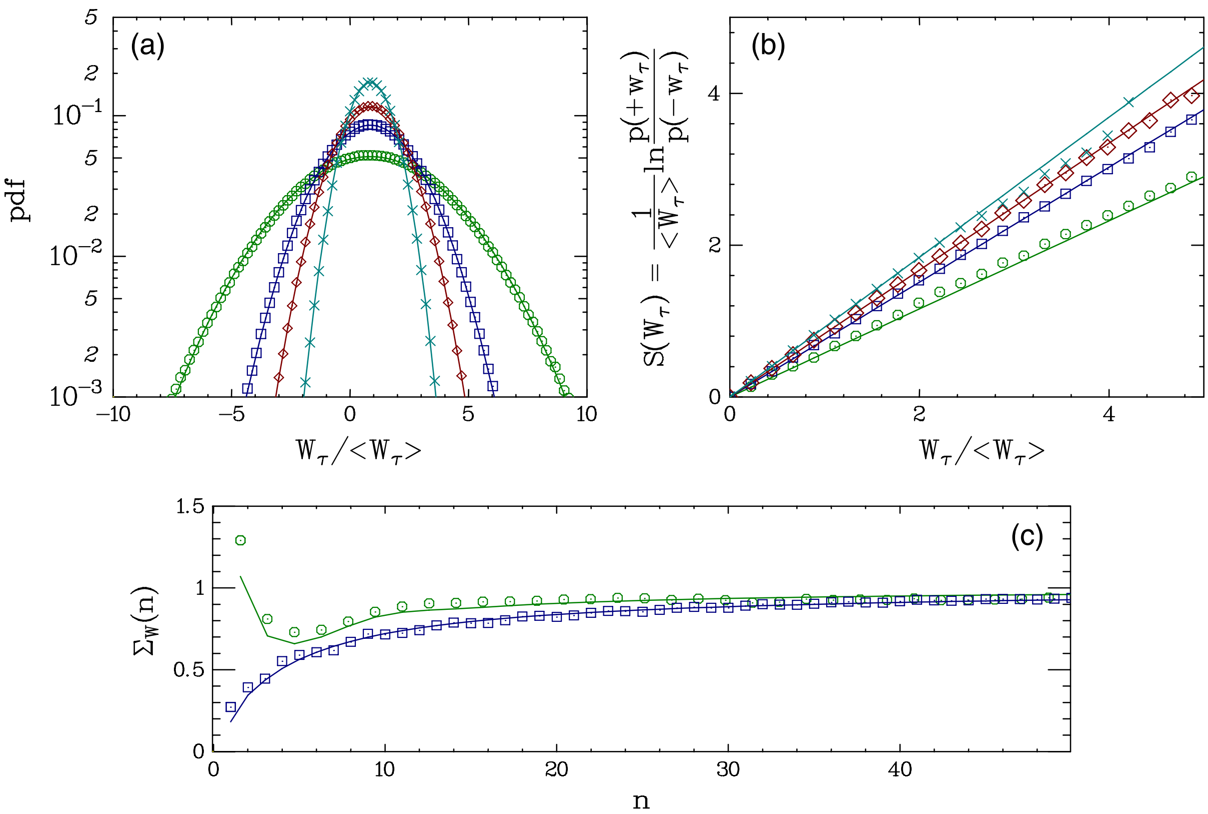

Figure 6. Sinusoidal forcing. (a) PDFs of the work w_n integrated over n periods of forcing, with $n = 7$ (○), $n = 15$ (□), $n = 25$ (◊) and $n = 50$ (×). (b) The function $S(w_n)$ measured at $\omega_d/2\pi = 64$ Hz is plotted as a function of w_n for several n: (○) $n = 7$; (□) $n = 15$ (◊) $n = 25$; (×) $n = 50$. For these two plots, continuous lines are theoretical predictions with no adjustable parameters (equations (A.11) and (A.14)). (c) The slopes $\Sigma_w(n)$, plotted as a function of n for two different driving frequencies $\omega_d = 64$ Hz (□) and 256 Hz (○); continuous lines are theoretical predictions from equation (21) with no adjustable parameters.

5.1. Work fluctuations

The work is written as a function of n, the number of periods of the forcing:

$$W_n = \frac{1}{k_B T} \int_{t_i}^{t_i+\tau_n} M(t') \frac{d\theta}{dt}(t')\, dt'. \tag{13}$$

The PDFs of w_n are plotted in figure 6(a). Work fluctuations are Gaussian for all values of n as in previous cases [33]. Thus symmetry functions are again linear in w_n (figure 6(b)). The slope $\Sigma_w(n)$ is not equal to 1 for all n but there is a correction in finite time (figure 6(c)). Nevertheless, $\Sigma_w(n)$ tends to 1 for large n, so the SSFT is satisfied. The convergence is very slow and we have to wait a large number of periods of forcing for the slope to be 1 (after 30 periods, the slope is still 0.9).

This behavior is independent of the amplitude of the forcing M_0 and consequently of the mean value of the work $\langle W_n \rangle$. The system satisfies the SSFT for all forcing frequencies ω_d but finite time corrections depend on ω_d, as can be seen in figure 6(c).

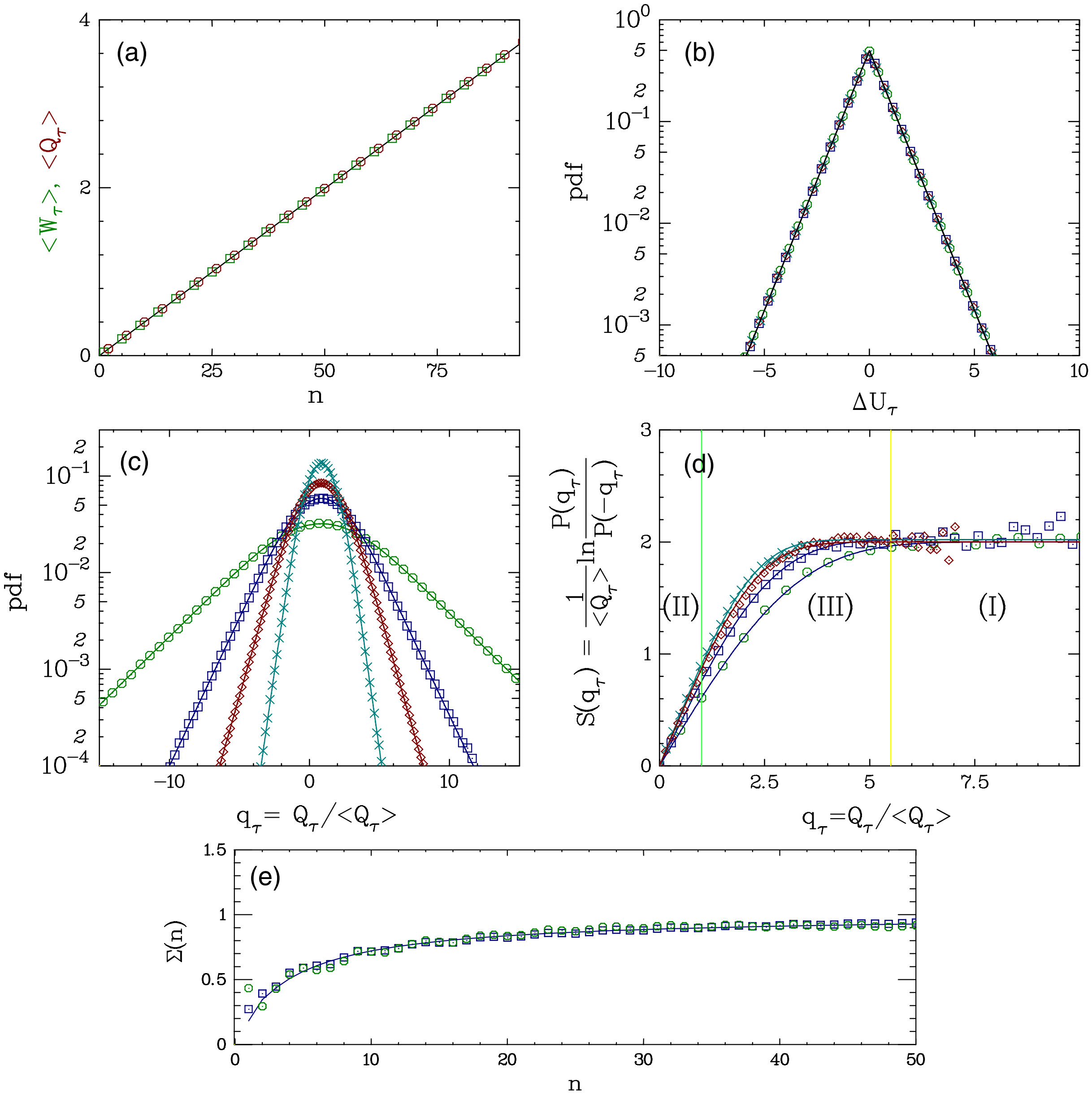

Figure 7. Sinusoidal forcing. (a) Average value of W_n (○) and Q_n (□). In the following plots, the integration time τ is a multiple of the period of forcing, $\tau = 2n\pi/\omega_d$, with $n = 7$ (○), $n = 15$ (□), $n = 25$ (◊) and $n = 50$ (×). Continuous lines are theoretical predictions with no adjustable parameters. (b) PDFs of ΔU_τ. (c) PDFs of q_τ. (d) Symmetry functions $S(q_\tau)$. (e) The slope $\Sigma_q(n)$ of $S(q_\tau)$ for $q_\tau < 1$, plotted as a function of n (○). The slope $\Sigma_w(n)$ of $S(w_\tau)$ plotted as a function of n (□). The continuous line is a theoretical prediction.

5.2. Heat fluctuations

We first make some comments on the average values. The average of ΔU_τ is obviously vanishing because the time τ is a multiple of the period of the forcing. $\langle W_n \rangle$ and $\langle Q_n \rangle$ have consequently the same behavior and they are linear in τ, as can be seen in figure 7(a),

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but the PDFs of heat fluctuations q_n have exponential tails (figure 7(c)). This can be understood by noticing that, from equation (6), $-Q_\tau = W_\tau - \Delta U_\tau$ and that ΔU_τ has an exponential PDF independent of n (figure 7(b)). Therefore, in a first approximation, the PDF of q_τ is a convolution of an exponential distribution (the PDF of ΔU_τ) and a Gaussian distribution (the PDF of w_τ).

Symmetry functions $S(q_n)$ are plotted in figure 7(d) for different values of n; three different regions appear:

(I) For large fluctuations q_n, $S(q_n)$ equals 2. When τ tends to infinity, this region spans from $q_n = 3$ to infinity.

(II) For small fluctuations q_n, $S(q_n)$ is a linear function of q_n. We then define $\Sigma_q(n)$ as the slope of the function $S(q_n)$, i.e. $S(q_n) = \Sigma_q(n) q_n$. This slope is plotted in figure 7(e) where we see that it tends to 1 when τ is increased. So, the SSFT holds in this region II which spans from $q_n = 0$ up to $q_n = 1$ for large τ.

(III) A smooth connection between the two behaviors.

We observe that $\Sigma_w(n)$ matches $\Sigma_q(n)$ experimentally, for all values of n (figure 7(e)). So the finite time corrections to the FR for the heat are the same as those of the FR for work: $\Sigma_w(n) = \Sigma_q(n)$.

These regions define the fluctuation relation from the heat dissipated by the oscillator. The limit for large τ of the symmetry function $S(q_\tau)$ is rather delicate and we will discuss it in section 8.2.

6. Discussion and conclusion on experimental results

In the previous sections, we have presented experimental results on a harmonic oscillator driven out of equilibrium by an external deterministic forcing M. We operated with two different time prescriptions: one in which M is a linear function of time, and one in which M is a sinusoidal function of time.

The energy injected into the system is the work W of the torque M. The PDFs of the work W are Gaussian whatever the time prescription of M is, and work fluctuations satisfy a TFT (M linear in time) and a SSFT (M linear or sinusoidal in time). This results for the harmonic oscillator, described by a second-order Langevin equation, confirm the theoretical predictions obtained for a first-order Langevin equation with a harmonic potential [33].

The energy dissipated by the system is represented by the heat Q, and we measured it using the first principle of thermodynamics (equation (6)). Heat probability distributions are not Gaussian and are very different from those of the work. They nevertheless satisfy a SSFT in both the case of a sinusoidal forcing and for a linear forcing. But they do not satisfy a TFT in the case of a linear forcing, because the symmetry functions are not linear for all values of dissipated heat q_τ.

In the next two sections, we use some experimental evidence to derive analytical expressions for the PDFs of work and the heat exchanged on an arbitrary time interval τ. We then derive FRs together with their finite time corrections.

7. Work fluctuations: theoretical predictions

In this section, we derive the analytical expression for the PDF of the work given to the system, and defined as the work of the torque applied to the pendulum, which is either linear or sinusoidal in time. Experimentally, we observed that the PDFs are always Gaussian, so we restrict our task to deriving expressions for the first two moments of the work distribution.

To do this, we use experimental observations on the fluctuations of the angle θ, as described in section 7.1 below. We then compute in section 7.2 the mean and the variance of the work W_τ in the different experimental situations, and then write formally the corresponding fluctuation relations, from which we obtain analytical expressions for the finite time corrections to the fluctuation theorems.

7.1. Angular fluctuations in the presence of forcing

We discuss here the angular fluctuations. We decompose the angle θ into a mean value $\langle\theta\rangle$ and a fluctuating part $\delta\theta$, writing $\theta = \langle\theta\rangle + \delta\theta$. The mean value corresponds to an ensemble average. It is obtained experimentally by averaging over realizations of the forcing, and it is presented in figures 2 and 5.

A first experimental observation is as follows. The measured mean response $\langle\theta\rangle$ is exactly equal to the solution of the deterministic second-order equation obtained when removing the noise term ($\eta = 0$) in the Langevin equation (1). We checked this from our data, and found in this way a value of the calibration A (see section 2.1) in perfect agreement with the one obtained from the application of the fluctuation dissipation theorem.

A second experimental observation concerns the probability distribution of $\delta\theta$ in out-of-equilibrium conditions. We know and observed that at equilibrium, $\delta\theta$ has a Gaussian distribution with variance $\sigma_\theta^2 = k_{\mathrm{B}}T/C$, and the associated momentum $\dot\theta$ has fluctuations $\delta\dot\theta$ which also have a Gaussian distribution, with a variance $k_{\mathrm{B}}T/I_{\mathrm{eff}}$. We observe that the statistical properties of angular fluctuations $\delta\theta$ when a torque $M(t)$ linear in time is applied are the same as the statistical properties at equilibrium, when no torque is applied. In figure 8(a), we plot the PDF of $\delta\theta$ measured at $M \neq 0$ together with the Gaussian fit of the PDF at equilibrium (continuous line). The two curves match perfectly within experimental accuracy. Thus we conclude that the external driving does not perturb the equilibrium distribution of angular fluctuations, so we use

$$P(\delta\theta, M \neq 0) = P(\delta\theta, M = 0) = \frac{1}{\sqrt{2\pi\sigma_\theta^2}} \exp\left(-\frac{\delta\theta^2}{2\sigma_\theta^2}\right). \tag{14}$$

The third experimental observation concerns time correlations. In figure 8(b), we plot the power spectral density function of $\delta\theta$ when applying an external forcing (∘). We compare it to the prediction from the fluctuation dissipation theorem at equilibrium (equation (2)) computed using the oscillator parameters. The two spectra are identical, so we can confidently use for our system a description in terms of a second-order Langevin dynamic where the noise term is not perturbed by the presence of the driving. From the power spectral density function of θ (equation (2)), we derive the autocorrelation function $R_{\delta\theta}(\tau)$ of $\delta\theta$ during a time interval τ. It is the same at equilibrium and out of equilibrium,

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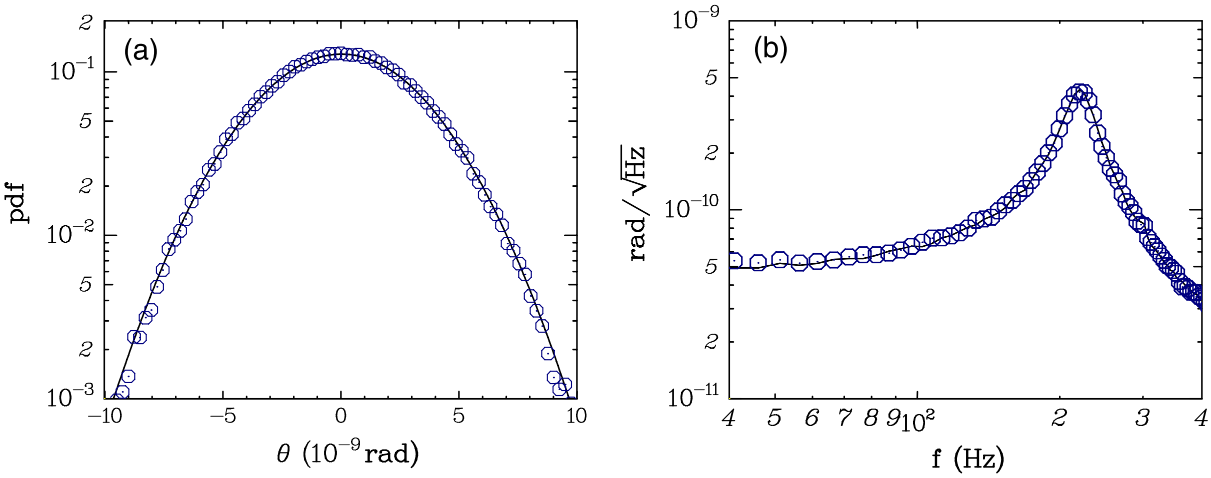

Figure 8. (a) PDF of the fluctuations $\delta\theta = \theta - \bar{\theta}(t)$ when the torque is applied (○), compared with a Gaussian fit of the PDF at equilibrium (continuous line). (b) The measured spectrum of $\delta\theta$ (○) is compared with the prediction from the fluctuation dissipation theorem in equilibrium (continuous line).

and decreases exponentially:

$$R_{\delta\theta}(\tau) = \langle \delta\theta(t+\tau)\delta\theta(t)\rangle = \frac{k_\mathrm{B}T}{C\sin(\varphi)} \exp\left(-\frac{|\tau|}{\tau_\alpha}\right)\sin(\psi|\tau| + \varphi), \tag{15}$$

where $\psi^2 \equiv (\omega_0)^2 - (1/\tau_\alpha)^2$ and φ is defined by $\cos(\varphi) = 1/(\omega_0\tau_\alpha)$ and $\sin(\varphi) = \psi/\omega_0$.

Thus we observe experimentally that when we drive the system out of equilibrium, the angular fluctuations $\delta\theta$ are identical (with respect to the expressions above) to those at equilibrium. This is reasonable because the driving amplitudes that we have used never drive the system into a non-linear regime. The behavior could be very different in this case. We verify the same properties for the sinusoidal time prescription of the torque, and use the equilibrium expression for the correlation function in the following sections.

7.2. Work distribution

In figures 3, 4 and 6, we see that the PDFs of the work are Gaussian for any integration time τ and whatever the forcing is. So these distributions are fully characterized by their mean value $\langle W_\tau\rangle$ and their variance $\sigma^2_{W_\tau} = \langle \delta W_\tau^2\rangle = \langle (W_\tau - \langle W_\tau\rangle)^2\rangle$. The external torque M is deterministic, so the mean value of the work done on the system can be written as

$$\langle W_\tau\rangle = \frac{1}{k_\mathrm{B}T}\int_{t_i}^{t_i+\tau} \tilde{M}(t')\langle\dot{\theta}(t')\rangle\,\mathrm{d}t'. \tag{16}$$

We have defined $\tilde{M}(t') = M(t') - aM(t_i)$. The value a depends on the time prescription of the torque that we apply to the oscillator. Choosing $a = 1$ gives a description of the linear ramp and $a = 0$ corresponds to the sinusoidal forcing.

The variance of the PDFs is

$$\sigma^2_{W_\tau} = \frac{1}{(k_\mathrm{B}T)^2}\int_{t_i}^{t_i+\tau}\int_{t_i}^{t_i+\tau} \tilde{M}(t_1)\cdot\tilde{M}(t_2)\langle\delta\dot{\theta}(t_2)\delta\dot{\theta}(t_1)\rangle\,\mathrm{d}t_1\,\mathrm{d}t_2. \tag{17}$$

This expression involves the autocorrelation function of the angular speed $\delta\dot{\theta}$, $(\langle \delta\dot{\theta}(t_2)\delta\dot{\theta}(t_1)\rangle)$. Using the expression for the autocorrelation function of angular fluctuations ($R_{\delta\theta}$, equation (15)), we can calculate exactly the expression for $\langle \delta\dot{\theta}(t_2)\delta\dot{\theta}(t_1)\rangle$:

$$\langle \delta\dot{\theta}(t_1)\delta\dot{\theta}(t_2)\rangle = -\frac{k_{\mathrm{B}}T}{I_{\mathrm{eff}}\sin(\varphi)}\exp\left(-\frac{|t_2-t_1|}{\tau_\alpha}\right)\sin(\psi|t_2-t_1|-\varphi). \tag{18}$$

We have calculated the mean value and the variance of the PDFs in the three situations of interest: stationary and transient cases with a forcing linear in time, and the stationary case with a forcing sinusoidal in time. Details and results can be found in the appendix. In all of the cases, we compare the theoretical PDFs and the symmetry functions with the experimental results. We have plotted in figures 3, 4 and 6 our theoretical PDFs and the corresponding symmetry functions with no adjustable parameters. Within experimental error bars, our analytical and experimental results are in excellent agreement. $S(w_\tau)$ is linear in w_τ because the PDFs of the work are Gaussian. We now want to calculate analytically the corrections to the slope $\Sigma_w(\tau)$ for finite time τ. For a Gaussian distribution, the symmetry function is

$$S(w_\tau) = \frac{2\langle W_\tau\rangle}{\sigma_W^2}w_\tau = \Sigma_w(\tau)w_\tau. \tag{19}$$

The expression for the slope $\Sigma_w(\tau)$ uses only the mean value and the variance of the Gaussian distribution. We define $\Sigma(\tau) = (1-\epsilon(\tau))^{-1}$, where the correction $\epsilon(\tau)$ is a decreasing function of τ. We obtain $\epsilon(\tau) = 0$ for the transient case, which is in agreement with a TFT. For the two steady states, there are corrections to the value 1; we find:

(i) Linear forcing

$$\epsilon(\tau) = \frac{1}{\psi\tau}\left[\frac{A}{\omega_0\tau} - \mathrm{e}^{-\tau/\tau_\alpha}\left(B + \frac{D}{\omega_0\tau}\right)\right]. \tag{20}$$

(ii) Sinusoidal forcing

$$\epsilon(\tau) = \frac{E}{\tau/\tau_\alpha} + \frac{F}{\tau/\tau_\alpha}\mathrm{e}^{-\tau/\tau_\alpha}. \tag{21}$$

Exact values of the coefficients A, B, D, E, F are given in the appendix. These two expressions are in perfect agreement with experimental results as can be seen in figures 4 and 6. These corrections depend on the kind of forcing and it is difficult to predict their form for an arbitrary forcing. Nevertheless, the two situations that we consider are useful as building blocks of such an arbitrary forcing, and they provide a very nice test of our method.

8. Heat fluctuations: theoretical predictions

We now determine an analytical expression for the PDF of the dissipated heat. To do so, we make the same hypothesis as in the case of the work (see section 7.1 above), and we complete them by making additional assumptions to simplify our derivations. We are interested in PDFs of the heat for integration time τ large compared to τ_α, so exponential corrections which are scaling like $\mathrm{e}^{-\tau/\tau_\alpha}$ can be neglected. In the case of sinusoidal forcing,

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this is correct after three or four periods of forcing ($\tau/\tau_\alpha = 1.64n$). Under this assumption, $\theta(t_i{+}\tau)$ and $\theta(t_i)$ are independent, and so are $(\mathrm{d}\theta/\mathrm{d}t)(t_i{+}\tau)$ and $(\mathrm{d}\theta/\mathrm{d}t)(t_i)$. Additionally, as the equation of motion of the oscillator is second order in time, θ and $\mathrm{d}\theta/\mathrm{d}t$ are independent at any given time t. We use the technique proposed in [7]. To obtain the PDF $p(Q_\tau)$ of the heat, we define its Fourier transform, the characteristic function, as

$$\hat{P}_\tau(s) \equiv \int_{-\infty}^{\infty} \mathrm{d}q_\tau\, \mathrm{e}^{\mathrm{i}sq_\tau} p(q_\tau). \tag{22}$$

We then write $p(q_\tau)$ using equation (6) as

$$p(q_\tau) = \int\int \mathrm{d}\theta\, \mathrm{d}\dot{\theta}\, \tilde{P}(\Delta U_\tau - Q_\tau, \theta(t_i+\tau), \theta(t_i), \dot{\theta}(t_i+\tau), \dot{\theta}(t_i)), \tag{23}$$

where $\tilde{P}$ is the joint distribution of the work W_τ, θ and $\mathrm{d}\theta/\mathrm{d}t$ at the beginning and at the end of the time interval τ. This distribution is expected to be Gaussian because W_τ is linear in $\dot{\theta}$ and additionally θ, $\dot{\theta}$ and W_τ are Gaussian. The details of the calculation are given in the appendix.

8.1. Linear forcing

The Fourier transform of the PDF of dissipated heat can be exactly calculated:

$$\hat{P}_\tau(s) = \frac{1}{1+s^2} \exp\left\{-d^2\mathrm{i}s\left(2\frac{\tau}{\tau_\alpha} + \mathrm{i}s\left[2\frac{\tau}{\tau_\alpha} + 2\right] + \frac{-16\cos(\varphi)^2 + 4 + 4\mathrm{i}s(4\cos(\varphi)^2+1)}{1+s^2}\right)\right\}.$$

As far as we know, there is no analytic expression for the inverse Fourier transform of this function, or for the PDF of dissipated heat. However we can make some comments. This expression is very similar to the one found in the case of a Brownian particle [7]. The factor $(1+s^2)^{-1}$ is the Fourier transform of an exponential PDF and this is directly connected to the exponential tails of the PDF. Moreover the PDF is not symmetric around its mean, because there is a non-vanishing third moment. In this expression, only two terms depend on τ. For large τ, this expression reduces to

$$\hat{P}_\tau(s) = \frac{1}{1+s^2} \exp\left\{-2\mathrm{i}d^2\frac{\tau}{\tau_\alpha}s(1+\mathrm{i}s)\right\}. \tag{24}$$

This expression will turn out to be similar to the one obtained with a sinusoidal forcing, as we will comment on in the next section.

Both expressions depend on the non-dimensional factor d defined as

$$d = \sqrt{\frac{1}{Ck_\mathrm{B}T}\frac{M_0}{\omega_0\tau_r}}. \tag{25}$$

All moments of the distribution of Q_τ are linear with d^2 and $\langle\dot{\theta}\rangle/\sqrt{\langle\delta\dot{\theta}^2\rangle} = d$. So d^2 compares the mean value of the angular speed to the root mean square of the angular speed fluctuations. This coefficient d^2 increases when the system is driven further from equilibrium. We consider it as a measure of the distance to equilibrium. In our system d is positive, but smaller than 1, so we are out of equilibrium but not very far from it ($d = 0.059$).

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8.2. Sinusoidal forcing

Just like in the experiments, we choose the integration time τ to be a multiple of the period of the forcing, so $\langle \Delta U_\tau \rangle = 0$ and therefore $\langle W_\tau \rangle = -\langle Q_\tau \rangle$. Within this framework, we find that the PDF of ΔU_τ is exponential:

$$P(\Delta U_\tau) = \tfrac{1}{2}\exp(-|\Delta U_\tau|). \tag{26}$$

It is independent of τ because ΔU_τ depends only on θ and $\mathrm{d}\theta/\mathrm{d}t$ at times t_i and $t_i+\tau$ which are uncorrelated. This expression is in perfect agreement with the experimental PDFs for all times (see figure 7(b)). Some algebra then yields for the characteristic function of Q

$$\hat{P}_\tau(s) = \frac{1}{1+s^2}\exp\left(\mathrm{i}\langle Q_\tau\rangle s - \frac{\sigma_W^2}{2}s^2\right). \tag{27}$$

The characteristic function of heat fluctuations is therefore the product of the characteristic function of an exponential distribution $(1/(1+s^2))$ with that of a Gaussian distribution $(\exp(\mathrm{i}\langle Q_\tau\rangle s - (\sigma_W^2/2)s^2))$. Thus the PDF of heat fluctuations is nothing but the convolution of a Gaussian and an exponential PDF, just as if W_τ and ΔU_τ were independent. The inverse Fourier transform can be computed exactly:

$$P(Q_\tau) = \frac{1}{4}\exp\left(\frac{\sigma_W^2}{2}\right)\left[\mathrm{e}^{Q_\tau - \langle Q_\tau\rangle}\,\mathrm{erfc}\left(\frac{Q_\tau - \langle Q_\tau\rangle + \sigma_W^2}{\sqrt{2\sigma_W^2}}\right)\right.$$
$$\left. +\ \mathrm{e}^{-(Q_\tau - \langle Q_\tau\rangle)}\,\mathrm{erfc}\left(\frac{-Q_\tau + \langle Q_\tau\rangle + \sigma_W^2}{\sqrt{2\sigma_W^2}}\right)\right], \tag{28}$$

where $\mathrm{erfc}(x) = 1 - \mathrm{erf}(x)$ stands for the complementary erf function. In figure 7(c), we have plotted the analytical PDF from equation (28) together with the experimental ones, using values of σ_W^2 and $\langle Q_\tau\rangle$ from the experiment and no adjustable parameters. The agreement is perfect for all values of n, i.e. for any time τ. From equation (28), we isolate three different regions for $S(q_\tau)$:

(I) If $Q_\tau > \sigma_W^2 + |\langle Q_\tau\rangle| = 3|\langle Q_\tau\rangle| + \mathcal{O}(1)$, then $S(q_\tau) = 2 + \mathcal{O}(1/\tau)$. This domain of S_τ corresponds to fluctuations larger than three times the average value. The PDF has exponential tails, corresponding to an exponential distribution with a non-vanishing mean.

(II) If $Q_\tau < \sigma_W^2 - |\langle Q_\tau\rangle| = |\langle Q_\tau\rangle| + \mathcal{O}(1)$, then $S(q_\tau) = \Sigma(n)q_\tau + \mathcal{O}(1/\tau)$ with $\Sigma_q(n) = 2|\langle Q_\tau\rangle|/\sigma_W^2 = \Sigma_w(n)$. In this domain, values of the heat are small and heat fluctuations behave like work fluctuations. The slope $\Sigma(\tau)$ is the same as the one found for work fluctuations. The exact correction to the asymptotic value 1 is plotted in figure 7(e) and again it describes perfectly the experimental behavior.

(III) For $\sigma_W^2 - |\langle Q_\tau\rangle| < Q_\tau < \sigma_W^2 + |\langle Q_\tau\rangle|$, there is an intermediate region connecting domains (I) and (II) by a second-order polynomial: $S(q_\tau) = 2 - (\Sigma(\tau)/4)(q_\tau - (1 + 2/\Sigma(\tau)))^2 + \mathcal{O}(1/\tau)$.

These three domains offer a perfect description of the three regions observed experimentally (figure 7(d)).

Now, we examine the limit of infinite τ in which the SSFT is supposed to hold. To do this, we distinguish two variables: the heat Q_τ and the normalized heat q_τ. Their asymptotic behaviors are different because the average heat $\langle Q_\tau \rangle$ depends on τ; more precisely it is linear in τ.

We discuss first Q_τ. The asymptotic shape of the PDF of Q_τ (equation (28)) for large τ is a Gaussian whose variance is σ_W^2, the variance of the PDF of W_τ. Thus, the PDF of Q_τ coincides with the PDF of W_τ for τ strictly infinite. As we have already shown, work fluctuations satisfy the conventional SSFT; therefore heat fluctuations also satisfy the conventional SSFT (equation (9)). We have found three different regions separated by two limit values: the mean and three times the mean. But in the limit of large times τ, the PDF shrinks and only region (II) is relevant. Region (II) corresponds to small fluctuations and it is bounded from above by $|\langle Q_\tau \rangle| + \mathcal{O}(1)$ with the average $\langle Q_\tau \rangle$ being linear in τ. So all the behavior of the fluctuations of Q_τ for large τ lies in region (II) where the symmetry function is linear and the SSFT holds.

We turn now to the normalized heat q_τ. As the average value of Q_τ is linear in τ, rescaling by $\langle Q_\tau \rangle$ is equivalent to a division by τ; the mean of q_τ is then 1. This normalization makes the two limit values constant. The boundary between regions (II) and (III) is $1+\mathcal{O}(1/\tau)$ and the boundary between (III) and (I) is $3+\mathcal{O}(1/\tau)$. The function $S(q_\tau)$ is not linear for large values of $q_\tau > 1$ but is linear just in region (II), for $q_\tau < 1$, i.e. for small fluctuations. So the SSFT is satisfied only for small fluctuations but not for all values of q_τ, and we obtain for q_τ a fluctuation relation which prescribes a symmetry function that is non-linear in q_τ.

These two different pictures, in terms of Q_τ and q_τ, result from taking two non-commutative limits differently. The first description using Q_τ implies that the limit τ infinite is taken before the limit of large Q_τ. The second description does the opposite. However, the probability of having large fluctuations decreases with τ and experimentally, for large τ, only the region (II) can be seen, and it is the region in which the SSFT holds.

As we have done in the case of the linear forcing, we introduce a non-dimensional factor d such as

$$d = \sqrt{\frac{1}{Ck_{\mathrm{B}}T}\frac{M_0\omega_d}{\omega_0\rho(\omega_d))}}, \tag{29}$$

$$\rho(\omega_d) = \sqrt{\left(1-\left(\frac{\omega_d}{\omega_0}\right)^2\right)^2 + 4\left(\frac{\omega_d}{\omega_0}\cos(\varphi)\right)^2}. \tag{30}$$

The moments of the distribution of Q_τ are linear with d^2 and, like the linear torque, d is equal to the amplitude of $\dot{\theta}$ divided by $\sqrt{\langle \delta\dot{\theta}^2 \rangle}$. We consider it also as a measure of the distance to equilibrium. In our system d is positive, but smaller than 1, so we are out of equilibrium but not very far from it: here $d = 0.18$.

9. Discussion and conclusion

We have studied the fluctuations of energy input and energy dissipation in a harmonic oscillator driven out of equilibrium. This oscillator is very well described by a second-order Langevin equation. We have performed experiments using a torsion pendulum driven out of equilibrium following a stationary protocol in which either the torque increases linearly in time, or it oscillates at a given frequency. We have also studied transient evolutions from the equilibrium state. We have defined the work given to the system as the work of the torque applied during a time τ. Accordingly we have defined the heat dissipated by the pendulum during this time τ, by writing the first principle of thermodynamics for between the two states separated by time τ.

Fluctuations relations are obtained experimentally for both the work and the heat, for the stationary and transient evolutions.

We have experimentally observed that angle fluctuations of the Brownian pendulum have the same statistical and dynamical properties at equilibrium and for any non-equilibrium driving. From this observation, we have derived expressions for the probability density functions of the work and the heat. In our system, fluctuations of the angle are Gaussian, and so are fluctuations of the work w_τ. So the symmetry functions $S(w_\tau)$ of the work are linear, and we have calculated exactly the time correction to the coefficient of proportionality between $S(w_\tau)$ and w_τ. These corrections match perfectly the experimental results, both in the case of a forcing linear in time and in the case of one sinusoidal in time. We have also computed the analytic expression for the Fourier transform of the PDFs of the dissipated heat. For the sinusoidal forcing, we have obtained for the first time an analytic expression for the PDF of the heat. This expression is in excellent agreement with the experimental measurements. For a torque linear in time, the PDF of the heat has no simple expression but its Fourier transform gives insight into the behavior of the symmetry function of the heat. It is very similar to the one obtained in the case of a first-order Langevin dynamics [7]. We emphasize here that our analytical derivations are strongly connected to experimental observations on the properties of the noise; and are therefore different from any previous theoretical approach.

We have introduced a dimensionless variable d which we think is a measure of the distance from equilibrium: the average dissipation rate is proportional to d, and it increases when the system is further from equilibrium. d is also proportional to the strength of the driving and in the fluctuation relations, it gives a proper unit for measuring the amplitude of fluctuations. So d plays the same role as the dissipation coefficient (the viscosity in our case) in the fluctuation dissipation theorem at equilibrium. We have an expression for d for the two different time prescriptions we have used. These expressions can be generalized:

$$d^2 = \frac{\langle \dot{\theta}^2 \rangle}{\langle \delta\dot{\theta}^2 \rangle}. \tag{31}$$

The numerator corresponds to the solution of the Langevin equation when removing the thermal noise term ($\eta = 0$). The denominator corresponds to the variance of thermal fluctuations of the angular speed $\delta\dot{\theta}$.

Acknowledgments

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Appendix A. Work fluctuations

In this section, we calculate the mean and the variance of the work done on the system in the following cases:

(i) Transient state, linear forcing.
(ii) Steady state, linear forcing.
(iii) Steady state, sinusoidal forcing.

A.1. The TFT, forcing linear in time

The torque is $M(t) = M_0 t/\tau_r$. The mean value of the angular displacement is the solution of equation (1):

$$\langle\theta\rangle = \frac{M_0}{\psi C\tau_r}(\mathrm{e}^{-t/\tau_\alpha}\sin(\psi t + 2\varphi) + \psi t - \sin(2\varphi)). \tag{A.1}$$

For the work done on the system, the PDFs are Gaussian for all integration time τ. The mean of the PDF of W_τ for a given τ is

$$\langle W_\tau\rangle = \frac{M_0^2}{k_\mathrm{B}T\psi C\tau_r^2}\left[\frac{1}{2}\psi\tau^2 + \tau\mathrm{e}^{-\tau/\tau_\alpha}\sin(\psi\tau + 2\varphi) + \frac{1}{\omega_0}(\mathrm{e}^{-\tau/\tau_\alpha}\sin(\psi\tau + 3\varphi) - \sin(3\varphi))\right], \tag{A.2}$$

and its variance is

$$\sigma_{W_\tau}^2 = \frac{2M_0^2}{k_\mathrm{B}T\psi C\tau_r^2}\left[\frac{1}{2}\psi\tau^2 + \tau\mathrm{e}^{-\tau/\tau_\alpha}\sin(\psi\tau + 2\varphi) + \frac{1}{\omega_0}(\mathrm{e}^{-\tau/\tau_\alpha}\sin(\psi\tau + 3\varphi) - \sin(3\varphi))\right], \tag{A.3}$$

$$\sigma_{W_\tau}^2 = 2\langle W_\tau\rangle. \tag{A.4}$$

A.2. The SSFT, forcing linear in time

The torque is $M(t) = M_0 t/\tau_r$. The mean value of the angular displacement is the solution of equation (1) after some τ_α. Thus the exponential term has vanished:

$$\langle\theta\rangle = \frac{M_0}{\psi C\tau_r}(\psi t - \sin(2\varphi)). \tag{A.5}$$

For the work done on the system, the PDFs are Gaussian for all integration time τ. The mean of the PDF is

$$\langle W_\tau\rangle = \frac{M_0^2}{2k_\mathrm{B}TC\tau_r^2}\tau^2, \tag{A.6}$$

and the variance is

$$\sigma_{W_\tau}^2 = \frac{2M_0^2}{k_\mathrm{B}T\psi C\tau_r^2}\left[\frac{1}{2}\psi\tau^2 + \tau\mathrm{e}^{-\tau/\tau_\alpha}\sin(\psi\tau + 2\varphi) + \frac{1}{\omega_0}(\mathrm{e}^{-\tau/\tau_\alpha}\sin(\psi\tau + 3\varphi) - \sin(3\varphi))\right]. \tag{A.7}$$

From this, we deduce

$$\epsilon(\tau) = \frac{1}{\psi\tau}\left\{A - \mathrm{e}^{-\tau/\tau_\alpha}\left(B + \frac{D}{\omega_0\tau}\right)\right\}, \tag{A.8}$$

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where

$$
\begin{aligned}
A &= 2\frac{\sin(3\varphi)}{\omega_0 \tau}, \\
B &= 2\sin(\psi\tau + 2\varphi), \\
D &= 2\sin(\psi\tau + 3\varphi).
\end{aligned}
$$

A.3. The SSFT, forcing sinusoidal in time

The torque is $M(t) = M_0 \sin(\omega_d t)$. The mean value of the angular displacement is

$$
\langle \theta \rangle = \theta_0 \sin(\omega_d t + \beta) \qquad \text{where } \theta_0 = \frac{M_0}{C\rho(\omega_d)}, \tag{A.9}
$$

where

$$
\begin{aligned}
\cos(\beta) &= \frac{1-(\omega_d/\omega_0)^2}{\rho(\omega_d)} \qquad \text{and} \qquad \sin(\beta) = \frac{-2\,(\omega_d/\omega_0)\cos(\varphi)}{\rho(\omega_d)}, \\
\rho(\omega_d) &= \sqrt{\left(1-\left(\frac{\omega_d}{\omega_0}\right)^2\right)^2 + 4\left(\frac{\omega_d}{\omega_0}\cos(\varphi)\right)^2}.
\end{aligned} \tag{A.10}
$$

For the work done on the system, the PDFs are Gaussian for all integration times τ. The mean of the PDF is

$$
\langle W_n \rangle = \frac{M_0^2}{k_{\rm B} T C} \left(\frac{\omega/\omega_0}{\rho(\omega)}\right)^2 (\tau/\tau_\alpha), \tag{A.11}
$$

and the variance is

$$
\sigma_n^2 = 2\langle W_n \rangle + E + F \mathrm{e}^{-\tau/\tau_\alpha}, \tag{A.12}
$$

where

$$
E = -\frac{\langle W_n\rangle (1 + (\omega/\omega_d)^2)\cos(2\beta)}{(\omega/\omega_0)^2 (\tau/\tau_\alpha)}, \tag{A.13}
$$

$$
\begin{aligned}
F = -\frac{\langle W_n\rangle}{(\omega/\omega_0)^2 \cdot (\tau/\tau_\alpha))} &[\sin(\psi\tau + \varphi)\cos(2\beta) + (\omega/\omega_0)^2 \sin(\psi\tau - \varphi)\cos(2\beta) \\
&+ (\omega/\omega_0)\sin(\psi\tau)\sin(2\beta)].
\end{aligned} \tag{A.14}
$$

Appendix B. Heat fluctuations

In this section, we calculate the Fourier transform of the PDF of the dissipated heat in two cases:

(i) Linear forcing.

(ii) Sinusoidal forcing.

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B.1. Linear forcing

We introduce first non-dimensional parameters:

$$\tilde{x}(t) = \sqrt{\frac{C}{k_\mathrm{B}T}}\left(\theta(t) - \frac{M(t)}{C}\right), \qquad \dot{x} = \sqrt{\frac{I_\mathrm{eff}}{k_\mathrm{B}T}}\dot{\theta}(t). \tag{B.1}$$

The mean value and the variance of $\tilde{x}$ and $\dot{x}$ can be simply expressed:

$$d = \sqrt{\frac{M_0^2}{Ck_\mathrm{B}T}}\frac{1}{\omega_0\tau_r}, \qquad \langle\tilde{x}\rangle = -2\cdot d\cdot\cos(\varphi), \quad \langle\dot{x}\rangle = d, \quad \langle\delta\tilde{x}^2\rangle = 1, \quad \langle\delta\dot{x}^2\rangle = 1, \tag{B.2}$$

where d is a non-dimensional value. Integrating by parts, the work W_τ can be rewritten as

$$W_\tau = d\cdot\omega_0[(t_i+\tau)x(t_i+\tau) - t_i x(t_i)] - \frac{(\mathrm{d}\omega_0)^2}{2}[(t_i+\tau)^2 - t_i^2] + W^*, \qquad W^* = -(\mathrm{d}\omega_0)\int_{t_i}^{t_i+\tau}\tilde{x}(t')\,\mathrm{d}t'. \tag{B.3}$$

With these definitions, we obtain $Q_\tau = \frac{1}{2}\Delta\tilde{x}_\tau + \frac{1}{2}\Delta\dot{x}_\tau - W^*$ and $\langle Q_\tau\rangle = -\langle W^*\rangle$. Like the distribution of W_τ, the distribution of W^* is Gaussian for all values of τ and we find

$$\langle W^*\rangle = 2d^2\tau/\tau_\alpha, \qquad \sigma_{W^*}^2 = 2d^2(2\tau/\tau_\alpha + 1 - 4\cos(\varphi)^2). \tag{B.4}$$

For convenience, we introduce a five-dimensional vector: $Y = (W^*, \tilde{x}(t_i+\tau), \tilde{x}(t_i), \dot{x}(t_i+\tau), \dot{x}(t_i))$. As explained in section 3.3 the probability density function $\tilde{P}$ is Gaussian and is thus fully characterized by the covariance matrix $\mathcal{C}$ defined as

$$\mathcal{C}_{ij} = \langle(Y_i - \langle Y_i\rangle)(Y_j - \langle Y_j\rangle)^\dagger\rangle, \tag{B.5}$$

where $Z^\dagger$ denotes the complex conjugate of Z. So the distribution $\tilde{P}$ is written as

$$\tilde{P}(Y) = \sqrt{\frac{1}{(2\pi)^5\det\mathcal{C}}}\exp\left(-\frac{1}{2}(Y - \langle Y\rangle)^\mathrm{T}C^{-1}(Y - \langle Y\rangle)\right), \tag{B.6}$$

where Z^T denotes the transpose of Z. We suppose that the integration time is larger than the relaxation time. Under this assumption, $\theta(t_i+\tau)$ and $\theta(t_i)$ are independent, and so are $\dot{\theta}(t_i+\tau)$ and $\dot{\theta}(t_i)$. As the equation of motion of the oscillator is second order in time, θ and $\dot{\theta}$ are independent at any given times t. With these hypotheses, we get

$$\begin{aligned}\langle\delta\tilde{x}(t_i)\delta\tilde{x}(t_i+\tau)\rangle &= \langle\delta\tilde{x}(t_i)\delta\dot{x}(t_i)\rangle = \langle\delta\tilde{x}(t_i)\delta\dot{x}(t_i+\tau)\rangle \\ &= \langle\delta\dot{x}(t_i)\delta\tilde{x}(t_i+\tau)\rangle = \langle\delta\dot{x}(t_i)\delta\dot{x}(t_i+\tau)\rangle \\ &= \langle\delta\dot{x}(t_i+\tau)\delta\tilde{x}(t_i+\tau)\rangle = 0.\end{aligned} \tag{B.7}$$

The other coefficients of the covariance matrix are

$$\begin{aligned}\langle \delta W^* \delta\tilde{x}(t_i)\rangle &= \langle \delta W^* \delta\tilde{x}(t_i+\tau)\rangle = -2d\cos(\varphi),\\ \langle \delta W^* \delta\dot{x}(t_i)\rangle &= \langle \delta W^* \delta\dot{x}(t_i+\tau)\rangle = -d.\end{aligned} \tag{B.8}$$

We now compute the Fourier transform of the PDF of the heat. We define two quantities:

$$e = \begin{pmatrix}1\\0\\0\\0\\0\end{pmatrix} \qquad N = \begin{pmatrix}0&0&0&0&0\\0&1&0&0&0\\0&0&-1&0&0\\0&0&0&1&0\\0&0&0&0&-1\end{pmatrix}. \tag{B.9}$$

One can write Q_τ as $Q_\tau = \frac{1}{2}Y^{\mathrm{T}}NY - e^{\mathrm{T}}Y$. The Fourier transform can thus be written as

$$\begin{aligned}\hat{P}_\tau(s) &= \int \frac{\mathrm{d}Y}{\sqrt{(2\pi)^5\det\mathcal{C}}}\exp(M),\\ M &= -\tfrac{1}{2}(\delta Y)^{\mathrm{T}}\mathcal{C}^{-1}(\delta Y) + \mathrm{i}s(\tfrac{1}{2}Y^{\mathrm{T}}NY - \mathrm{e}^{\mathrm{T}}Y).\end{aligned} \tag{B.10}$$

We use a new variable defined as

$$Y' = Y - (1-\mathrm{i}s\mathcal{C}\cdot N)^{-1}(\langle Y\rangle - \mathrm{i}s\cdot\mathcal{C}\cdot e). \tag{B.11}$$

With this definition, the argument in the exponential M can be rewritten as

$$\begin{aligned}M &= -\tfrac{1}{2}Y'(\mathcal{C}^{-1} - \mathrm{i}sN)Y' + \gamma,\\ \gamma &= \frac{\mathrm{i}s}{2}[(N\langle Y\rangle - e)^{\mathrm{T}}(1-\mathrm{i}s\mathcal{C}N)^{-1}(\langle Y\rangle - \mathrm{i}s\mathcal{C}e) - \langle Y\rangle^{\mathrm{T}}e].\end{aligned} \tag{B.12}$$

Changing the integration variable to Y' yields

$$\begin{aligned}\hat{P}_\tau(s) &= \int \frac{\mathrm{d}Y'}{\sqrt{(2\pi)^5\det\mathcal{C}}}\exp\left(-\frac{1}{2}Y'^{\mathrm{T}}(\mathcal{C}^{-1}-\mathrm{i}sN)Y'\right)\cdot\exp(\gamma)\\ &= \frac{\exp(\gamma)}{\sqrt{\det(1-\mathrm{i}s\mathcal{C}\cdot N)}}.\end{aligned} \tag{B.13}$$

To get an explicit expression for $\hat{P}_\tau$, the inverse of the matrix $(1-\mathrm{i}s\mathcal{C}\cdot N)$ is required in the expression for γ and its determinant. These are obtained as follows. We find

$$1-\mathrm{i}s\mathcal{C}\cdot N = \begin{pmatrix}1 & \mathrm{i}s(2d\cos(\varphi)) & \mathrm{i}s(-2d\cos(\varphi)) & \mathrm{i}sd & -\mathrm{i}sd\\ 0 & 1-\mathrm{i}s & 0 & 0 & 0\\ 0 & 0 & 1+\mathrm{i}s & 0 & 0\\ 0&0&0&1-\mathrm{i}s&0\\ 0&0&0&0&1+\mathrm{i}s\end{pmatrix}.$$

The determinant of the matrix is $(1+s^2)^2$. For the inverse of this matrix, we get

$$(1-\mathrm{i}s\mathcal{C}\cdot N)^{-1} = \begin{pmatrix}1 & -\frac{\mathrm{i}s}{1-\mathrm{i}s}(2d\cos(\varphi)) & \frac{\mathrm{i}s}{1+\mathrm{i}s}(2d\cos(\varphi)) & -\frac{\mathrm{i}s}{1-\mathrm{i}s}d & \frac{\mathrm{i}s}{1+\mathrm{i}s}d\\ 0 & \frac{1}{1-\mathrm{i}s} & 0 & 0 & 0\\ 0 & 0 & \frac{1}{1+\mathrm{i}s} & 0 & 0\\ 0&0&0&\frac{1}{1-\mathrm{i}s}&0\\ 0&0&0&0&\frac{1}{1+\mathrm{i}s}\end{pmatrix}.$$

We deduce γ:

$$\gamma = -\mathrm{i}s\langle W^*\rangle - \frac{s^2}{2}\left[\sigma_W^2 + 2d^2(1+4\cos(\varphi)^2) + \frac{4\mathrm{i}sd^2}{1+s^2}(4\cos(\varphi)^2-1) + \frac{4s^2d^2}{1+s^2}(4\cos(\varphi)^2+1)\right]. \tag{B.14}$$

So the analytic expression for the Fourier transform of the PDF of the heat dissipated during a linear forcing is

$$\hat{P}_\tau(s) = \frac{1}{1+s^2}\exp\left\{-d^2\mathrm{i}s\left(2\frac{\tau}{\tau_\alpha} + \mathrm{i}s\left[2\frac{\tau}{\tau_\alpha}+2\right] + \frac{-16\cos(\varphi)^2+4+4\mathrm{i}s(4\cos(\varphi)^2+1)}{1+s^2}\right)\right\}. \tag{B.15}$$

B.2. Sinusoidal forcing

We determine in a first time period the Gaussian joint distribution $\tilde{P}$ of W_τ, $\theta(t_i)$, $\theta(t_i+\tau)$, $\dot\theta(t_i)$ and $\dot\theta(t_i+\tau)$. For notational convenience, we introduce a five-dimensional vector: $\vec{X} = (W_\tau, \theta(t_i+\tau), \theta(t_i), \dot\theta(t_i+\tau), \dot\theta(t_i))$. The PDF $\tilde{P}$ is fully characterized by the covariance matrix $\mathcal{C}$:

$$\mathcal{C}_{ij} = \langle (X_i - \langle X_i\rangle)(X_j - \langle X_j\rangle)^\dagger\rangle, \tag{B.16}$$

where $Z^\dagger$ denotes the complex conjugate of Z. We suppose that the integration time is larger than the relaxation time. Under this assumption, $\theta(t_i+\tau)$ and $\theta(t_i)$ are independent, and so are $\dot\theta(t_i+\tau)$ and $\dot\theta(t_i)$. As the equation of motion of the oscillator is second order in time, θ and $\dot\theta$ are independent at any given times t. With these hypotheses, we get

$$\begin{aligned}\langle\delta\theta(t_i)\delta\theta(t_i+\tau)\rangle &= \langle\delta\theta(t_i)\delta\dot\theta(t_i)\rangle = \langle\delta\theta(t_i)\delta\dot\theta(t_i+\tau)\rangle \\ &= \langle\delta\dot\theta(t_i)\delta\theta(t_i+\tau)\rangle = \langle\delta\dot\theta(t_i)\delta\dot\theta(t_i+\tau)\rangle \\ &= \langle\delta\dot\theta(t_i+\tau)\delta\theta(t_i+\tau)\rangle = \langle W_\tau\theta(t_i)\rangle \\ &= \langle W_\tau\theta(t_i+\tau)\rangle = \langle W_\tau\dot\theta(t_i)\rangle \\ &= \langle W_\tau\dot\theta(t_i+\tau)\rangle = 0.\end{aligned} \tag{B.17}$$

The covariance matrix is a diagonal matrix:

$$\mathcal{C} = \begin{pmatrix} \sigma_W^2 & 0 & 0 & 0 & 0 \\ 0 & k_\mathrm{B}T/C & 0 & 0 & 0 \\ 0 & 0 & k_\mathrm{B}T/C & 0 & 0 \\ 0 & 0 & 0 & k_\mathrm{B}T/I_\mathrm{eff} & 0 \\ 0 & 0 & 0 & 0 & k_\mathrm{B}T/I_\mathrm{eff}\end{pmatrix}. \tag{B.18}$$

ΔU_τ is a function of the positions and velocities at the beginning (t_i) and at the end $(t_i+\tau)$. Thus, ΔU_τ and W_τ can be considered as independent. The PDF of Q_τ is the convolution of the PDF of W_τ which is Gaussian and the PDF of ΔU_τ:

$$P(Q_\tau) = \int_{-\infty}^{+\infty} P_{W_\tau}(z)P_{\Delta U_\tau}(Q_\tau+z)\,\mathrm{d}z. \tag{B.19}$$

We first calculate exactly the PDF of the variation of the internal energy. We have shown that $\theta(t_i)$, $\theta(t_i+\tau)$, $\dot{\theta}(t_i)$ and $\dot{\theta}(t_i+\tau)$ are independent. The Fourier transform of the PDF is

$$\hat{P}_{\Delta U_\tau}(s) = \hat{P}_{E_p(t_i+\tau)}(s)\cdot\hat{P}_{E_c(t_i+\tau)}(s)\cdot\hat{P}_{E_p(t_i)}(-s)\cdot\hat{P}_{E_c(t_i)}(-s), \tag{B.20}$$

where $E_p = (1/2k_{\mathrm{B}}T)C\theta^2$ and $E_c = (1/2k_{\mathrm{B}}T)I_{\mathrm{eff}}\dot{\theta}^2$. The distribution of θ is Gaussian with variance $k_{\mathrm{B}}T/C$. The distribution of E_p and the distribution of E_c are the same:

$$P_{E_p}(x) = P_{E_c}(x) = \frac{1}{\sqrt{\pi x}}\exp(-x). \tag{B.21}$$

The Fourier transform of this distribution is $\hat{P}(s) = (1-\mathrm{i}s)^{-1/2}$. This distribution is the same for E_p and E_c at t_i and $t_i+\tau$. Thus the Fourier transform of the variation of internal energy is

$$\hat{P}_{\Delta U_\tau}(s) = (1+s^2)^{-1}, \tag{B.22}$$

and the probability is

$$P(\Delta U_\tau) = \tfrac{1}{2}\exp(-|\Delta U_\tau|). \tag{B.23}$$

As ΔU_τ and W_τ are independent, the Fourier transform of the dissipated heat can be calculated:

$$\hat{P}_{Q_\tau}(s) = \frac{\exp\Big(\mathrm{i}\langle Q_\tau\rangle - (\sigma_W^2/2)s^2\Big)}{1+s^2}. \tag{B.24}$$

This expression can be inverted because it is simply the convolution of a Gaussian distribution with an exponential distribution. So we find equation (28).

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