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Work, dissipation, and fluctuations in nonequilibrium physics

Experimental study of work fluctuations in a harmonic oscillator

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Abstract

The work fluctuations of a harmonic oscillator in contact with a thermostat and driven out of equilibrium by an external force are studied experimentally. For the work both the transient and stationary state fluctuation theorems hold. The finite time corrections are very different from those of a first order Langevin equation. The heat and work fluctuations are studied when a periodic forcing is applied to the oscillator. The importance of the choice of the 'good work' to compute the free energy from the Jarzynski equality is discussed. ***To cite this article: S. Joubaud et al., C. R. Physique 8 (2007).***

Résumé

Étude expérimentale des fluctuations du travail dans un oscillateur harmonique. Nous étudions expérimentalement les fluctuations du travail d'une force externe sur un oscillateur harmonique en contact avec un bain thermique. Nous trouvons que les théorèmes de fluctuations pour les états transitoires et stationnaires sont vérifiés. Toutefois les corrections de temps fini pour l'état stationnaire sont très différentes de celles calculées dans le cadre de l'équation de Langevin du premier ordre. Nous étudions aussi le forçage périodique de l'oscillateur. Enfin nous discutons l'importance du choix du « bon travail » pour calculer l'énergie libre en partant de l'égalité de Jarzynski. ***Pour citer cet article : S. Joubaud et al., C. R. Physique 8 (2007).***

Keywords: Fluctuation theorems; Work; Out of equilibrium

Mots-clés : Théorèmes de fluctuation ; Travail ; Hors-équilibre

1. Introduction

Thermal fluctuations play a very important role in the out of equilibrium dynamics of small systems such those that one can find in nanotechnologies and biophysics. Indeed in these systems the amount of injected energy is often comparable to that of thermal fluctuations, which may produce unwanted and unexpected behavior. For example very large fluctuations may force the system to move in the opposite direction of the one imposed by the external forces. In the same way the heat exchanges with the thermal bath are such that the heat may instantaneously flow from a cold

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source to a hot one. Of course these are not violations of the second principle of thermodynamics which fixes only the mean values and does not make any statement for fluctuations. The recent fluctuation theorems FTs [1–7] allow one to compute the probability of these negative events for the work and for the heat flux. It is interesting 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 either the Jarzynski equality (JE) [9,8] or the Crooks relation (CR) [10]. Indeed the JE and CR take advantage of these work fluctuations and relate ΔF to the probability distribution function (PDF) of the work performed on the system to drive it from A to B along any path γ (either reversible or irreversible) in the system parameter space. In this article we will study the possibility of using these theorems on real experimental data. Indeed the proofs of FTs and JE are based on a certain number of hypothesis; experimenting on real devices is useful not only to check those hypothesis, but also to check whether the predicted effects are observable or remain only a theoretical tool. There are not many experimental tests of FTs. Some of them are performed in dynamical systems [11] in which the interpretation of the results is very difficult. Other experiments are performed on stochastic systems, one on a Brownian particle in a moving optical trap [12] and another on electrical circuits driven out of equilibrium by injecting in it a small current [13]. The last two systems are described by first order Langevin equations and the results agree with the predictions of Refs. [7,6]. In this paper we study the out-of-equilibrium fluctuations of a harmonic oscillator whose damping is mainly produced by the viscosity of the surrounding fluid, which acts as a thermal bath of temperature T. The test using a harmonic oscillator is particularly important because the harmonic oscillator is the basis of many physical processes [14,15]. The article is organized as follow. In the next section we will briefly describe the experimental set-up. The fluctuation theorem will be studied is section three. In Section 4 we will describe the results for the work and heat for a the stationary state fluctuation theorem when the oscillator is submitted to a periodic driving. In Section 5 the JE and CR are used to compute the free energy. The importance of the choice of the 'good work' for the JE is pointed out too. We show indeed that a definition of work which satisfies FT cannot be used to compute the free energy with JE. Finally we conclude in Section 6.

2. Experimental set-up

We recall here only the main features of the experimental set-up, more details can be found in Refs. [16,18]. The oscillator is a torsion pendulum composed by a brass wire and a glass mirror glued in the middle of this wire. It is enclosed in a cell filled by a water–glycerol solution at 60% concentration. The motion of this pendulum can be described by a second order Langevin equation:

$$I_{\mathrm{eff}}\frac{\mathrm{d}^2\theta}{\mathrm{d}t^2}+\nu\frac{\mathrm{d}\theta}{\mathrm{d}t}+C\theta=M+\sqrt{2k_BT\nu}\eta \tag{1}$$

where θ is the angular displacement of the pendulum, I_{eff} is the total moment of inertia of the displaced masses, ν is the oscillator viscous damping, C is the elastic torsional stiffness of the wire, M is the external torque, k_B the Boltzmann constant and η the noise, delta-correlated in time. In our system the measured parameters are the stiffness $C=4.5\times 10^{-4}\ \mathrm{N\,m\,rad^{-1}}$, the resonant frequency $f_o=\sqrt{C/I_{\mathrm{eff}}}/(2\pi)=217$ Hz and the relaxation time $\tau_\alpha=2I_{\mathrm{eff}}/\nu=9.5$ ms. The external torque M is applied by means of a tiny electric current J flowing in a coil glued behind the mirror. The coil is inside a static magnetic field, hence $M\propto J$. The measurement of θ is performed by a differential interferometer, which uses two laser beams impinging on the pendulum mirror [16,18]. 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_o. The calibration accuracy of the apparatus, tested at $M=0$ using the Fluctuation Dissipation Theorem, is better than 3% (see [18]).

3. Fluctuation theorems

It is important to make a distinction between *Stationary State Fluctuation Theorem* (SSFT) and *Transient Fluctuation Theorem* (TFT) (as defined in Refs. [7,6]). TFT implies that the initial state when the force is applied to the system is an equilibrium one. In contrast SSFT concerns out of equilibrium stationary states where all transients have already

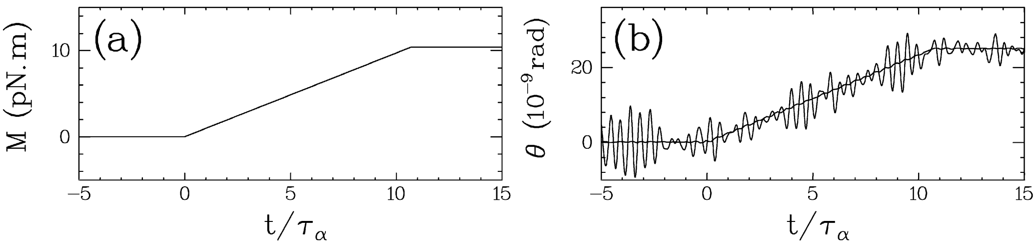

Fig. 1. (a) Typical driving torque applied to the oscillator. (b) Response of the oscillator to the external torque (gray line). The dark line represents the mean response $\bar{\theta}(t)$ to the applied torque $M(t)$.

relaxed. To study SSFT and TFT we apply to the oscillator a time dependent torque $M(t)$ as depicted in Fig. 1(a), and we consider the work W_τ done by $M(t)$ over a time τ:

$$W_\tau = \frac{1}{k_B T} \int_{t_i}^{t_i+\tau} \left[M(t) - M(t_i)\right] \frac{\mathrm{d}\theta}{\mathrm{d}t}\, \mathrm{d}t \tag{2}$$

By definition, the TFT implies that $t_i = 0$ in Eq. (2) whereas $t_i \geqslant 3\tau_\alpha$ for SSFT. As a second choice for $M(t)$, the linear ramp with a rising time τ_r is replaced by a sinusoidal forcing; this leads to a new form of stationary state which has never been considered in the context of FT. We examine first the linear forcing $M(t) = M_o t/\tau_r$ (Fig. 1(a)), with $M_o = 10.4$ pN m and $\tau_r = 0.1$ s $= 10.7\tau_\alpha$. The response of the oscillator to this excitation is comparable to the thermal noise amplitude, as can be seen in Fig. 1(b) where $\theta(t)$ is plotted during the same time interval of Fig. 1(a). Because of thermal noise the power W_τ injected into the system (Eq. (2)) is itself a strongly fluctuating quantity.

The FTs state [7] that the probability density functions (PDF) $P(W_\tau)$ of W_τ satisfies:

$$\ln\left[\frac{P(W_\tau)}{P(-W_\tau)}\right] = \Sigma(\tau) W_\tau \tag{3}$$

where for TFT

$$\Sigma(\tau) = 1, \quad \forall\tau \tag{4}$$

and for SSFT

$$\Sigma(\tau) \to 1 \quad \text{for } \tau \to \infty \tag{5}$$

(see Refs. [6,7] for a clear discussion on the difference between TFT and SSFT).

3.1. Transient fluctuation theorem

We consider first the TFT. The probability density functions $P(W_\tau)$ of W_τ are plotted in Fig. 2(a) for different values of τ. We see that the PDFs are Gaussian for all τ and the mean value of W_τ is a few $k_B T$. We also notice that the probability of having negative values of W is rather high for the small τ. The function

$$S(W_\tau) \equiv \ln\left[\frac{P(W_\tau)}{P(-W_\tau)}\right] \tag{6}$$

is plotted in Fig. 2(b). It is a linear function of W_τ for any τ, that is $S(W_\tau) = \Sigma(\tau) W_\tau$. Within experimental error, we measure the slope $\Sigma(\tau) = 1$. PDF, as can be observed on Fig. 2(b). Thus for our harmonic oscillator the TFT is verified for any time τ. This was expected [2,6], and a derivation of this generic result for a second order Langevin dynamics is given in Refs. [15,19].

3.2. Stationary state fluctuation theorem

We now consider the SSFT with $t_i \geqslant 3\tau_\alpha$ in Eq. (2). We find that the PDFs of W_τ, plotted in Fig. 3(a), are Gaussian with many negative values of W_τ for short τ. The function $S(W_\tau)$, plotted in Fig. 3(b), is still a linear function of

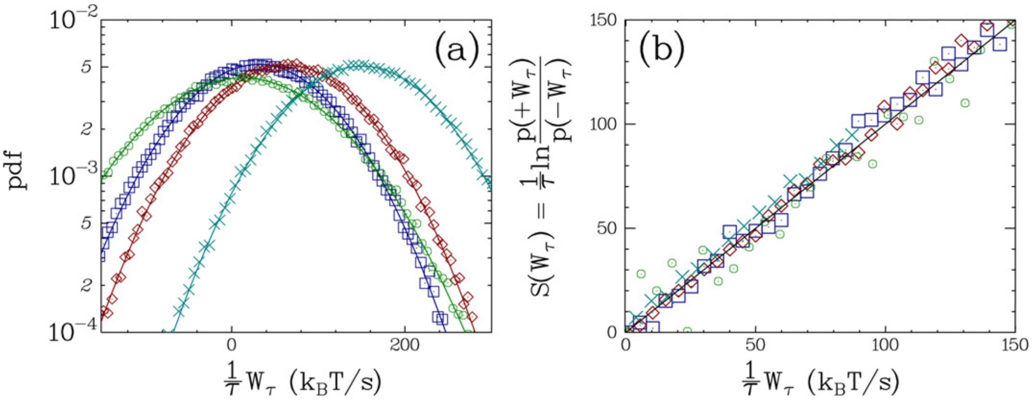

Fig. 2. TFT. (a) $P(W_\tau)$ for TFT for various τ/τ_α: 0.31 (○), 1.015 (□), 2.09 (◇) and 4.97 (×). Continuous lines are Gaussian fits. (b) TFT; $S(W_\tau)$ computed with the PDF of (a). The straight continuous line has slope 1, i.e., $\Sigma(\tau) = 1$, $\forall\tau$.

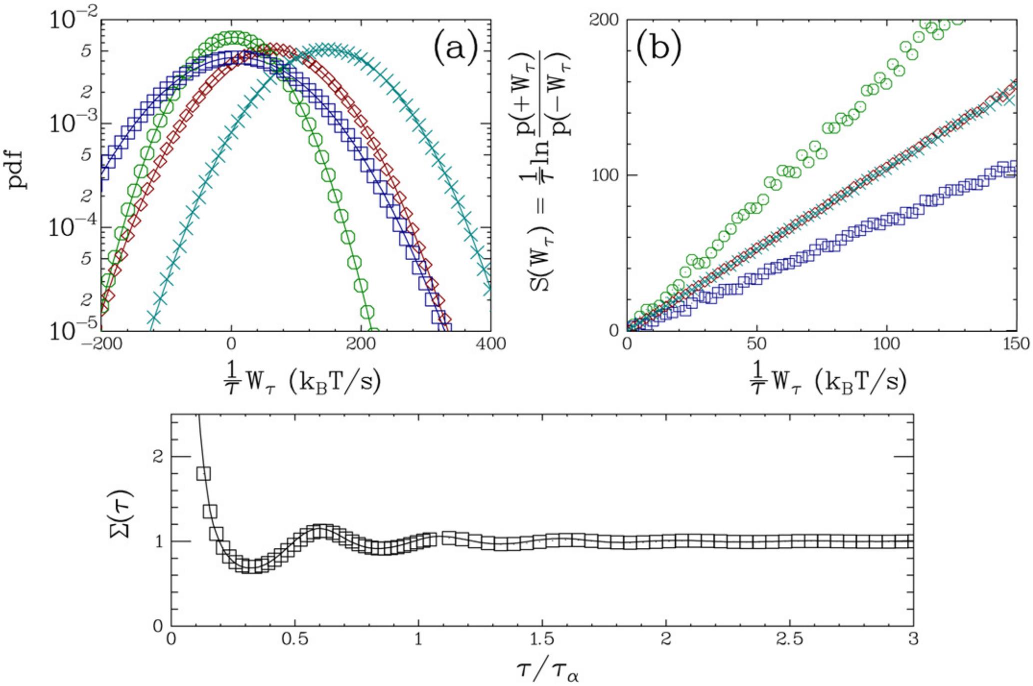

Fig. 3. SSFT with a ramp forcing. (a) PDF of W_τ for various τ/τ_α: 0.019 (○), 0.31 (□), 2.09 (◇) and 4.97 (×). (b) Corresponding functions $S(W_\tau)$. (c) The slope $\Sigma(\tau)$ of $S(W_\tau)$ is plotted versus τ (□: experimental values; continuous line: theoretical prediction from Refs. [15,19] with no adjustable parameter).

W_τ, but, in contrast to TFT, the slope $\Sigma(\tau)$ depends on τ. In Fig. 3(c) the measured values of $\Sigma(\tau)$ are plotted as a function of τ. The function $\Sigma(\tau) \to 1$ for $\tau \gg \tau_\alpha$. Thus SSFT is verified only for large τ. The finite time corrections of SSFT, which present oscillations whose frequency is close to f_0, agree quite well with the theoretical prediction computed for a second order Langevin dynamics [15]. We stress that the finite time correction is in this case very different from that computed in Refs. [6,7] for the first order Langevin equation. The results of Figs. 2 and 3 have been checked for several M_o/τ_r without noticing any difference. The errors bars in the figures are within the size of the symbols, and they come only from the calibration errors of the harmonic oscillator parameters, and statistics of realizations (typically 5×10^5 cycles have been used).

4. Periodic forcing

We describe in this section the results of the periodic forcing. In this case $M(t) = M_o \sin\omega_d t$ and the work expression (Eq. (2)) is replaced by

$$W_n = W_{\tau=\tau_n} = \frac{1}{k_B T} \int_{t_i}^{t_i+\tau} M(t) \frac{\mathrm{d}\theta}{\mathrm{d}t}\, \mathrm{d}t \tag{7}$$

where τ is a multiple of the period of the driving ($\tau = 2n\pi/\omega_d$ with n integer). The starting phase $t_i\omega_d$ is averaged over all possible t_i to increase statistics. This periodic forcing is a stationary state that has never been studied in detail in the context of FT. As already done for the first order Langevin equation [6,7,17], we want to consider here also the heat fluctuations, that is the energy dissipated by the oscillator towards the heat bath. Multiplying Eq. (1) by $\frac{\mathrm{d}\theta}{\mathrm{d}t}$ and then integrating between t_i and $t_i + \tau$, we obtain exactly the first law of thermodynamics. The change in the internal energy ΔU_τ over a time τ is:

$$\Delta U_\tau = U(t_i + \tau) - U(t_i) = Q_\tau + W_\tau \tag{8}$$

where Q_τ is the heat given to the system. Equivalently, $(-Q_\tau)$ is the heat dissipated by the system. For a harmonic oscillator described by a second order Langevin equation (1) the internal energy $U(t)$ and the heat Q_τ have the following expressions:

$$U(t) = \frac{1}{k_B T}\left[\frac{1}{2} I_{\text{eff}}\left[\frac{\mathrm{d}\theta(t)}{\mathrm{d}t}\right]^2 + \frac{1}{2} C\theta(t)^2\right] \tag{9}$$

$$Q_\tau = \Delta U_\tau - W_\tau = -\frac{1}{k_B\ T} \int_{t_i}^{t_i+\tau} \nu \left[\frac{\mathrm{d}\theta}{\mathrm{d}t}(t')\right]^2 \mathrm{d}t' + \frac{1}{k_B\ T} \int_{t_i}^{t_i+\tau} \eta(t') \frac{\mathrm{d}\theta}{\mathrm{d}t}(t')\, \mathrm{d}t' \tag{10}$$

The first term in Eq. (10) corresponds to the viscous dissipation and is always positive, whereas the second term can be interpreted as the work of the thermal noise which have a fluctuating sign.

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: $w_\tau = \frac{W_\tau}{\langle W_\tau \rangle}$ ($q_\tau = \frac{Q_\tau}{\langle Q_\tau \rangle}$). Averages are time-averages, and they are proportional to τ on the stationary state under consideration.

As an example we consider a measurement performed at $M_o = 0.78$ pN m and at $\omega_d/(2\pi) = 64$ Hz. The PDFs of w_τ, ΔU_τ and q_τ are plotted in Fig. 4 for different values of n. The average of ΔU_τ is clearly zero because the time τ is a multiple of the period of the forcing. The PDFs of the work (Fig. 4(a)) are Gaussian for any n whereas the PDFs of heat fluctuations q_τ have exponential tails (Fig. 4(c)). These exponential PDFs can be understood taking into account that, from Eq. (10), $-Q_\tau = W_\tau - \Delta U_\tau$ and that ΔU_τ has an exponential PDF independent of n (Fig. 4(b)). In the case of the periodic forcing the PDF of q_τ can be exactly computed (see Ref. [19]):

$$P(Q_\tau) = \frac{1}{4}\exp\left(\frac{\sigma_W^2}{2}\right)\left[\mathrm{e}^{Q_\tau - \langle Q_\tau\rangle} \operatorname{erfc}\left(\frac{Q_\tau - \langle Q_\tau \rangle + \sigma_W^2}{\sqrt{2\sigma_W^2}}\right) + \mathrm{e}^{-(Q_\tau - \langle Q_\tau\rangle)} \operatorname{erfc}\left(\frac{-Q_\tau + \langle Q_\tau \rangle + \sigma_W^2}{\sqrt{2\sigma_W^2}}\right)\right] \tag{11}$$

where erfc stands for the complementary Erf function and σ_W^2 is the work variance. In Fig. 4(c), we have plotted the analytical PDF from Eq. (11) together with the experimental ones, using the values of σ_W^2 and $\langle Q_\tau \rangle$ from the experiment. The agreement is perfect for all values of n and with no adjustable parameter, using Eq. (11).

To quantify the symmetry of the PDF around the origin, we define the function S as:

$$S(e_\tau) \equiv \frac{1}{\langle E_\tau \rangle} \ln\left[\frac{P(e_\tau)}{P(-e_\tau)}\right] \tag{12}$$

where e_τ stands for either w_τ or q_τ and E_τ stands for either W_τ or Q_τ. The question we ask is whether:

$$\lim_{\tau\to\infty} S(e_\tau) = e_\tau \tag{13}$$

as required by SSFT. $S(q_\tau)$ is plotted in Fig. 4(d) for different values of n; three regions appear:

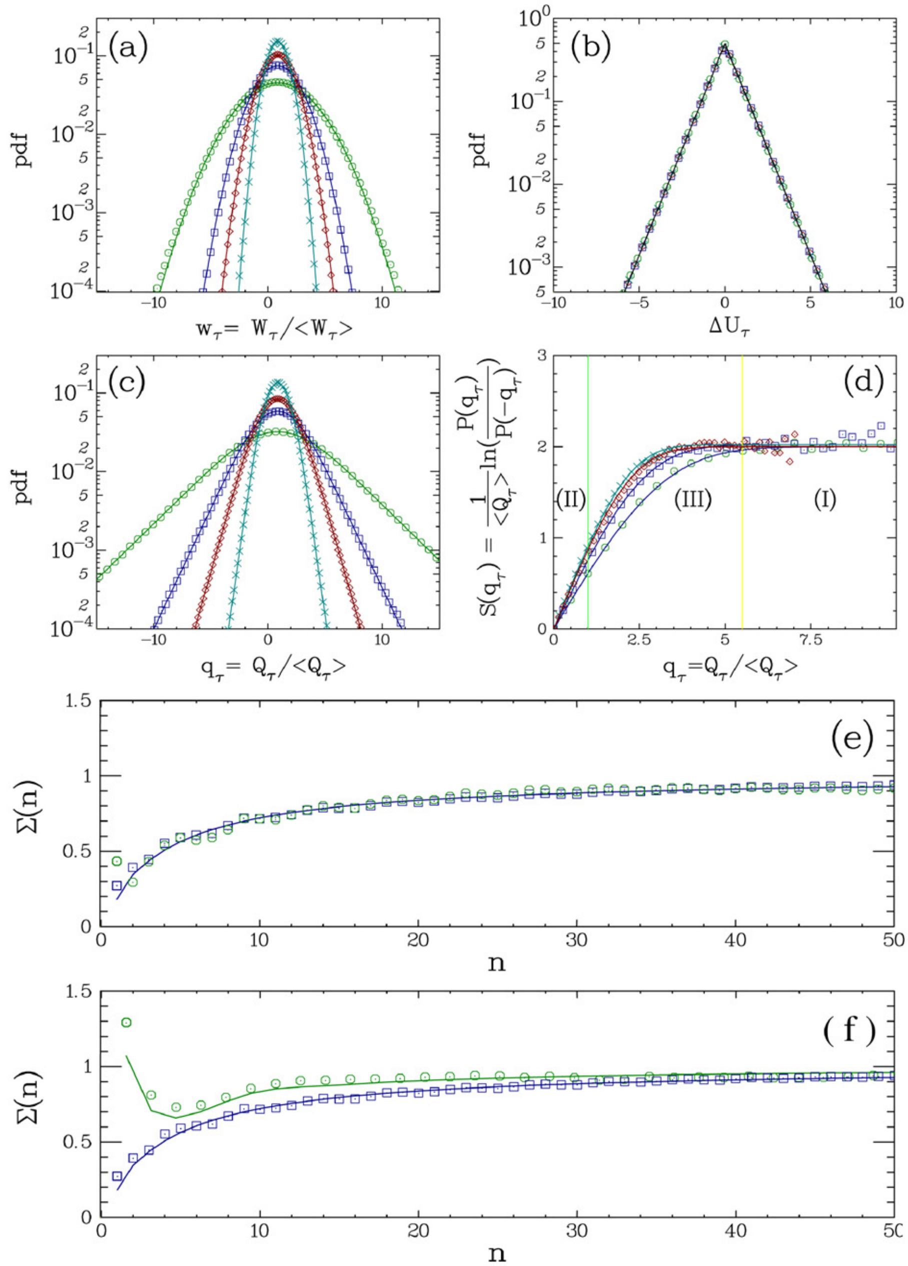

Fig. 4. Sinusoidal forcing: (a) PDFs of w_τ; (b) PDFs of ΔU_τ; (c) PDFs of q_τ; (d) functions $S(q_\tau)$. In all plots, the integration time τ is a multiple of the period of forcing, $\tau = 2n\pi/\omega_d$, with $n = 7$ (○), $n = 15$ (□), $n = 25$ (◇) and $n = 50$ (×). Continuous lines are theoretical predictions with no adjustable parameter. (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 (□). Continuous line is theoretical prediction. (f) The slopes $\Sigma(n)$, plotted as a function of n for two different driving frequencies $\omega_d = 64$ Hz (□) and 256 Hz (○); continuous lines are theoretical predictions from Refs. [15,19] with no adjustable parameter.

(i) For large fluctuations q_τ, $S(q_\tau)$ equals 2. When τ tends to infinity, this region spans from $q_\tau = 3$ to infinity.
(ii) For small fluctuations q_τ, $S(q_\tau)$ is a linear function of q_τ. We then define $\Sigma_q(n)$ as the slope of the function $S(q_\tau)$, i.e. $S(q_\tau) = \Sigma_q(n) q_\tau$. This slope is plotted in Fig. 4(e) where we see that it tends to 1 when τ is increased. So, SSFT holds in this region II which spans from $q_\tau = 0$ up to $q_\tau = 1$ for large τ.
(iii) A smooth connection between the two behaviors.

The PDF of the work being Gaussian, the functions $S(w_\tau)$ are proportional to w_τ for any τ, i.e. $S(w_\tau) = \Sigma_w(n) w_\tau$ (Ref. [15]). $\Sigma_w(n)$ is plotted in Fig. 4(e) and we observe that it matches experimentally $\Sigma_q(n)$, for all values of n. So the finite time corrections to the FT for the heat are the same than the ones of FT for work [15]: $\Sigma_w(n) = \Sigma_q(n) = 1 + K/n + 1/n\mathrm{O}(\mathrm{e}^{-\tau_n/\tau_\alpha})$, where K is a constant.

We find that the scenario plotted in Fig. 4(a)–(e) is the same for any driving frequency ω_d [15,19]. However the finite time corrections of $\Sigma_w(n)$ are a function of ω_d. The function $\Sigma_w(n)$, measured at $\omega_d/2\pi = 64$ Hz, is compared with that measured at $\omega_d/2\pi = 256$ Hz in Fig. 4(f). The convergence rate is quite different in the two cases, which agree with the theoretical predictions for a second order Langevin equation (see Refs. [15,19]).

We also notice that in the case of the sinusoidal forcing, the convergence is very slow in Figs. 4(e) and 4(f), we see that it takes several dozens of excitation period (500 ms for $\omega_d/2\pi = 64$ Hz) to get $\Sigma(n) = 1$ within one percent. On the contrary for a ramp forcing, this is achieved in about (20 ms), i.e. a few τ_α (see Fig. 3(c)).

In this section we have seen that also in the case of the sinusoidal forcing the agreement between the computed and measured finite time corrections is very good. These results prove not only that FTs asymptotically hold for any kind of forcing, but also that finite time corrections strongly depend on the specific dynamics. The detailed theoretical analysis of this behavior for a second order Langevin equation can be found in Ref. [19].

5. TFT and the Jarzynski equality the Crooks relation

In this section we want to discuss the relationship between TFT and JE. The Jarzynski equality (JE) relates the free energy difference ΔF between two equilibrium states A and B of a system in contact with a heat reservoir to the PDF of the work performed on the system to drive it from A to B along any path γ in the system parameter space. Actually thermal fluctuations are here very useful because they allow the system to explore all possible paths from A to B. Specifically, let us consider the work done by the external torque on the harmonic oscillator described in Section 3. The external torque $M(t)$ drives the system from $M(0) = 0$ (equilibrium state A) to $M(t > \tau_r) = M_o$ (equilibrium state B). Jarzynski defines the work performed by $M(t)$ to drive the system from A to B as

$$W^J = -\int_0^{\tau_r} \dot{M}\theta \,\mathrm{d}t = -[M\theta]_0^{\tau_r} - W^{\mathrm{cl}} \tag{14}$$

where

$$W^{\mathrm{cl}} = -\int_0^{\tau_r} M\dot{\theta} \,\mathrm{d}t = -W_{\tau_r} k_B T \tag{15}$$

is the classical work such that $-W^{\mathrm{cl}}/(k_B T)$ is equal to W_{τ_r} defined in Eq. (2). Here we define W^{cl} such that it has the same sign of W^J. Thus W^J and W^{cl} are related but they are not the same and they differ by a boundary term, which makes an important difference in the fluctuations of these two quantities. This difference between the W and W_{cl}, has been already pointed out in Ref. [20]. One can consider an ensemble of realizations of the 'switching process' from A to B with initial conditions all starting in the same initial equilibrium state. Then the work may be computed for each trajectory in the ensemble. The JE states that [9]

$$\Delta F = -\frac{1}{\beta} \log\bigl\langle \exp\bigl[-\beta W^J\bigr]\bigr\rangle \tag{16}$$

where $\langle\cdot\rangle$ denotes the ensemble average, $\beta^{-1} = k_B T$. In other words $\langle \exp[-\beta W_{\mathrm{diss}}]\rangle = 1$, since we can always write $W = \Delta F + W_{\mathrm{diss}}$ where W_{diss} is the dissipated work. In our experiment we can also check the CR which is related to the JE and which gives useful and complementary information on the dissipated work. Crooks considers the forward work W_{f} to drive the system from A to B and the backward work W_{b} to drive it from B to A. If the work pdfs during the forward and backward processes are $\mathrm{P_f}(W^J)$ and $\mathrm{P_b}(-W^J)$, one has [10,8]

$$\frac{\mathrm{P_f}(W^J)}{\mathrm{P_b}(-W^J)} = \exp\bigl(\beta\bigl[W^J - \Delta F\bigr]\bigr) = \exp[\beta W_{\mathrm{diss}}] \tag{17}$$

A simple calculation from Eq. (17) leads to Eq. (16). However, from an experimental point of view this relation is extremely useful because one immediately sees that the crossing point of the two pdfs, that is the point where

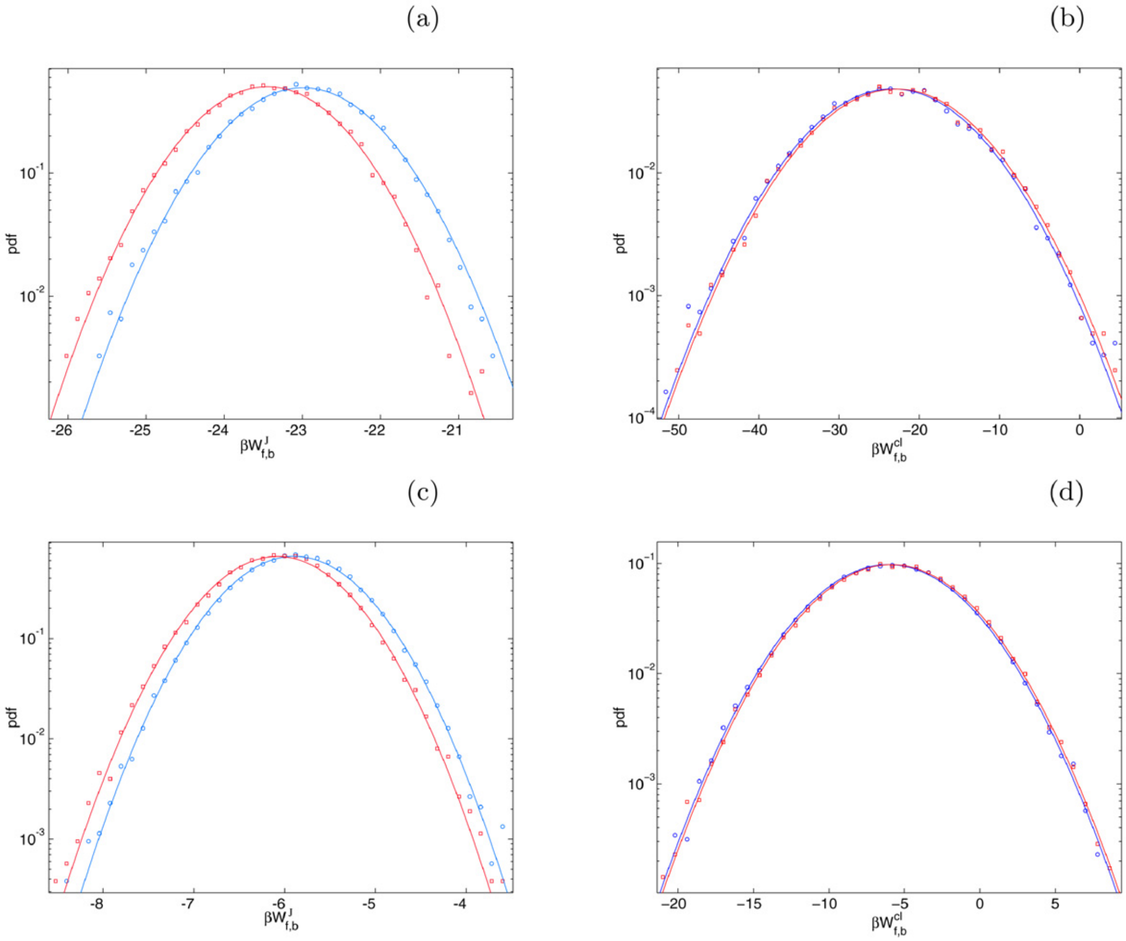

Fig. 5. $M_o = 11.9$ pN m (a) $P_f(W)$ and $P_b(-W)$, (b) $P_f(W^{cl})$ and $P_b(-W^{cl})$; $M_o = 6.1$ pN m: (c) $P_f(W)$ and $P_b(-W)$, (d) $P_f(W^{cl})$ and $P_b(-W^{cl})$ (experimental forward and backward pdfs are represented by $\circ$ and $\square$ respectively, whereas the continuous lines are Gaussian fits).

$P_f(W^J) = P_b(-W^J)$, is precisely ΔF. Thus one has another mean to check the computed free energy by looking at the pdfs crossing point $W_\times$.

Many details of the test of the JE and CR in the harmonic oscillator can be found in Ref. [18]. Here we want only to stress the difference between the fluctuations of the classical and the Jarzynski works. This can be seen in Fig. 5 where we plot the pdfs of W^J (Figs. 5(a), (c)) and W^{cl} (Figs. 5(b), (d)) for the forward and backward processes measured for two values of M_o specifically $M_o = 11.9$ pN m (Figs. 5(a), (b)) and $M_o = 6.1$ pN m (Figs. 5(a), (b)). The stiffness C of the oscillator was 7.5×10^{-4} N m rad^{-1} in this experiment. In Fig. 5, bullets are the experimental data and the continuous lines their fitted Gaussian pdfs. Comparing the pdfs of W^J and W^{cl} for the same M_o we see that the variance of W^{cl} is much larger than that of W^J. Indeed W^{cl} presents both positive and negative values and, as we have seen in Section 3, $P(-W^{cl})$ satisfies TFT. Thus it is clear that if W^J satisfies Eq. (16) this equation cannot be satisfied by W^{cl}. Indeed using the measured values of W^J in Eq. (16) one finds $\beta\Delta F = -23.3 \pm 0.4$ for $M_o = 11.9$ and $\beta\Delta F = -6.3 \pm 0.3$ for $M_o = 6.1$. These values correspond to $\Delta F = -\frac{M_o^2}{2C}$ for the driven harmonic oscillator. In Fig. 5, the pdfs $P_f(W)$ and $P_b(-W)$ cross at $\beta W \simeq -23.5$ (Fig. 5(a)) and in $\beta W \simeq -6.1$ (Fig. 5(c)), which again correspond to the expected values. Thus we see that JE and CR can be safely applied on experimental data to measure ΔF if the work W^J defined in Eq. (14) is used. In Ref. [18] it has been shown that this result is true independently of the ratio τ_r/τ_α and of the maximum amplitude of M_o. This has been checked at the largest M_o and the shortest rising time τ_r allowed by our apparatus.

The fact that the JE and CR are satisfied only by W^J but not by W^{cl} can be easily understood by noticing that a variable that satisfies TFT cannot be used in Eq. (16). Indeed one may rewrite Eq. (16) as:

$$\exp(-\beta\Delta F) = \langle\exp(-\beta\widetilde{W})\rangle = \int_{-\infty}^{\infty} \exp(-\beta\widetilde{W}) P(\widetilde{W})\,\mathrm{d}\widetilde{W} \tag{18}$$

where $\widetilde{W}$ is an energy injected into the system on a time τ. If $P(\widetilde{W})$ satisfies TFT then from Eqs. (3) and (4):

$$P(\widetilde{W}) = \exp(-\beta\widetilde{W}) P(-\widetilde{W}), \quad \forall\tau$$

Replacing this identity in Eq. (18) one finds:

$$\int_{-\infty}^{\infty} \exp(-\beta\widetilde{W}) P(\widetilde{W})\,\mathrm{d}W = \int_{-\infty}^{\infty} \exp(-\beta\widetilde{W}) P(-\widetilde{W}) \exp(\beta\widetilde{W})\,\mathrm{d}\widetilde{W} = 1 \tag{19}$$

showing that if $\widetilde{W}$ satisfies TFT then it cannot be used to compute ΔF. Thus one concludes that as W^{cl} satisfies TFT it cannot satisfy the JE as it shown in Eq. (19). This observation points out the importance of the choice of the 'good variables' in order to use the JE to compute the free energy difference in a more complex system. Several other limitations for a safe application of JE and CR on real data have been already discussed in Ref. [18].

6. Conclusions

In conclusion we have applied the FTs and JE to the work fluctuations of an oscillator driven out of equilibrium by an external force. The experimental results agree with theoretical predictions both for TFT and SSFT (Eqs. (3)–(5)). Indeed we observe that in the transient case when the system starts in equilibrium (TFT) the FT (Eq. (3)) holds for any time, whereas when the system is in a stationary out of equilibrium regime (SSFT), Eq. (3) holds only asymptotically. The SFFT presents a complex convergence to the asymptotic behavior which strongly depends on the form of the driving. The exact formula of this convergence can be computed using several experimental evidences of the statistics of the fluctuation. The details of derivation of the finite time correction and of the PDF for the heat will be the subject of a long paper [19]. We have also discussed the importance of the choice of the variable in order to safely apply JE. The results reported in this article are useful for many applications going from biological systems to nanotechnology, where the harmonic oscillator is the simplest building block.

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