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Fluctuations of the total entropy production in stochastic systems

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Abstract. - Fluctuations of the total entropy are experimentally investigated in two stochastic systems in a non-equilibrium steady state : an electric circuit with an imposed mean current and a harmonic oscillator driven out of equilibrium by a periodic torque. In these two linear systems, we study the total entropy production which is the entropy created to maintain the system in the non-equilibrium steady state. Fluctuation theorem holds for the total entropy production in the two experimental systems, both for all observation times and for all fluctuation magnitudes.

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Thermodynamics of systems at equilibrium has been developed by defining the internal energy, the injected work, and the dissipated heat. The first law of Thermodynamics describes energy conservation and gives a relation between those three energies. The second law of Thermodynamics imposes that the entropy variation is positive for a closed system. Statistical Physics further gives a microscopic definition of entropy, which allows analytical results on entropy production. The extension of Thermodynamics to systems in non-equilibrium steady states is an active field of research. Within this context, the first law has been extended for stochastic systems described by a Langevin equation [1–3]. It has been noted that the second law is not verified at all times but only in average, *i.e.* over macroscopic times : entropy production can have instantaneously negative values. The probabilities of getting positive and negative entropy production are quantitatively related in non-equilibrium systems by the Fluctuation Theorem (FT). This theorem has been first demonstrated in deterministic systems [4–6] and secondly extended to stochastic dynamics [7–10]. FTs for work and heat fluctuations have been theoretically and experimentally studied in Brownian systems described by the Langevin equation [2, 3, 11–18]. For these systems in non-equilibrium steady state, Fluctuation Theorems hold only in the limit of infinite time:

$$\Phi(a) \equiv \ln \left(\frac{p(X_\tau = +a)}{p(X_\tau = -a)} \right) \rightarrow \frac{a}{k_B T} \text{ for } \tau \rightarrow \infty \quad (1)$$

where k_B is the Boltzmann constant, T the temperature of the heat bath and $p(X_\tau)$ is the probability density function (PDF) of X_τ . Φ is called symmetry function and X_τ

stands for either injected work or dissipated heat, averaged over a time lag τ . For the injected work, eq. 1 is valid for all fluctuation magnitudes a ; for the dissipated heat, eq. 1 is satisfied for values lower than the mean value [13].

We are interested here in the total entropy production in a non-equilibrium steady state (NESS), introduced in ref. [19–21] and directly related to previous work on house-keeping heat [22, 23]. Entropy production has been studied both theoretically and experimentally in several systems [24–30]. In [19], Seifert and Speck have shown that the total entropy production for a stochastic system described by a first order Langevin equation in a NESS satisfies a Detailed Fluctuation Theorem (DFT) :

$$\Phi(a) = \ln \left(\frac{p(X_\tau = +a)}{p(X_\tau = -a)} \right) = \frac{a}{k_B T} \quad \forall \tau \quad \forall a \quad (2)$$

The relation (2) is valid for all integration time τ and all fluctuation magnitudes of the total entropy production. This relation is closely related to the Jarzynski and Crooks non-equilibrium work relations [31, 32] which can be exploited to measure equilibrium free energy in experiments [33–37] and it has been extended to Markov processes [38].

In this Letter, we measure the total entropy production in two out-of-equilibrium systems and show that this quantity verifies eq. (2). In the first part of the letter, we recall the general definition of dissipated heat, "trajectory-dependent" entropy and total entropy production. In the second part, we detail our two experimental systems. The first one is an electric circuit maintained in a NESS by an injected mean current. The second system is a torsion

pendulum driven in a NESS by forcing it with a periodic torque.

The heat dissipated by the system is the heat given to the thermostat during a time τ ; we note it Q_τ . It is related to the work W_τ , given to the system during the time τ , and to the variation of internal energy $\Delta_\tau U$ during this period, thanks to the first law of Thermodynamics:

$$Q_\tau = W_\tau - \Delta_\tau U. \quad (3)$$

Expressions of W_τ and $\Delta_\tau U$ for our two experimental setups are given below. Following notations of ref [19], we define the entropy variation in the system during a time τ as :

$$\Delta s_{m,\tau} = \frac{1}{T} Q_\tau \quad (4)$$

where T is the temperature of the heat bath. For thermostated systems, entropy change in medium behaves like the dissipated heat. The non-equilibrium Gibbs entropy is :

$$S(t) = -k_B \int d\vec{x} p(\vec{x}(t), t, \lambda_t) \ln p(\vec{x}(t), t, \lambda_t) = \langle s(t) \rangle \quad (5)$$

where λ_t denotes the set of control parameters at time t and $p(\vec{x}(t), t, \lambda_t)$ is the probability density function to find the particle at a position $\vec{x}(t)$ at time t , for the state corresponding to λ_t . This expression allows the definition of a "trajectory-dependent" entropy :

$$s(t) \equiv -k_B \ln p(\vec{x}(t), t, \lambda_t) \quad (6)$$

The variation $\Delta s_{\text{tot},\tau}$ of the total entropy s_{tot} during a time τ is the sum of the entropy change in the system during τ and the variation of the "trajectory-dependent" entropy in a time τ , $\Delta s_\tau \equiv s(t + \tau) - s(t)$:

$$\Delta s_{\text{tot},\tau} \equiv s_{\text{tot}}(t + \tau) - s_{\text{tot}}(t) = \Delta s_{m,\tau} + \Delta s_\tau \quad (7)$$

In this letter, we study fluctuations of $\Delta s_{\text{tot},\tau}$ computed using (4) and (6). We will show that $\Delta s_{\text{tot},\tau}$ satisfies a DFT (eq. (2)). In ref. [38], the relevance of boundary terms like Δs_τ has already been pointed out.

Our first experimental system is an electric circuit composed of a resistance $R = 9.22 \text{ M}\Omega$ in parallel with a capacitance $C = 278 \text{ pF}$ [15]. The time constant of the circuit is $\tau_0 \equiv RC = 2.56 \text{ ms}$. The voltage V across the dipole fluctuates due to Johnson-Nyquist thermal noise. We drive the system out of equilibrium by injecting a constant controlled current $I = 1.06 \cdot 10^{-13} \text{ A}$. After some τ_0 , the system is in a NESS. Electric laws give in this setup [15] :

$$\tau_0 \frac{dV}{dt} + V = RI + \xi, \quad (8)$$

where ξ is the Gaussian thermal noise, delta-correlated in time of variance $2k_B T R$.

Multiplying (8) by V and integrating it between t and $t + \tau$, we define the work W_τ , injected into the system, and

the dissipated heat Q_τ , together with the internal energy U :

$$W_\tau \equiv \int_t^{t+\tau} V(t') I dt' \quad (9)$$

$$Q_\tau \equiv \int_t^{t+\tau} V(t') i_R(t') dt' \quad (10)$$

$$\Delta_\tau U \equiv \frac{1}{2} C (V(t + \tau)^2 - V(t)^2) = W_\tau - Q_\tau \quad (11)$$

where i_R is the current flowing in the resistance : $i_R = I - C \frac{dV}{dt}$. This system has only one degree of freedom, so the trajectory in phase space is defined by the voltage $V(t)$ alone, and the only external parameter is the constant current I . So the variation of the "trajectory-dependent" entropy during a time τ is :

$$\Delta s_\tau = -k_B \ln \left(\frac{p(V(t + \tau))}{p(V(t))} \right) \quad (12)$$

Fluctuation relations for the injected work and the dissipated heat (or entropy change in medium) in this system have been reported in [15]. Let us recall the experimental results for the dissipated heat $T \cdot \Delta s_{m,\tau}$, for several values of the integration time. Its average value $\langle T \cdot \Delta s_{m,\tau} \rangle$ is equal to the average of injected work and linear in τ . The PDFs of $T \cdot \Delta s_{m,\tau}$ are plotted in figure 1a) for four values of τ/τ_0 . They are not Gaussian for small times τ and extreme events have an exponential distribution. We now describe new results in this system. The PDF of the "trajectory-dependent" entropy Δs_τ is plotted in figure 1b) ; we have superposed to it the PDF of $\Delta s_{m,\tau}$ at equilibrium ($I = 0 \text{ A}$). These two PDFs are independent of the integration time. The two curves match perfectly within experimental errors. Therefore the "trajectory-dependent" entropy is equal in this case to the fluctuations of the entropy exchanged with the thermal bath at equilibrium. The average value of this "trajectory-dependent" entropy is zero within experimental errors ; so the total entropy production has the same average value than the entropy $\Delta s_{m,\tau}$. The PDFs of the total entropy $\Delta s_{\text{tot},\tau} / \langle \Delta s_{\text{tot},\tau} \rangle$, computed by adding Δs_τ to $\Delta s_{m,\tau}$, are plotted in figure 1c) for different values of τ ; they are all Gaussian.

In figure 1d), we have plotted the symmetry functions of the dissipated heat ($T \Delta s_{m,\tau}$) together with those of the total entropy. $\Phi(\Delta s_{m,\tau})$ is a non linear function of $\Delta s_{m,\tau}$. The linearity is recovered for $\Delta s_{m,\tau} < \langle \Delta s_{m,\tau} \rangle$. The slope tends to 1 for large integration time. Entropy change in medium satisfies relation (1) [15]. On the contrary, the symmetry functions for the total entropy are linear with $\Delta s_{\text{tot},\tau}$ for all integration times τ and for all values of $\Delta s_{\text{tot},\tau}$: $\Phi(\Delta s_{\text{tot},\tau}) = \Sigma(\tau) \Delta s_{\text{tot},\tau}$. The slope $\Sigma(\tau)$ is equal to 1 for all integration times within experimental errors. Measurements can be done for other values of injected current and we find the same results. Thus total entropy satisfies relation (2).

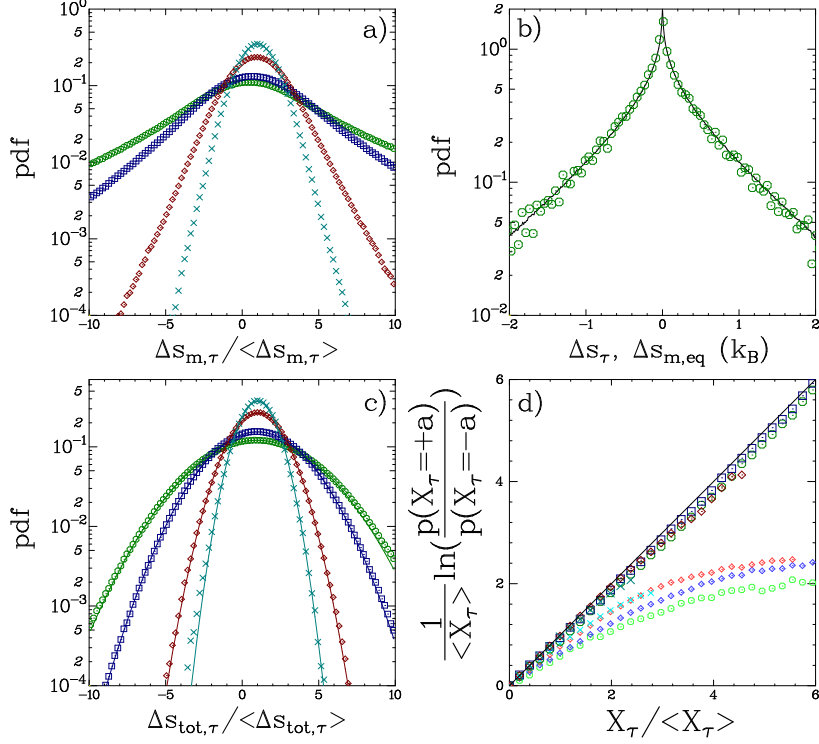


Fig. 1: Resistance. a) PDFs of the normalized entropy variation in the system $\Delta s_{m,\tau}/\langle\Delta s_{m,\tau}\rangle$, with $\tau/\tau_0 = 2.4$ (\circ), $\tau/\tau_0 = 4.8$ (\square), $\tau/\tau_0 = 14.5$ (\diamond) and $\tau/\tau_0 = 29$ (\times). b) PDF of the variation of "trajectory-dependent" entropy Δs_τ for $\tau/\tau_0 = 4.8$. The distribution is independent on τ/τ_0 . Continuous line is experimental PDF of the entropy variation at equilibrium ($\Delta s_{m,\tau,eq}$ at $I = 0$ A). c) PDFs of the total entropy production $\Delta s_{tot,\tau}/\langle\Delta s_{tot,\tau}\rangle$, with $\tau/\tau_0 = 2.4$ (\circ), $\tau/\tau_0 = 4.8$ (\square), $\tau/\tau_0 = 14.5$ (\diamond) and $\tau/\tau_0 = 29$ (\times). d) Symmetry functions Φ for $\Delta s_{m,\tau}/\langle\Delta s_{m,\tau}\rangle$ (small symbols in light colors) and $\Delta s_{tot,\tau}/\langle\Delta s_{tot,\tau}\rangle$ (large symbols in dark colors) for the same values of τ/τ_0 .

This experimental result can be explained using a first order Langevin equation and noting that fluctuations of the voltage $\delta V(t) = V(t) - \langle V(t) \rangle$, when a current is applied, are identical to those at equilibrium [15]. Thus the voltage $V(t)$ has a Gaussian distribution with mean $\langle V(t) \rangle = R.I$ and variance $(k_B T/C)$, whereas its auto-correlation function is the same out of equilibrium and at equilibrium:

$$\langle \delta V(t+\tau)\delta V(t) \rangle = \frac{k_B T}{C} e^{-(\tau/\tau_0)}. \quad (13)$$

So we can compute the expression of the "trajectory-dependent" entropy from eq. (12) and we find:

$$T.\Delta s_\tau = \frac{1}{2}C\delta V(t+\tau)^2 - \frac{1}{2}C\delta V(t)^2 \quad (14)$$

Fluctuations of the voltage are identical to those at equilibrium, thus "trajectory-dependent" entropy is equal to the variation of internal energy divided by T at equilibrium and to the opposite of the entropy variation in the system at equilibrium. Using eq. (7), (10) and (14), the expression of the total entropy is :

$$T.\Delta s_{tot,\tau} = I \int_t^{t+\tau} V(t') - I\tau_0 (\delta V(t+\tau) - \delta V(t)) dt' \quad (15)$$

We experimentally see that the PDF of $\Delta s_{tot,\tau}$ is Gaussian, so fully characterized by its mean value and its variance. Its average value is linear in τ ($\langle\Delta s_{tot,\tau}\rangle = RI^2\tau/T$) and equals the mean injected work divided by the temperature T . Its variance is computed using eq. (13) and we obtain $\sigma_{\Delta s_{tot,\tau}}^2 = 2RI^2k_B\tau/T$. For a Gaussian distribution, the symmetry function of $\Delta s_{tot,\tau}$ is linear with $\Delta s_{tot,\tau}$, that is $\Phi(\Delta s_{tot,\tau}) = \Sigma\Delta s_{tot,\tau}$. The slope Σ is related to the mean and the variance of the total entropy : $\Sigma = 2\langle\Delta s_{tot,\tau}\rangle/\sigma_{\Delta s_{tot,\tau}}^2 = 1/k_B$. Experimentally, we have normalized the total entropy by k_B , and the slope is equal to 1 for any τ as shown in fig. 1d).

We now consider the second experimental system. It is a torsion pendulum in a viscous fluid which acts as a thermal bath at temperature T . The system is driven out of equilibrium by an external deterministic time dependent torque M . All the details of the experimental setup can be found in [3]. The torsional stiffness of the oscillator is $C = 4.65 \cdot 10^{-4}$ N.m.rad $^{-1}$, its viscous damping ν , its total moment of inertia I_{eff} , its resonant frequency $f_0 = \omega_0/(2\pi) = \sqrt{C/I}/(2\pi) = 217$ Hz and its relaxation time $\tau_\alpha = \nu/(2I_{eff}) = 9.5$ ms. The angular motion of the

oscillator obeys a second order Langevin equation :

$$\frac{d^2\theta}{dt^2} + \frac{2}{\tau_\alpha} \frac{d\theta}{dt} + \omega_0^2\theta = \frac{M + \eta}{C}, \quad (16)$$

where η is the thermal noise, delta-correlated in time of variance $2k_B T\nu$. The work injected into the system between t_i and $t_i + \tau$ is :

$$W_\tau = \int_{t_i}^{t_i+\tau} M(t') \frac{d\theta}{dt}(t') dt'. \quad (17)$$

The dissipated heat is computed according to eq. (3) where, in this case, the internal energy $U(t)$ is :

$$U(t) = \frac{1}{2} C \theta(t)^2 + \frac{1}{2} I_{\text{eff}} \dot{\theta}(t)^2 \quad (18)$$

We investigate a periodic forcing : $M(t) = M_0 \sin(\omega_d t)$ ($M_0 = 0.78$ pN.m and $\omega_d/(2\pi) = 64$ Hz). The integration time τ is chosen to be a multiple of the period of the forcing : $\tau_n = 2n\pi/\omega_d$. The average responses of the system $\langle \theta(t) \rangle$ and $\langle \dot{\theta}(t) \rangle$ are periodic function of the pulsation ω_d and the system is in a steady state. Results for injected work and dissipated heat in this case are reported in [3,17].

The "trajectory-dependent" entropy is not as simple as in the case of the resistance. The system has two independent degrees of freedom (θ and $\dot{\theta}$) and its expression is :

$$\Delta s_{\tau_n} = -k_B \ln \left(\frac{p(\theta(t_i + \tau_n), \varphi) \cdot p(\dot{\theta}(t_i + \tau_n, \varphi))}{p(\theta(t_i + \tau_n), \varphi) \cdot p(\dot{\theta}(t_i + \tau_n, \varphi))} \right) \quad (19)$$

The DFT (eq. (2)) is valid for each fixed starting phase $\varphi = t_i \omega_d$ [21]. For computing correctly the total entropy, we have to calculate the PDFs of the angular position and the angular velocity for each initial phase φ . Then we compute the "trajectory-dependent" entropy. As fluctuations of θ and $\dot{\theta}$ are independent of φ [3]. These distributions correspond to the equilibrium fluctuations of θ and $\dot{\theta}$ around the mean trajectory defined by $\langle \theta(t) \rangle$ and $\langle \dot{\theta}(t) \rangle$. As a consequence, we can average Δs_{τ_n} over φ which improves a lot the statistical accuracy. We stress that it is not equivalent to calculate first the PDFs over all values of φ — which would correspond here to the convolution of the PDF of the fluctuations with the PDF of a periodic signal — and then compute the trajectory dependent entropy.

In figure 2a), we recall the main results for the dissipated heat $T\Delta s_{m,\tau_n}$. Its average value $\langle T.\Delta s_{m,\tau_n} \rangle$ is linear in τ_n and equal to the injected work. The PDFs of $T.\Delta s_{m,\tau_n}$ are not Gaussian and extreme events have an exponential distribution. Let us now describe new results in this system. The PDF of the "trajectory-dependent" entropy is plotted in fig. 2b); it is independent of n . We superpose to it the PDF of the variation of internal energy divided by T at equilibrium : the two curves match perfectly within experimental errors, so the "trajectory-dependent" entropy can again be considered as the entropy exchanged with

the thermostat if the system is at equilibrium. The average value of Δs_{τ_n} is zero, so the average value of the total entropy is equal to the average of injected power divided by T . In fig. 2c), we plot the PDFs of the normalized total entropy for four typical values of integration time. We find that the PDFs are Gaussian for any time.

The symmetry functions of the dissipated heat $\Phi(\Delta s_{m,\tau_n})$ and the total entropy $\Phi(\Delta s_{\text{tot},\tau_n})$ are plotted in fig. 2d). For the dissipated heat, the symmetry function is a non linear function of $\Delta s_{m,\tau}$ and we observe a linear behavior for $\Delta s_{m,\tau_n} < \langle \Delta s_{m,\tau_n} \rangle$ with a slope that tends to 1 for large time. For the normalized total entropy, the symmetry functions are linear with $\Delta s_{\text{tot},\tau_n}$ for all values of $\Delta s_{\text{tot},\tau_n}$ and the slope is equal to 1 for all values of τ_n . Note that it is not exactly the case for the first values of τ_n because these are the times over which the statistical errors are the largest and the error in the slope is large.

In ref. [3], we have already shown that, when a torque is applied, the fluctuations around $\langle \theta(t) \rangle$ have the same statistics and the same dynamics as fluctuations at equilibrium. Using the expression of the distribution of the angular position and the angular velocity, we can compute the "trajectory-dependent" entropy from eq. (19):

$$\begin{aligned} T.\Delta s_{\tau_n} &= \frac{1}{2} C (\delta\theta(t_i + \tau_n)^2 - \delta\theta(t_i)^2) \\ &+ \frac{1}{2} I_{\text{eff}} (\delta\dot{\theta}(t_i + \tau_n)^2 - \delta\dot{\theta}(t_i)^2) \end{aligned} \quad (20)$$

where $\delta\theta$ and $\delta\dot{\theta}$ are the fluctuations around the mean trajectory : $\theta(t) = \langle \theta(t) \rangle + \delta\theta(t)$ and $\dot{\theta}(t) = \langle \dot{\theta}(t) \rangle + \delta\dot{\theta}(t)$. The "trajectory-dependent" entropy is equivalent to the variation of internal energy for the system at equilibrium divided by the temperature of the bath. The total entropy is :

$$\begin{aligned} T.\Delta s_{\text{tot},\tau_n} &= W_{\tau_n} - \frac{1}{2} C \bar{\theta}(t_i) (\delta\theta(t_i + \tau_n) - \delta\theta(t_i)) \\ &- \frac{1}{2} I_{\text{eff}} \dot{\bar{\theta}}(t_i) (\delta\dot{\theta}(t_i + \tau_n) - \delta\dot{\theta}(t_i)) \end{aligned} \quad (21)$$

Experimentally, we observe that the PDF of the total entropy is Gaussian. We can calculate the mean value and the variance of the total entropy for any τ_n . We find that $\langle T.\Delta s_{\text{tot},\tau_n} \rangle$ is equal to the injected work. Using the first law of thermodynamics and the equation of motion, we write the dissipated heat as the difference between the viscous dissipation and the work of the thermal noise :

$$T.\Delta s_{m,\tau_n} = \int_{t_i}^{t_i+\tau_n} \nu \dot{\theta}(t')^2 dt' - \int_{t_i}^{t_i+\tau_n} \dot{\theta}(t') \eta(t') dt' \quad (22)$$

This expression holds at equilibrium as well as out of equilibrium. The only difference is that when out of equilibrium $\langle \theta(t) \rangle \neq 0$ and $\langle \dot{\theta}(t) \rangle \neq 0$. After some algebra the total entropy is :

$$T.\Delta s_{\text{tot},\tau_n} = \nu \int_{t_i}^{t_i+\tau_n} \langle \dot{\theta}(t') \rangle^2 dt'$$

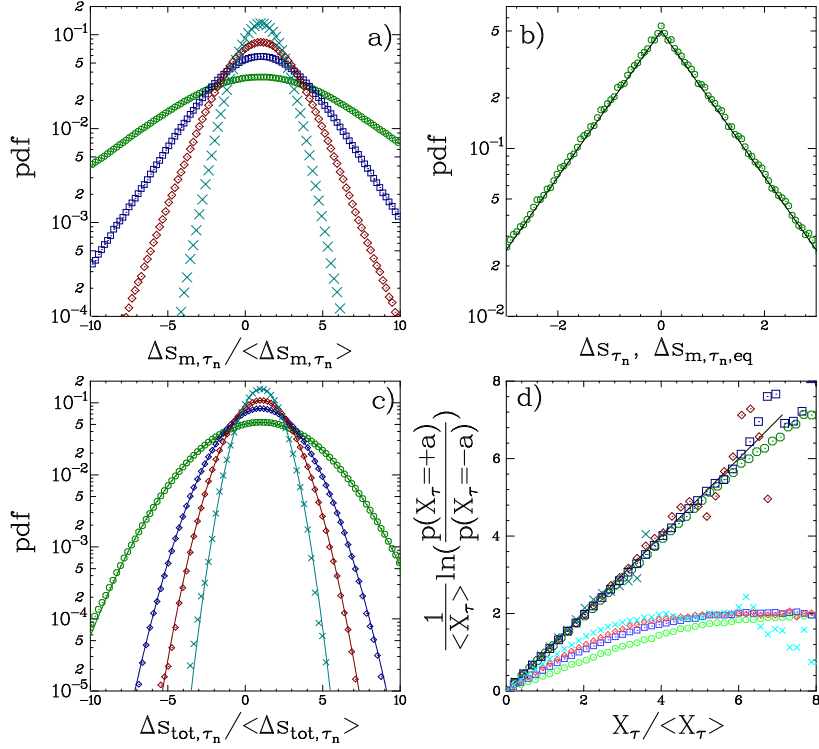


Fig. 2: Torsion pendulum. a) PDFs of the normalized entropy variation $\Delta s_{m,\tau_n}/\langle\Delta s_{m,\tau_n}\rangle$ integrated over n periods of forcing, with $n = 7$ (\circ), $n = 15$ (\square), $n = 25$ (\diamond) and $n = 50$ (\times). b) PDFs of Δs_{τ_n} , the distribution is independent of n and here $n = 7$. Continuous line is the theoretical prediction for equilibrium entropy exchanged with thermal bath $\Delta s_{m,\tau_n,eq}$. c) PDFs of the normalized total entropy $\Delta s_{tot,\tau_n}/\langle\Delta s_{tot,\tau_n}\rangle$, with $n = 7$ (\circ), $n = 15$ (\square), $n = 25$ (\diamond) and $n = 50$ (\times). d) Symmetry functions for the normalized entropy variation in the system (small symbols in light colors) and for the normalized total entropy (large symbols in dark colors) for the same values of n .

$$\begin{aligned}
 & + 2\nu \int_{t_i}^{t_i+\tau_n} \langle \dot{\theta}(t') \rangle \delta \dot{\theta}(t') dt' \\
 & - \int_{t_i}^{t_i+\tau_n} \langle \dot{\theta}(t') \rangle \eta(t') dt' \quad (23)
 \end{aligned}$$

The average value of the total entropy is $\nu \int_{t_i}^{t_i+\tau_n} \langle \dot{\theta}(t') \rangle^2 dt'$ and its variance is :

$$\begin{aligned}
 \langle \sigma_{\Delta s_{tot,\tau_n}}^2 \rangle & = 2k_B \langle \Delta s_{tot,\tau_n} \rangle + B/T^2 \\
 B & = 4\nu \int \int dudv \langle \dot{\theta}(u) \rangle \langle \dot{\theta}(v) \rangle \psi(u, v) \quad (24) \\
 \psi(u, v) & = \nu \langle \delta \dot{\theta}(u) \delta \dot{\theta}(v) \rangle - \langle \delta \dot{\theta}(u) \eta(v) \rangle \quad (25)
 \end{aligned}$$

The first term in the function ψ is the autocorrelation function of the angular velocity. This function is symmetric around $u = v$. The second term is the correlation function of the angular velocity with the noise. Due to the causality principle, this term vanishes if $u < v$. Changing variables to $r = (u + v)/2$ and $s = u - v$, eq. (24) can be rewritten :

$$B = \int_{t_i}^{t_i+\tau_n} dr \int_0^{\tau_n} \langle \dot{\theta}(r + s/2) \rangle \langle \dot{\theta}(r - s/2) \rangle \tilde{\psi}(r, s) \quad (26)$$

$$\tilde{\psi}(r, s) = 2\nu \langle \delta \dot{\theta}(s) \delta \dot{\theta}(0) \rangle - \langle \delta \dot{\theta}(s) \eta(0) \rangle \quad (27)$$

After some algebra we can show that the correlation function $\langle \delta \dot{\theta}(s) \eta(0) \rangle$ is two times the autocorrelation function $\langle \delta \dot{\theta}(s) \delta \dot{\theta}(0) \rangle$, therefore $\tilde{\psi} = 0$. Thus we obtain that the variance of the total entropy is equal to $2k_B \langle \Delta s_{tot,\tau_n} \rangle$. The Fluctuation Relation for the total entropy is : $\Phi(\Delta s_{tot,n}) = 1/k_B \Delta s_{tot,n}$ for all times τ , for all values of $\Delta s_{tot,n}$ and for any kind of stationary forcing.

For our two experimental systems, we have obtained that the "trajectory-dependent" entropy can be considered as the entropy variation in the system in a time τ that one would have if the system was at equilibrium. Therefore the total entropy is the additional entropy due to the presence of the external forcing : this is the part of entropy which is created due to the non-equilibrium stationary process. The derivation we gave for a second order Langevin equation can be extended to a first order Langevin equation : total entropy (or excess entropy) satisfies the Fluctuation Theorem for all times and for all kind of stationary intensity injected in the circuit or all kind of stationary external torque. The ratio between the average value of the total entropy at $\tau = \tau_\alpha$ (relaxation time) and the variance σ_{eq}^2 of fluctuations the entropy variation at equilibrium characterizes the distance from equilibrium d

:

$$d^2 = \frac{\langle \Delta s_{\text{tot}, \tau \alpha} \rangle}{\sigma_{\text{eq}}} = \sqrt{\frac{3n_d}{8} \frac{\sigma_{\Delta s_{\text{tot}, \tau \alpha}}^2}{\sigma_{\text{eq}}^2}} \quad (28)$$

where n_d is the number of degrees of freedom. For the second equality, we use the Gaussianity of $\Delta s_{\text{tot}, \tau}$, *i.e.* $\sigma_{\Delta s_{\text{tot}, \tau}}^2 = 2k_B \langle \Delta s_{\text{tot}, \tau} \rangle$ and the variance of the fluctuation of entropy variation at equilibrium in terms of k_B , *i.e.* $\sigma_{\text{eq}}^2 = 3/2n_d k_B^2$. It turns out that this expression for d is the same that was defined in [3] with a completely different approach. Eq. (28) indicates that, when the system is driven far from equilibrium, σ_{eq} becomes negligible. As a consequence the fluctuations of the total entropy become equal to the fluctuations of the entropy variation in the system in a time τ . In other words, the PDFs of the dissipated heat far from equilibrium are Gaussian.

In conclusion, we have studied the total entropy when the system is driven in a non-equilibrium steady state. We have shown that the Fluctuation Theorem for the total entropy is valid not only in the limit of large times, as it is the case for injected work and dissipated heat, but also for all integration times and all fluctuation amplitudes. In the two examples we have discussed, the total entropy corresponds to the difference between the entropy change in medium out of equilibrium and at equilibrium.

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