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# Fluctuations of the total entropy production in stochastic systems

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**Abstract.** - Fluctuations of the excess heat in an out of equilibrium steady state are experimentally investigated in two stochastic systems : 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 excess heat that represents the difference between the dissipated heat out of equilibrium and the dissipated heat at equilibrium. Fluctuation theorem holds for the excess heat in the two experimental systems for all observation times and for all fluctuation magnitudes.

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 gave a microscopic definition of entropy, which allowed analytical results on entropy production. The extension of Thermodynamics to non-equilibrium systems in 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 over macroscopic times, *i.e.* entropy production fluctuates can instantly be negative. 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]. Work and heat fluctuations have been theoretically and experimentally studied in some Brownian systems described by the Langevin equation [2, 3, 11–17]. For these systems in a non-equilibrium steady state, Fluctuation Theorems hold only in the limit of infinite time:

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

$\Phi$  is called symmetry function and  $X_\tau$  stands for either injected work or dissipated heat, averaged over a time lag  $\tau$ . For the injected work the relation is valid for all fluctuation magnitudes ; for the dissipated heat, the relation is satisfied for values lower than the mean value.

We are interested here in the total entropy production or the excess heat, using the definition of a "trajectory-dependent" heat [18, 19]. Entropy production has been studied both theoretically and experimentally in several systems [20–26]. In two recent theoretical articles, Seifert and Speck have shown that the total entropy production for a stochastic system described by a Langevin equation in a non equilibrium steady state satisfies a detailed fluctuation theorem [27, 28] :

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

The relation 2 is valid for all integration time  $\tau$  and all fluctuation magnitudes of the excess heat. This relation is closely related to the Jarzynski and Crooks non equilibrium work relations [29–31] which can be exploited to measure equilibrium free energy in experiments [32–36].

In this Letter, we measure the excess heat 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" heat and excess heat. In the second part, we detail our two experimental systems. The first one is an electric circuit maintained in a non-equilibrium steady state by an injected mean current and described by a first order Langevin equation. The second system is a torsion pendulum driven in a non-equilibrium steady state by forcing it with a periodic torque; this system is described by a second order Langevin equation.

The heat dissipated by the system is the heat given to the thermostat during a time  $\tau$  ; we note it  $Q_\tau$ . On one hand, it is related to the work  $W_\tau$ , given to the system during the time  $\tau$ , 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  $W_\tau$  and  $\Delta_\tau U$  for our two experimental setups are given below. Following refs [18, 19], we write the dissipated heat as the sum of two terms : the excess heat  $Q_{ex,\tau}$  and the "trajectory-dependent" heat  $Q_{G,\tau}$  :

$$Q_\tau = Q_{ex,\tau} + Q_{G,\tau} \quad (4)$$

The nonequilibrium Gibbs entropy is :

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

where  $\lambda_t$  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 a state corresponding to  $\lambda_t$ . This expression suggests a form of a "trajectory-dependent" entropy  $s(t) \equiv \ln p(\vec{x}(t), t, \lambda_t)$  and therefore a "trajectory-dependent" heat :

$$Q_{G,\tau} \equiv -k_B T \ln \left( \frac{p(\vec{x}(t+\tau), t+\tau, \lambda_{t+\tau})}{p(\vec{x}(t), t, \lambda_t)} \right) \quad (6)$$

In this letter, we study fluctuations of  $Q_\tau$  computed using (4) and (6). This allow us to estimate excess entropy production defined as

$$\Delta S_{ex,\tau} = \frac{1}{T} Q_{ex,\tau} \quad (7)$$

where  $t$  is the temperature of the heat bath. We will show that  $\Delta S_{ex,\tau}$  satisfies eq. 2 for all times  $\tau$  and for all fluctuation magnitudes.

The first experimental system is an electric circuit composed of a resistance  $R = 9.22 \text{ M}\Omega$  in parallel with a capacitance  $C = 278 \text{ pF}$  [14]. 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 current  $I = 1.06 \cdot 10^{-13} \text{ A}$ . After some  $\tau_0$ , the system is in a non-equilibrium steady state. Electric laws give :

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

where  $\xi$  is the thermal noise delta-correlated in time. Multiplying (8) by  $V$  and integrating between  $t$  and  $t + \tau$ , we define the work  $W_\tau$ , injected into the system, and the dissipated heat  $Q_\tau$ , together with the internal energy  $U$  :

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

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

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

Fluctuations relations for the injected work and the dissipated heat in this system have been reported in [14]. 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 "trajectory-dependent" heat is :

$$Q_{G,\tau} = -k_B T \ln \left( \frac{p(V(t+\tau))}{p(V(t))} \right) \quad (12)$$

Let us recall the experimental results for the dissipated heat  $Q_\tau$  for several values of the integration time. We normalize the dissipated heat by its average value  $\langle Q_\tau \rangle$  which is equal to the average of injected work and linear with  $\tau$  as expected. The probability density functions (PDFs) of  $Q_\tau$  are plotted in figure 1a) for four values of  $\tau/\tau_0$ . They are not Gaussian for small times  $\tau$  and extreme events have an exponential distribution. The PDF of the "trajectory-dependent" heat  $Q_{G,\tau}$  is plotted in figure 1b); it is the same for all times. We have superposed to these results the PDFs of  $Q_\tau$  at equilibrium ( $I = 0 \text{ A}$ ) which are independent of the integration time. The two curves matches perfectly within experimental error. Therefore the "trajectory-dependent" heat is equal in this case to the heat dissipated by the system at equilibrium. The average value of this "trajectory-dependent" heat is zero within experimental error ; so the excess heat have the same average value than the dissipated heat. The PDFs of the normalized excess heat  $Q_{ex,\tau}/\langle Q_{ex,\tau} \rangle$ , computed by subtracting  $Q_{G,\tau}$  from  $Q_\tau$ , are plotted in figure 1c) for different values of  $\tau$ ; they are all Gaussian. In figure 1d), we have plotted the symmetry functions of the dissipated heat together with those of the excess heat. The symmetry functions for the dissipated heat  $\Phi(Q_\tau)$  are not linear in  $Q_\tau$  and can be divided in three regions [14]: a linear region with a slope which tends to 1 for large integration time ( $Q_\tau < \langle Q_\tau \rangle$ ), a second region where the symmetry function tends to the constant value 2 when  $\tau$  tends to infinity ; this region corresponds to extreme events ( $Q_\tau > 3\langle Q_\tau \rangle$ ). The third region is a smooth connection between the two behaviors. On the contrary, the symmetry functions for the excess heat are linear with  $Q_{ex,\tau}$  for all integration times  $\tau$  :  $\Phi(Q_\tau) = \Sigma(\tau)Q_\tau$ . 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.

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 [14]. Thus the voltage  $V(t)$  has a Gaussian probability distribution with mean  $\langle V(t) \rangle = R.I$  and variance  $(k_B T/C)$ , whereas its autocorrelation 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-

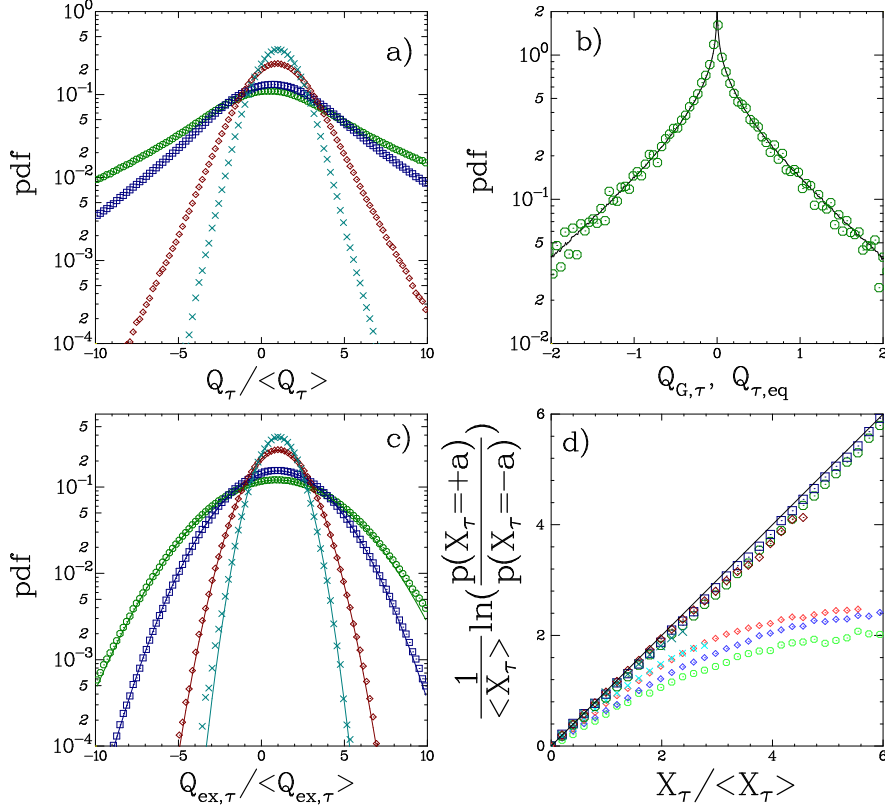


Fig. 1: Resistance. a) PDFs of the normalized dissipated heat  $Q_\tau/\langle Q_\tau \rangle$ , with  $\tau/\tau_0 = 2.4$  ( $\circ$ ),  $\tau/\tau_0 = 4.8$  ( $\square$ ),  $\tau/\tau_0 = 14.5$  ( $\diamond$ ) and  $\tau/\tau_0 = 29$  ( $\times$ ). b) PDF of the "trajectory-dependent" heat  $Q_\tau$  for  $\tau/\tau_0 = 4.8$ . The distribution is independent on  $\tau/\tau_0$ . Continuous line is experimental PDF of the dissipated heat in equilibrium ( $Q_{\tau,eq}$  at  $I = 0$  A). c) PDFs of the normalized excess heat  $Q_{ex,\tau}/\langle Q_{ex,\tau} \rangle$ , 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  $\Phi$  for the normalized dissipated heat (small symbols in light colors) and the normalized excess heat (large symbols in dark colors) for the same values of  $\tau/\tau_0$ .

dependent" heat from eq. 12 and we find:

$$Q_{G,\tau} = -\frac{1}{2}C\delta V(t+\tau)^2 + \frac{1}{2}C\delta V(t)^2 \quad (14)$$

Thus "trajectory-dependent" heat is the opposite of the dissipated heat at equilibrium : the excess heat vanishes at equilibrium. Using eq. 4 and eq. 14, the expression of the excess heat is :

$$Q_{ex,\tau} = I \int_t^{t+\tau} V(t') - I\tau_0 (\delta V(t+\tau) - \delta V(t)) \quad (15)$$

The excess heat has a linear dependence on  $V(t)$  which have a Gaussian distribution [37] so the PDF of  $Q_{ex,\tau}$  is Gaussian for any  $\tau$ . Its average value is linear in  $\tau$  ( $\langle Q_{ex,\tau} \rangle = RI^2\tau$ ) and equals the mean injected work. Its variance  $\sigma_{Q_{ex,\tau}}^2$  can be computed using the expression of the autocorrelation function of the voltage  $V(t)$  given in (13) We obtain  $\sigma_{Q_{ex,\tau}}^2 = 2RI^2k_B T\tau$ . For a Gaussian distribution, the symmetry function of  $Q_{ex,\tau}$  is linear with  $Q_{ex,\tau}$ , that is  $\Phi(Q_{ex,\tau}) = \Sigma Q_{ex,\tau}$  and the slope  $\Sigma$  is related to the mean and the variance of the excess heat :  $\Sigma = 2\langle Q_{ex,\tau} \rangle / \sigma_{Q_{ex,\tau}}^2 = 1/k_B T$ . In the figures of the

present paper, all the energies are normalized by  $k_B T$ , and the slope is equal to 1 for any  $\tau$  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 experimental setup are reported in ref. [3]. The torsional stiffness of the oscillator is  $C = 4.65 \cdot 10^{-4}$  N.m.rad $^{-1}$ , its viscous damping  $\nu$ , its total moment of inertia  $I_{eff}$ , its resonance 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  $\eta$  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 the difference performed on the work given to the system and the variation of internal energy between  $t_i$  and  $t_i + \tau$  :

$$Q_\tau = W_\tau - \Delta_\tau U \quad (18)$$

where  $U(t)$  is the internal energy :

$$U(t) = \frac{1}{2}C\theta(t)^2 + \frac{1}{2}I_{\text{eff}}\dot{\theta}(t)^2 \quad (19)$$

Results for injected work and dissipated heat are reported in [3, 16]. 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  $\tau$  is chosen to be a multiple of the period of the forcing :  $\tau_n = 2n\pi/\omega_d$  and the starting phase  $t_i\omega_d$  is averaged over all possible  $t_i$  to increase statistics. The system is clearly in a steady state. The average response of the system is periodic. In the following we will note  $W_n$ ,  $Q_n$ ,  $Q_{G,n}$  and  $Q_{ex,n}$  the values of  $W_{\tau_n}$ ,  $Q_{\tau_n}$ ,  $Q_{G,\tau_n}$  and  $Q_{ex,\tau_n}$ .

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

$$Q_{G,n} = -k_B T \ln \left( \frac{p(\theta(t_i + \tau_n), \varphi) \cdot p(\dot{\theta}(t_i + \tau_n), \varphi)}{p(\theta(t_i + \tau_n), \varphi) \cdot p(\dot{\theta}(t_i + \tau_n), \varphi)} \right) \quad (20)$$

The probability depends on the starting phase  $\varphi = t_i\omega_d$ . We calculate the PDF of the angular position and the angular velocity which depends on  $\varphi$ , next we compute the "trajectory-dependent" heat. Finally we average over  $\varphi$ . This is not equivalent to calculate first the PDF over all values of  $\varphi$ , which corresponds here to the convolution of the PDF of the fluctuations and the PDF of a periodic signal, and then compute the "trajectory-dependent" heat. In fact, we consider here only the PDF of the fluctuations around the average trajectory  $\langle \theta(t) \rangle$ .

In figure 2a), we recall the main results for the dissipated heat. We have normalized the dissipated heat by its average value  $\langle Q_n \rangle$ , which is linear in  $n$  and equal to the injected work. The PDFs of  $Q_n$  are not Gaussian and extreme events have an exponential distribution. 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 at equilibrium : the two curves matches perfectly within experimental error, so the "trajectory-dependent" heat can be considered as the heat exchanged with the thermostat if the system is at equilibrium. The average value of  $Q_{G,n}$  is zero, so the average value of the excess heat is equal to the average of injected power. In fig. 2c), we plot the PDFs of the normalized excess heat for four typical values of integration time. We find that the PDFs are Gaussian for any time. The symmetry functions of the dissipated heat  $\Phi(Q_n)$  and  $\Phi(Q_{ex,n})$  are plotted in fig. 2d). We can distinguish three behaviors for the dissipated heat : a linear

behavior for  $Q_n < \langle Q_n \rangle$  with a slope which tends to 1 for large time, a behavior where the symmetry functions are constant equal to 2. This region corresponds to extreme events ( $Q_n > 3\langle Q_n \rangle$ ). In the third region, there is a smooth connection between the two behaviors. For the normalized excess heat, the symmetry functions are linear with  $Q_{ex,n}$  for all values of  $Q_{ex,n}$  and the slope is equal to one for all values of  $n$ . It is not exactly the case for the first values of  $n$  because it is the time in 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 of the fluctuations at equilibrium. Using the expression of the distribution of the angular position and the angular velocity, we can compute the "trajectory-dependent" heat from eq. (20):

$$Q_{G,n} = \frac{1}{2}C(\delta\theta(t_i + \tau_n)^2 - \delta\theta(t_i)^2) + \frac{1}{2}I_{\text{eff}}(\delta\dot{\theta}(t_i + \tau_n)^2 - \delta\dot{\theta}(t_i)^2) \quad (21)$$

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" heat is equivalent to the variation of internal energy for the system at equilibrium. The excess heat is :

$$Q_{ex,n} = W_n - \frac{1}{2}C\bar{\theta}(t_i)(\delta\theta(t_i + \tau_n) - \delta\theta(t_i)) - \frac{1}{2}I_{\text{eff}}\dot{\bar{\theta}}(t_i)(\delta\dot{\theta}(t_i + \tau_n) - \delta\dot{\theta}(t_i)) \quad (22)$$

As  $Q_{ex,n}$  is linear in the two independent degrees of freedom, which both have Gaussian distributions, it is normal to find that the excess heat have a Gaussian distribution [28]. So we can calculate the mean value and the variance of the excess heat for any  $n$ . We find that  $\langle Q_{ex,n} \rangle$  is equal to the injected work for any  $n$ .

The excess heat is the difference between the total heat exchanged with the thermostat and the heat exchanged with the thermostat at equilibrium. Using the first law of thermodynamics and the equation of motion, we can write the dissipated heat as the difference between the viscous dissipation and the work of the thermal noise :

$$Q_{G,n} = \int_{t_i}^{t_i + \tau_n} \nu \dot{\theta}(t')^2 dt' - \int_{t_i}^{t_i + \tau_n} \dot{\theta}(t') \eta(t') dt' \quad (23)$$

This expression holds at equilibrium as well as out of equilibrium. The only difference is that when out of equilibrium  $\theta(t) = \langle \theta(t) \rangle + \delta\theta(t)$  ; and  $\dot{\theta}(t) = \langle \dot{\theta}(t) \rangle + \delta\dot{\theta}(t)$ . It is then clear that when there is no driving, the heat dissipated at equilibrium is the same replacing  $\dot{\theta}$  by  $\delta\dot{\theta}$ . After some algebra the excess heat is :

$$Q_{ex} = \nu \int_{t_i}^{t_i + \tau_n} \langle \dot{\theta}(t') \rangle^2 dt' + 2\nu \int_{t_i}^{t_i + \tau_n} \langle \dot{\theta}(t') \rangle \delta\theta(t') dt' - \int_{t_i}^{t_i + \tau_n} \langle \dot{\theta}(t') \rangle \eta(t') dt' \quad (24)$$



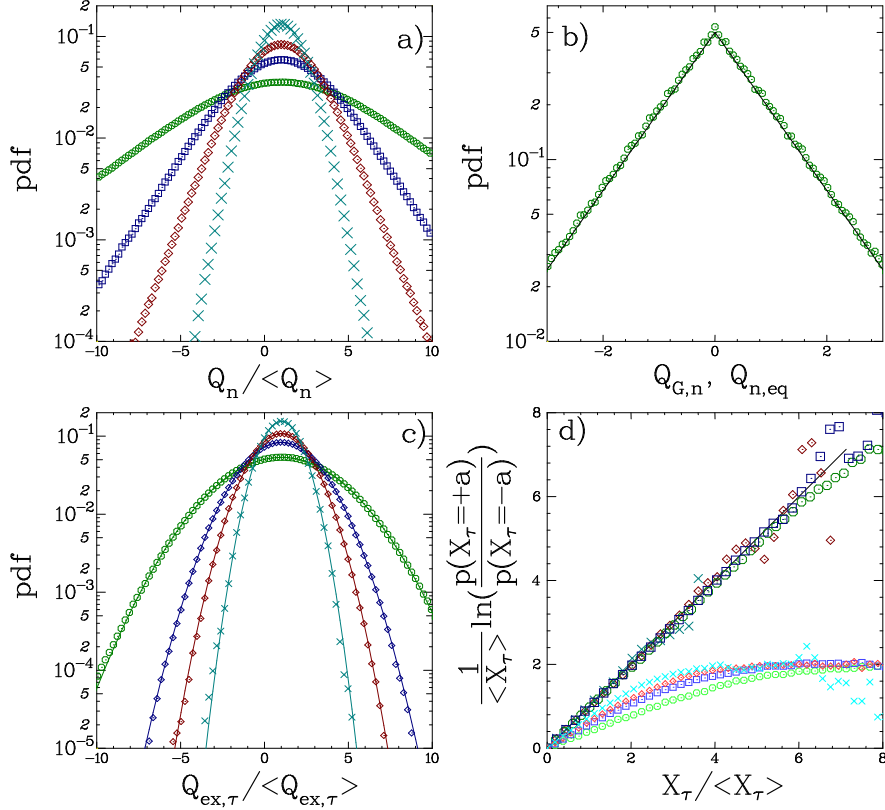


Fig. 2: Torsion pendulum. a) PDFs of the normalized dissipated heat  $Q_n/\langle Q_n \rangle$  integrated over  $n$  periods of forcing, with  $n = 7$  ( $\circ$ ),  $n = 15$  ( $\square$ ),  $n = 25$  ( $\diamond$ ) and  $n = 50$  ( $\times$ ). b) PDFs of  $Q_{G,n}$ , the distribution is independent of  $n$  and here  $n = 7$ . Continuous line is the theoretical prediction for equilibrium dissipated heat  $Q_{n,eq}$ . c) PDFs of the normalized excess heat  $Q_{ex,n}/\langle Q_{ex,n} \rangle$ , with  $n = 7$  ( $\circ$ ),  $n = 15$  ( $\square$ ),  $n = 25$  ( $\diamond$ ) and  $n = 50$  ( $\times$ ). d) Symmetry functions for the normalized dissipated heat (small symbols in light colors) and for the normalized excess heat (large symbols in dark colors) for the same values of  $n$ .

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

$$\langle \sigma_{Q_{ex,n}}^2 \rangle = 2k_B T \langle Q_{ex} \rangle + B$$

$$B = 4\nu \int \int dudv \langle \dot{\theta}(u) \rangle \langle \dot{\theta}(v) \rangle \psi(u, v) \quad (25)$$

$$\psi(u, v) = \nu \langle \delta \dot{\theta}(u) \delta \dot{\theta}(v) \rangle - \langle \delta \theta(u) \eta(v) \rangle \quad (26)$$

The first term in the function  $\psi$  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  $u < v$ . Using a variable change  $r = (u + v)/2$  and  $s = u - v$ , eq. 25 can be rewritten :

$$B = \int_{t_i}^{t_i+\tau_n} dr \int_0^{\tau_n} \langle \dot{\theta}(r + s/2) \rangle \langle \dot{\theta}(r - s/2) \rangle \tilde{\psi}(r, s) \quad (27)$$

$$\tilde{\psi}(r, s) = 2\nu \langle \delta \dot{\theta}(s) \delta \dot{\theta}(0) \rangle - \langle \delta \theta(s) \eta(0) \rangle \quad (28)$$

After some algebra we can show that the correlation function of the angular velocity and the noise is two times the

autocorrelation function of the angular velocity, therefore  $\tilde{\psi} = 0$ . Thus we obtain that the variance of the excess heat is equal to  $2k_B T \langle Q_{ex,n} \rangle$ . The Fluctuation Relation for the excess heat is :  $\Phi(Q_{ex,n}) = Q_{ex,n}$  for all times  $\tau$ , for all values of  $Q_{ex,n}$  and for any kind of stationary forcing.

For our two experimental cases, we have obtained that the "trajectory-dependent" heat can be considered as the dissipated heat we would have if the system was at equilibrium. Therefore the excess heat is the additional heat due to the presence of the external forcing : this is the part of heat which is dissipated due to the non-equilibrium process. The derivation we gave for a second order Langevin equation can be extended to a first order Langevin equation : excess heat (or excess entropy) satisfies the Fluctuation Theorem for all times for all kind of stationary intensity injected in the circuit or all kind of stationary external torque. Our derivation holds also if the system is not in a steady state : the probability we then have to consider in the computation of the "trajectory-dependent" heat is the probability of the fluctuations around the trajectory. The ratio between the average value of the excess heat at  $\tau = \tau_\alpha$  (relaxation time) and the variance of the

dissipated heat at equilibrium characterizes the distance from equilibrium  $d$  :

$$d^2 = \frac{\langle Q_{\text{ex},\tau\alpha} \rangle}{\sigma_{Q_{\tau\alpha,eq}}} = \sqrt{\frac{3n_d}{8}} \frac{\sigma_{Q_{\text{ex},\tau\alpha}}^2}{\sigma_{Q_{\tau\alpha,eq}}^2} \quad (29)$$

where  $n_d$  is the number of degrees of freedom. For the second equality, we use the Gaussianity of  $Q_{\text{ex},\tau}$ , *i.e.*  $\sigma_{Q_{\text{ex},\tau}}^2 = 2k_B T \langle Q_{\text{ex},\tau} \rangle$  and the variance of  $Q_{\tau,eq}$  in terms of  $k_B T$ , *i.e.*  $\sigma_{Q_{\tau,eq}}^2 = 3/2n_d k_B T$ . It turns out that this expression for  $d$  is the same defined in [3] with a completely different approach. Eq. 29 indicates that, when the system is driven far from equilibrium,  $\sigma_{Q_{\tau,eq}}$  becomes negligible. As a consequence the fluctuations of the excess heat become equal to the fluctuations of the dissipated heat. In other words, the PDFs of the dissipated heat far from equilibrium are Gaussian.

In conclusion, we have studied the excess heat when the system is driven in a non-equilibrium steady state. We have shown that the Fluctuation Theorem for the excess heat 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 excess heat corresponds to the difference between the total dissipated heat and heat fluctuations at equilibrium.

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