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# Heat fluctuation theorem for a relaxing system

J. R. Gomez-Solano,\* A. Petrosyan, and S. Ciliberto  
*Laboratoire de Physique, École Normale Supérieure de Lyon,  
 CNRS UMR 5672, 46, Allée d'Italie, 69364 Lyon CEDEX 07, France*  
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We measure the energy fluctuations of a Brownian particle confined by an optical trap in an aging gelatin after a very fast quench (less than 1 ms). The strong nonequilibrium fluctuations due to the assemblage of the gel, are interpreted, within the framework of fluctuation theorem, as a heat flux from the particle towards the bath. We derive, from a simple model, an analytical expression of the heat probability distribution, which fits the experimental data and satisfies a fluctuation relation similar to that of a system in contact with two baths at different temperatures.

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The heat flux between two reservoirs at different temperatures is an important and useful example of an out of equilibrium process. In small systems this heat flux is a strongly fluctuating quantity and the probability distribution of these fluctuations has been recently widely studied, within the context of fluctuation theorems [1]. These studies have been mainly devoted to the steady state, that is when the temperatures  $T_A$  and  $T_B$  of the two reservoirs,  $A$  and  $B$ , are kept constant. In such a case the probability distribution  $P(Q_\tau)$  of exchanging with the reservoir  $A$  the heat  $Q_\tau$  in a time  $\tau$ , is related to the that of exchanging the quantity  $-Q_\tau$  according:

$$\ln \frac{P(Q_\tau)}{P(-Q_\tau)} = \Delta\beta Q_\tau \quad (1)$$

where  $\Delta\beta = (1/T_B - 1/T_A)/k_B$ ,  $k_B$  is the Boltzmann constant and  $k_B\Delta\beta Q_\tau$  can be easily identified as the entropy production during the time  $\tau$  [1–3]. This equation has been derived for several theoretical models [3–7] in the stationary regime. However the non stationary case, although very useful for applications, has been studied only in some specific models [8, 9] of systems relaxing towards equilibrium. Thus one may wonder whether a relation like Eq. (1) may still hold, how it is eventually modified and what kind of information on the system can be obtained [8, 9].

These important questions have never been analyzed in any experiment. Thus the purpose of this letter is to give new insight to this problem, by measuring the energy fluctuations of a Brownian particle used as a probe inside a gelatin relaxing towards its solid-like state (gel), after a very fast quench, from above to below the gelation temperature  $T_{gel}$ . The main result of our investigation is that these fluctuations can be interpreted as a heat flux from the particle towards the bath. The measured  $P(Q_\tau)$  satisfies an equation formally equivalent to Eq. (1), but in this case  $\Delta\beta$  is a decreasing function of time. The  $P(Q_\tau)$  can be fitted by an analytical expression that we derive from a Langevin equation for a Brownian particle coupled with two baths, which fully justifies our observations.

The experiment has been performed using gelatin, a

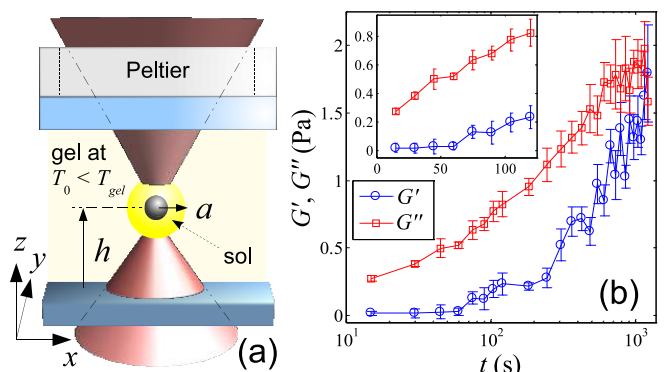


FIG. 1. (a) Schematic representation of the experimental setup to perform a local quench in a sol droplet around a trapped particle in the gel bulk. (b) Time evolution of the storage and loss moduli of the gelatin droplet at  $f = 5$  Hz after the quench. Inset: expanded view at early aging time.

thermoreversible gel obtained from denatured collagen. Above  $T_{gel}$  an aqueous gelatin solution is in a liquid viscous phase (sol), whereas below  $T_{gel}$  the formation of a network of cross-linked filaments leads to an elastic solid-like phase (gel) [10]. In this gel phase the gelatin viscoelastic properties slowly evolve toward equilibrium and share some common phenomenological features with glassy dynamics [11–13]. We are interested in this transient out-of-equilibrium regime, that we use to study the fluctuations of the energy fluxes from and to the heat bath in the nonstationary case. A similar problem has been theoretically analyzed for the first time in Refs [8, 9] for a model of aging spin glasses. It has been found that a relation like Eq. (1) can be applied to a relaxing system to obtain quantitative informations on the heat exchanges with the bath. We show in this letter that this approach, exploited only once in real experiments [14], can be indeed very useful for understanding the properties of a Brownian particle in an out-of-equilibrium bath.

In the present experiment, an aqueous gelatin solution (type-B pig skin) at a concentration of 10%wt is pre-

pared following the usual protocol described in detail in [13]. For this sample  $T_{gel} = 29^\circ\text{C}$ . This solution fills a transparent cell the temperature of which is controlled by a Peltier element [Fig. 1(a)], at  $T_0 = 26 \pm 0.05^\circ\text{C} < T_{gel}$ . Thus the solution inside the cell is in the solid-like phase. A silica bead, of radius  $r = 1 \mu\text{m}$ , is kept inside the gelatin in the focal position of a tightly focused laser beam ( $\lambda = 980 \text{ nm}$ ) at a power of 20 mW. At this power the laser produces on the particle an elastic force of stiffness  $k = 2.9 \text{ pN}/\mu\text{m}$ . Because of light absorption, the temperature of the trapped particle is  $T = 27^\circ\text{C}$ , which is still smaller than  $T_{gel}$ . Therefore the bead is inside the solid gel in the beam focus at a distance  $h = 25 \mu\text{m}$  from the cell wall, see Fig.1(a) [15]. Starting from this condition, the laser power is increased to 200 mW and the local temperature around the focus rises to  $38^\circ\text{C} > T_{gel}$ . As a result the gel melts and a liquid droplet of radius  $a = 5 \mu\text{m}$ , is formed around the trapped bead inside the the solid gel bulk, as sketched in Fig. 1(a). After 180 s, the laser power is suddenly decreased again to 20 mW so that the temperature is homogenized by heat diffusion into the bulk in less than 1 ms resulting in a very efficient quench of the droplet to the final equilibrium temperature  $T < T_{gel}$ . At  $T$  the liquid inside the droplet solidifies in about 1 hour and the particle, trapped in the center of the drop by the focused beam, is a probe of this relaxation dynamics. The quenching procedure is repeated 60 times in order to perform the proper ensemble averages.

Immediately after the quench we record the time evolution of the  $x$  position [see Fig. 1(a)] of the trapped particle measured by a position sensitive detector whose output is sampled at 8 kHz and acquired by a computer. In order to characterize the particle dynamics we measure the time evolution of the elastic  $G'$  and viscous  $G''$  moduli of the gel inside the droplet, using active microrheology [14]. This is done by applying a time-dependent sinusoidal force (of frequency  $f = 5 \text{ Hz}$  and amplitude 87 fN) to the particle through the modulation of the beam focus position and measuring the response of the bead at  $f$ . The results are shown in Fig. 1(b). One can clearly distinguish two different regimes. First, for  $t \lesssim 60 \text{ s}$  after the quench there is a transient regime where the droplet is purely viscous,  $G' = 0$ , whereas  $G''$  increases in time. For  $t > 200 \text{ s}$  the liquid gelatine inside the drop has a behavior similar to that observed in macroscopic samples [10, 13] i.e.  $G'$  and  $G''$  reach a logarithmic growth  $\sim \log t$ , with  $G'$  growing faster than  $G''$  so that the liquid drop is actually undergoing gelation. We will study the nonequilibrium statistical properties of the bead dynamics in the very first 200 s after the quench where the liquid gelatin inside the drop is mainly viscous and its elasticity ( $k_g = 6\pi r G'$ ) is negligible with respect to  $k$ .

We begin by analyzing the variance  $\sigma_x(t)^2$  of  $x$  at time  $t$  after the quench.  $\sigma_x(t)^2$  is computed over 60 independent quenches and over a short time window  $\delta t = 0.1 \text{ s}$  around each value of  $t$  in order to improve the statistics,

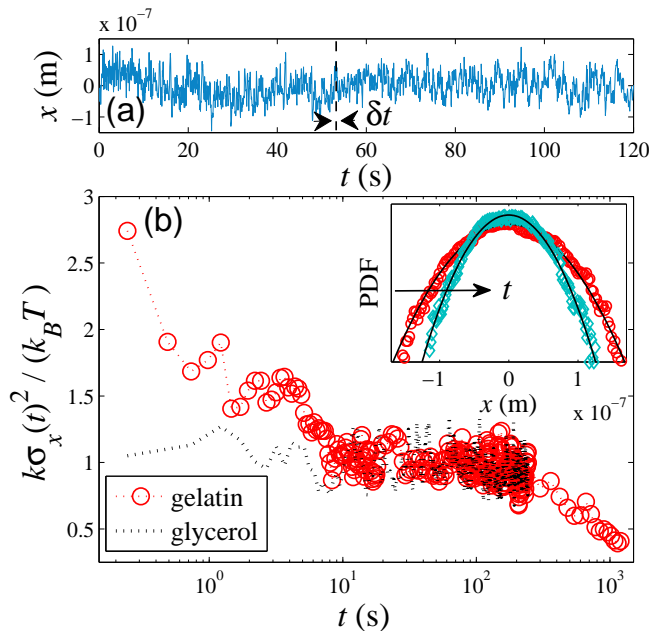


FIG. 2. (a) Time evolution of  $x$  after a quench.  $\sigma_x(t)^2$  is computed over  $\delta t = 0.1 \text{ s}$  and over 60 independent quenches. (b) Time evolution of  $\sigma_x(t)^2$  (normalized by  $k_B T/k$ ) after the quenches performed in gelatin (o) and glycerol (dashed line). Inset: Probability density of  $x$  at  $t = 0.5 \text{ s}$  and  $50 \text{ s}$  for the quench in gelatin. The solid lines are Gaussian fits.

as depicted in Fig. 2(a). The time evolution of  $\sigma_x(t)^2$  is plotted in Fig. 2(b). At the beginning,  $\sigma_x(t)^2$  is almost three times the equipartition value  $k_B T/k$  that would be obtained at equilibrium. This shows the presence of a nonthermal stochastic force on the particle due to the transient formation of the gel network. This force weakens compared to the thermal fluctuations becoming negligible at  $\sim 20 \text{ s}$  so that  $\sigma_x(t)^2$  slowly decreases in time, reaching the equilibrium value for  $t \lesssim 20 \text{ s}$ . This relaxation timescale is two orders of magnitude larger than the initial viscous relaxation time of the particle:  $\tau_k = 3rG''/(kf) = 65 \text{ ms}$ . Finally for  $t \gtrsim 200 \text{ s}$ ,  $\sigma_x(t)^2$  starts again to decrease because of the appearance of a  $k_g$ , confirming the direct measure of  $G'$ , shown in Fig. 1(b), and justifying that for  $t \leq 200 \text{ s}$  the gelatin elasticity is negligible, i.e.  $k_g \ll k$ . During this relaxation process  $x$  remains Gaussian as shown in the inset of Fig. 2(b).

In Fig. 2(b) we also plot the time evolution of  $\sigma_x(t)^2$  measured, after the same quenching procedure, in a Newtonian fluid (glycerol 60%wt in water) with the same viscosity of the initial sol phase of the gelatine. In this case, the particle dynamics must settle into an equilibrium state in a time  $\sim \tau_k$  after the quench [16]. Indeed in Fig. 2(b) we see that, in glycerol,  $\sigma_x(t)^2 = k_B T/k$  for all  $t$  within the experimental accuracy. This confirms that no experimental artifact is present and that the observed dependence of  $\sigma_x(t)^2$  in gelatin is a real nonequilibrium effect due to the sol-gel transition.

We now focus on the fluctuations of the heat exchanged between the particle and the droplet for  $t < 200$  s, *i.e.* when the elasticity of the gelatin inside the drop is negligible ( $k_g \ll k$ ). From the previous experimental results for  $\sigma_x$ , the nonequilibrium dynamics of  $x$  after the quench can be modelled by the overdamped Langevin equation

$$\gamma_t \dot{x}_t = -kx_t + \zeta_t^T + \zeta_t^{NT}. \quad (2)$$

In Eq. (2)  $\gamma_t = 3rG''/f$  is the age-dependent viscous drag coefficient,  $-kx_t$  is the harmonic force exerted by the optical trap,  $\zeta_t^T$  and  $\zeta_t^{NT}$  are the thermal and nonthermal fluctuating forces on the particle due to the gelatin chains. Both are zero mean forces with  $\zeta_t^T$  satisfying  $\langle \zeta_t^T \zeta_s^T \rangle = 2k_B T \gamma_t \delta(t-s)$  and  $\zeta_t^{NT}$  slowly correlated in time. Multiplying Eq. (2) by  $\dot{x}_t$  and integrating over the time interval  $[t, t+\tau]$  one obtains the energy balance [17]

$$Q_{t,\tau} = \frac{k}{2}(x_{t+\tau}^2 - x_t^2), \quad (3)$$

where  $Q_{t,\tau}$ , the heat exchanged between the particle and the gelatin droplet, is

$$Q_{t,\tau} = - \int_t^{t+\tau} \gamma_s \dot{x}_s^2 ds + \int_t^{t+\tau} (\zeta_s^T + \zeta_s^{NT}) \dot{x}_s ds, \quad (4)$$

In Eq. (4) the first integral accounts for the heat delivered by the particle to the environment by viscous dissipation whereas the second one represents the heat injected by the two kinds of fluctuating forces. According to Eq. (3) the mean heat transferred during  $[t, t+\tau]$  is

$$\langle Q_{t,\tau} \rangle = (k/2)[\sigma_x(t+\tau)^2 - \sigma_x(t)^2] \leq 0$$

which reveals the existence of a mean heat flux from the particle to the surroundings over the timescale  $\tau$  because of the relaxation of  $\sigma_x$ . The maximum value  $|\langle Q_{t,\tau} \rangle| \approx k_B T$  takes place at  $t = 0$  s and for  $20 \text{ s} \lesssim \tau \lesssim 60 \text{ s}$ . Non-negligible values of the mean heat compared to  $k_B T$  persist for several seconds after the quench. Nevertheless, as  $t$  increases,  $|\langle Q_{t,\tau} \rangle|$  decreases becoming negligible and experimentally undetectable for  $t \gtrsim 20$  s.

The probability density function  $P_t(q_\tau)$  of the normalized heat  $q_{t,\tau} = Q_{t,\tau}/(k_B T)$  can be readily computed from the experimental trajectories  $x_t$  using Eq. (3).  $P_t(q_\tau)$  is computed over the 60 initial quenches and over a short time window  $\delta t = 0.1$  s around each  $t$  and  $t+\tau$ , as sketched in Fig 2(a). We focus on a large value of  $\tau$  in order to probe timescales comparable to the relaxation of the nonthermal fluctuations. Fig. 3(a) shows the profile of  $P_t(q_\tau)$  at different times  $t$  after the quench for  $\tau = 30$  s.  $P_t(q_\tau)$  is highly non-Gaussian with a spike at  $q_\tau = 0$  and slowly decaying tails for all the values of  $t$ . Immediately after the quench the profile is strongly asymmetric with a long tail occurring at negative fluctuations. As  $t$  increases the asymmetry of  $P_t(q_\tau)$  decreases becoming effectively symmetric at  $t \gtrsim 20$  s for our experimental resolution.

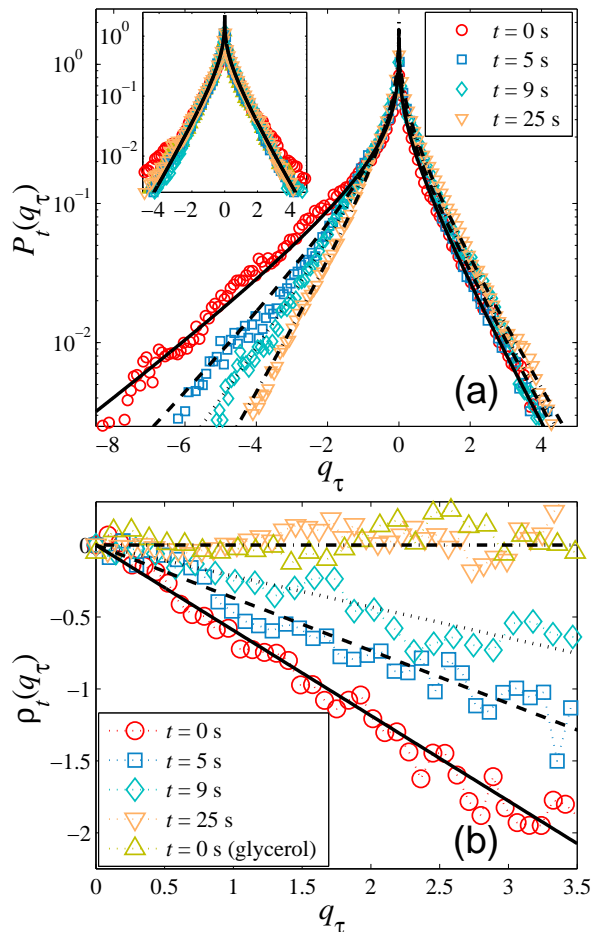


FIG. 3. (a) Probability density  $P_t(q_\tau)$  of the normalized heat  $q_{t,\tau}$  for  $\tau = 30$  s at different times  $t$  after the quench. The theoretical lines are computed using Eq. (5). Inset:  $P_t(q_\tau)$  computed, at the same  $t$  and  $\tau$  during a quench performed in glycerol. The solid line corresponds to the theoretical equilibrium profile. (b) Asymmetry function of the  $P_t(q_\tau)$  shown in (a). The straight lines are obtained using Eq. (7).

As in Eq.(1), the *asymmetry function*  $\rho_t(q_\tau) = \ln[P_t(q_\tau)/P_t(-q_\tau)]$  is commonly used to measure the asymmetry of  $P(q_\tau)$  between the positive and the negative values of the fluctuations. The function  $\rho_t(q_\tau)$ , computed from the  $P_t(q_\tau)$  shown in Fig. 3(a), is plotted in Fig 3(b). It is a linear function of its argument  $q_\tau$ :  $\rho_t(q_\tau) = -\Delta\beta_{t,\tau}q_\tau$ . The slope  $\Delta\beta_{t,\tau}$  decreases as  $t$  increases approaching the symmetric value  $\Delta\beta_{t,\tau} = 0$  as  $|\langle Q_{t,\tau} \rangle| \ll k_B T$ . This linear relation is formally similar to Eq.(1) except for the time dependent  $\Delta\beta_{t,\tau}$ .

The asymmetry of  $P_t(q_\tau)$  can be directly linked to the nonstationarity of the aging bath through the quantity  $\sigma_x$  in a very simple way. Using Eq. (3) and the experimental fact that  $x$  is Gaussian [Fig. 2(b)], the analytical

expression of  $P_t(q_\tau)$  for large  $\tau$  can be computed [15] :

$$P_t(q_\tau) = \frac{A_{t,\tau}}{\pi} K_0(B_{t,\tau}|q_\tau|) \exp\left(-\frac{\Delta_{t,\tau} A_{t,\tau}}{2} q_\tau\right), \quad (5)$$

where  $K_0$  is the zeroth-order modified Bessel function of the second kind and

$$\begin{aligned} A_{t,\tau} &= \frac{k_B T}{k \sigma_x(t) \sigma_x(t+\tau)}, \\ \Delta_{t,\tau} &= \frac{\sigma_x(t)}{\sigma_x(t+\tau)} - \frac{\sigma_x(t+\tau)}{\sigma_x(t)}, \\ B_{t,\tau} &= A_{t,\tau} \sqrt{1 + \Delta_{t,\tau}^2/4} \end{aligned} \quad (6)$$

In Eq. (5) the asymmetry of the density is completely determined by the parameter  $\Delta_{t,\tau}$  in the exponential. At equilibrium  $\Delta_{t,\tau} = 0$ ,  $A_{t,\tau} = B_{t,\tau} = 1$  regardless of  $t$  and  $\tau$ , so that one recovers the symmetric equilibrium profile  $P_t(q_\tau) = K_0(|q_\tau|)/\pi$  with  $\langle q_{t,\tau} \rangle = 0$  [18, 19]. In Fig. 3(a) for each experimental  $P_t(q_\tau)$  we plot the theoretical profile given by the analytical formula (5) using the respective experimental value of  $\sigma_x$  shown in Fig. 2(b). The excellent agreement confirms that the Langevin model (2) is suitable to describe the particle dynamics and the asymmetric heat exchange with the gelatin bath after the quench. Once again, we check that the long-lived asymmetry occurs because of the intricate nonequilibrium nature of the bath. In the inset of Fig. 3(a) we plot  $P_t(q_\tau)$  with  $\tau = 30$  s for the local quenches performed in glycerol.  $P_t(q_\tau)$  quickly converges to the equilibrium profile and it is always symmetric with respect to  $q_\tau = 0$ .

From Eq. (5) one obtains the explicit expression for the asymmetry function  $\rho_t(q_\tau) = -\Delta\beta_{t,\tau} q_\tau$  and  $\Delta\beta_{t,\tau}$

$$\Delta\beta_{t,\tau} = \frac{k_B T}{k} \left[ \frac{1}{\sigma_x(t+\tau)^2} - \frac{1}{\sigma_x(t)^2} \right]. \quad (7)$$

Hence, the linearity of  $\rho_t(q_\tau)$  is analytically satisfied for all the values of the heat fluctuations and for all  $t$  even when  $P(q_\tau)$  is strongly non-Gaussian. In Fig. 3(b) we plot the straight lines with the slope  $\Delta\beta_{t,\tau}$  given by Eq. (7) and computed using the experimental values of  $\sigma_x$ . The agreement with the experimental data is very good verifying a fluctuation relation, as Eq. (1). For comparison we also plot  $\rho_t(q_\tau)$  for the quench in glycerol at  $t = 0$  and  $\tau = 30$  s. In this case the heat exchange process is always symmetric.

Eq.(7) gains a very intuitive interpretation if one introduces an equipartition-like relation for the particle motion for  $0 \leq t \lesssim 60$  s:  $k_B T_{eff}(t) = k \sigma_x(t)^2$ . Here  $T_{eff}$  is the effective temperature perceived by the particle due to its coupling with the nonequilibrium gelatin environment. In this way the parameter  $\Delta\beta_{t,\tau}$  can be written conveniently as

$$\Delta\beta_{t,\tau} = \left( \frac{1}{T_{eff}(t+\tau)} - \frac{1}{T_{eff}(t)} \right) T, \quad (8)$$

so that Eq. (7) takes the form of Eq. (1). Hence  $\Delta S_\tau = -k_B \Delta\beta_{t,\tau} q_{t,\tau}$  can be naturally identified as the entropy produced by the breakdown of the time-reversal symmetry due to the effective temperature imbalance at two different times after the quench. As the gelatin droplet ages  $\Delta S_\tau$  slows down and the particle exhibits an equilibrium-like dynamics for the experimental timescales. We point out that unlike Eq. (1) derived in Refs. [3–7] for nonequilibrium steady states, Eq. (7) holds for a nonstationary regime created by the nonequilibrium bath.

In conclusion, we have experimentally studied the fluctuations of the heat exchanged between a trapped Brownian particle and a nonstationary bath after a quench. In the particular case of gelatin, the nonequilibrium assemblage of the fiber network after the quench gives rise to nonthermal forces comparable to the thermal fluctuations acting on the particle. The relaxation of these forces as the bath ages creates an asymmetric heat flux from the particle to the environment. We have shown that the distribution of the heat satisfies a fluctuation relation even when the bath is in a nonstationary state. Our results suggest that this fluctuation relation may appear as a very robust symmetry property of heat exchange processes in other kinds of relaxing systems.

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\* juan.gomez\_solano@ens-lyon.fr

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