Entropy production and time asymmetry in nonequilibrium fluctuations

David Andrieux, Pierre Gaspard, Sergio Ciliberto, Nicolas Garnier, Sylvain Joubaud, Artyom Petrosyan

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D. Andrieux and P. Gaspard
Center for Nonlinear Phenomena and Complex Systems,
Université Libre de Bruxelles, Code Postal 231, Campus Plaine, B-1050 Brussels, Belgium

S. Ciliberto, N. Garnier, S. Joubaud, and A. Petrosyan
Laboratoire de Physique, CNRS UMR 5672, Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon Cédex 07, France

The time-reversal symmetry of nonequilibrium fluctuations is experimentally investigated in two out-of-equilibrium systems namely, a Brownian particle in a trap moving at constant speed and an electric circuit with an imposed mean current. The dynamical randomness of their nonequilibrium fluctuations is characterized in terms of the standard and time-reversed entropies per unit time of dynamical systems theory. We present experimental results showing that their difference equals the thermodynamic entropy production in units of Boltzmann's constant.

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Newton's equations ruling the motion of particles in matter are known to be time-reversal symmetric. Yet, macroscopic processes present irreversible behavior in which entropy is produced according to the second law of thermodynamics. Recent works suggest that this thermodynamic time asymmetry could be understood in terms similar as those used for other symmetry breaking phenomena in condensed matter physics. The breaking of time-reversal symmetry should concern the fluctuations in systems driven out of equilibrium. These fluctuations may be described in terms of the probabilities weighting the different possible trajectories of the systems. Albeit the time-reversal symmetry of the microscopic Newtonian dynamics says that each trajectory corresponds to a time-reversed one, it turns out that distinct forward and backward trajectories may have different probability weights if the system is out of equilibrium. For example, the probability for a driven Brownian particle of having a trajectory from a point A to a point B is different of having the same reverse trajectory from B to A.

This important observation can be further elaborated to establish a connection with the entropy production. We consider the paths or histories $\boldsymbol{z} = (z_0, z_1, z_2, ..., z_{n-1})$ obtained by sampling the trajectories $z(t)$ at regular time intervals τ. The probability weight of a typical path is known to decay as

$$P_+(z_0, z_1, z_2, ..., z_{n-1}) \sim \exp(-n\tau h) \tag{1}$$

as the number n of time intervals increases [1, 2, 3, 4]. The decay rate h is known as the entropy per unit time of dynamical systems theory [1, 2, 3, 4]. This quantity characterizes the temporal disorder, i.e., the dynamical randomness of the stochastic process. We can compare (1) with the probability weight of the time-reversed path $\boldsymbol{z}^{\mathrm{R}} = (z_{n-1}, ..., z_2, z_1, z_0)$ in the nonequilibrium system with reversed driving constraints (denoted by the minus sign):

$$P_-(z_{n-1}, ..., z_2, z_1, z_0) \sim \exp(-n\tau h^{\mathrm{R}}) \; . \tag{2}$$

It can be shown that, out of equilibrium, the probabilities of the time-reversed paths decay faster than the probabilities of the paths themselves [5]. We can interpret this as a breaking of the time-reversal symmetry in the invariant probability distribution describing the nonequilibrium steady state, the fundamental underlying Newtonian dynamics still being time-reversal symmetric. The decay rate h^{R} in Eq. (2) is called the time-reversed entropy per unit time and characterizes the dynamical randomness of the time-reversed paths [5, 6]. The remarkable result is that the difference between both quantities h^{R} and h gives the entropy production of irreversible thermodynamics

$$\frac{1}{k_{\mathrm{B}}} \frac{d_{\mathrm{i}}S}{dt} = h^{\mathrm{R}} - h \tag{3}$$

where k_{B} is Boltzmann's constant [5, 6, 7, 8, 9]. In this sense, entropy production would find its origin in the time asymmetry of dynamical randomness. At equilibrium, the entropy production vanishes and both quantities h^{R} and h are equal, as expected from the principle of detailed balance.

The purpose of the present Letter is to provide experimental evidence for the above connection in two nonequilibrium fluctuating systems. The first system is a Brownian particle in a fluid at inverse temperature $\beta = (k_{\mathrm{B}}T)^{-1}$ and bounded by a laser trap with a time-dependent potential $V(x_t, t)$ where x_t is the particle position at time t. This potential is harmonic and driven at the velocity u so that $V(x_t, t) = (k/2)(x_t - ut)^2$ with stiffness k. The surrounding fluid is responsible for a friction force $-\alpha dx_t/dt$ and the corresponding Langevin fluctuating force. In the experimental setup, $k = 9.62\ 10^{-6}$ kg s^{-2} and the relaxation time $\tau_R = \alpha/k = 3.05\ 10^{-3}$ s. The second system is an electric circuit driven out of equilibrium by a current source which imposes the mean current I. The current in the circuit fluctuates because of the intrinsic thermal noise of the circuit (Nyquist noise) [10, 11]. Specifically the circuit is composed of a capacitance $C = 278$ pF in parallel with a resistance $R = 9.22$ MΩ so that the time constant of the circuit is $\tau_R = RC = 2.56\ 10^{-3}$ s. This electric circuit and the driven Brownian particle, although physically different, are known to be formally equivalent by the correspondence $\alpha \leftrightarrow R$, $k \leftrightarrow 1/C$ and $u \leftrightarrow I$ while x_t corresponds to the charge q_t inside the resistor at the time t [10, 11]. The variables x_t and q_t are acquired at a sampling frequency $1/\tau = 8192$ Hz. In both experiments, the temperature is $T = 298$ K.

The proposed method is very closely related to the experiments recently undertaken to measure nonequilibrium fluctuation relations [11, 12, 13]. Here, we investigate the possibility to extract the dissipated heat and the entropy production from quantities – the so-called entropies per unit time – characterizing the dynamical randomness of the paths and the corresponding time-reversed paths with also a reversal of the sign of the nonequilibrium constraint. The entropies per unit time can be calculated from two long time series with sufficient temporal and spatial resolutions, measured in two similar experiments but one driven with an opposite constraint, i.e., $u \to -u$ and $I \to -I$. The experiment thus consists in recording a pair of long temporal series in each of the two different experimental setups.

We present the proposed method in the case of the Brownian particle in a moving trap. Following Ref. [14], the heat Q_t dissipated along a random trajectory during a time interval t is given by

$$Q_t = \int_0^t \frac{dx_{t'}}{dt'} F(x_{t'} - ut')\, dt' \ . \tag{4}$$

where $F(x_t, t) = -\partial V(x_t, t)/\partial x_t = -k(x_t - ut)$ is the force exerted by the potential $V(x_t, t)$ of the trap. This dissipated heat is a random variable that has been shown to obey an extended fluctuation theorem due to his non-Gaussian tail [14]. After a long enough time, the system reaches a nonequilibrium steady state, in which the entropy production is related to the mean value of the dissipated heat according to

$$\frac{d_{\rm i}S}{dt} = \frac{1}{T}\frac{d\langle Q_t\rangle}{dt} = \frac{\alpha u^2}{T} \ . \tag{5}$$

Our aim is thus to show that one can extract the heat dissipated during an individual path by comparing the probabilities of this path with the time-reversed path having also reversed the displacement of the potential, i.e., $u \to -u$.

We first make the change to the comoving frame with the minimum of the potential so that $z \equiv x - ut$. After initial transients, the system will reach a steady state characterized by a stationary probability distribution. As we are interested in the probability of a given succession of states corresponding to a discretization of the signal at small time intervals τ, a multi-time random variable is defined according to $\boldsymbol{Z} = [Z(t_0), Z(t_0 + \tau), \ldots, Z(t_0 + n\tau - \tau)]$ which corresponds to the signal during the time period $t - t_0 = n\tau$. For a stationary process their distribution do not depend on the initial time t_0. From the point of view of probability theory, the process is defined by the n-time joint probabilities $P_\sigma(\boldsymbol{z}; d\boldsymbol{z}, \tau, n) = \Pr\{\boldsymbol{z} < \boldsymbol{Z} < \boldsymbol{z} + d\boldsymbol{z}; \sigma\} = p_\sigma(\boldsymbol{z})d\boldsymbol{z}$, where $p_\sigma(\boldsymbol{z})$ is the probability density for $\boldsymbol{Z}$ to take the value $\boldsymbol{z} = (z_0, z_1, \ldots, z_{n-1})$ at times $t_0 + i\tau$ for a nonequilibrium driving $\sigma = u/|u| = \pm 1$. In the overdamped case, the motion of the Brownian particle can be modeled as a Langevin equation with a Gaussian white noise. Thanks to the Markovian nature of this process, the joint probabilities can be decomposed into the products of the Green functions $G(z_i, z_{i-1}; \tau)dz_i$ for $i = 1, \ldots, n$. $G(z, z_0; t)$ gives the probability density to be at position z at time t given that the initial position was z_0 [15, 16]. To extract the dissipation occurring along a single trajectory, one has to look at the ratio of the probability of the forward path over the probability of the reversed path having also reversed the displacement of the potential. Indeed, taking the logarithm of this ratio and the continuous limit $\tau \to 0$, $n \to \infty$ with $n\tau = t$, we find

$$\ln \frac{P_+(\boldsymbol{z}; {\rm d}\boldsymbol{z}, \tau, n)}{P_-(\boldsymbol{z}^{\rm R}; {\rm d}\boldsymbol{z}, \tau, n)} = \beta u \int_0^t F(z_{t'})\, dt' - \beta\Big[V(z_t) - V(z_0)\Big] \tag{6}$$

which is exactly the heat Q_t in Eq. (4) expressed in the z variable and multiplied by the inverse temperature. This relation holds at the level of the paths of the particle. A similar relation but concerning the distribution of the work done on a time-dependent system has been derived by Crooks [17, 18]. We emphasize that the reversal of u is essential for the logarithm of this ratio of probability to present a behavior growing linearly in time.

This calculation shows that the heat dissipated along a single trajectory can be calculated from a ratio of probabilities involving this trajectory and its time reversal with the supplementary condition that the sign of u be reversed as well. Now, due to the continuous nature in time and in space of the process, one has to consider (ϵ, τ) quantities, i.e. quantities defined on cells of size ϵ and measured at time intervals τ. Therefore, let us consider the probability $P_+(\boldsymbol{Z}_m; \epsilon, \tau, n)$ for the path to remain within a distance ϵ of some reference path $\boldsymbol{Z}_m$, made of n successive positions of the Brownian particle observed at time intervals τ for the forward process. The probability is obtained by searching for the recurrences of M such reference paths or patterns in the time series. Next, we can introduce the quantity $P_-(\boldsymbol{Z}_m^{\rm R}; \epsilon, \tau, n)$ which is the probability for a reversed path of the reversed process to remain within a distance ϵ of the reference path $\boldsymbol{Z}_m$ (of the forward process) for n successive positions. According to a numerical procedure proposed by Grassberger, Procaccia and others [1, 2] the entropy per unit time can be estimated by the linear growth of the mean 'pattern entropy' defined as

$$H(\epsilon, \tau, n) = -\frac{1}{M} \sum_{m=1}^{M} \ln P_+(\boldsymbol{Z}_m; \epsilon, \tau, n) \qquad (7)$$

and, similarly,

$$H^{\mathrm{R}}(\epsilon, \tau, n) = -\frac{1}{M} \sum_{m=1}^{M} \ln P_-(\boldsymbol{Z}_m^{\mathrm{R}}; \epsilon, \tau, n) \qquad (8)$$

for the reversed process. The (ϵ,τ)-entropies per unit time $h(\epsilon, \tau)$ and $h^{\mathrm{R}}(\epsilon, \tau)$ are defined by the linear growth of the mean pattern entropy as a function of the time $n\tau$ of the sequences [1, 2, 4]. The mean entropy production in the nonequilibrium stationary state should thus be given by the difference between these two quantities:

$$\frac{1}{k_{\mathrm{B}}} \frac{d_{\mathrm{i}}S}{dt} = \lim_{\epsilon \to 0} \lim_{\tau \to 0} \left[h^{\mathrm{R}}(\epsilon, \tau) - h(\epsilon, \tau) \right] . \qquad (9)$$

It is important to note that the probability of the reversed paths are compared and averaged over the paths of the forward process in order to obtain Eq. (9). The entropy production is thus expressed as the difference of two usually very large quantities which increase for ϵ, τ going to zero with a scaling law in ϵ^{-2} as shown in Ref. [4, 19]. Nevertheless, the difference remains finite and gives the entropy production. Equation (9) has the general form of large-deviation dynamical relationships recently derived in the context of nonequilibrium statistical thermodynamics [6].

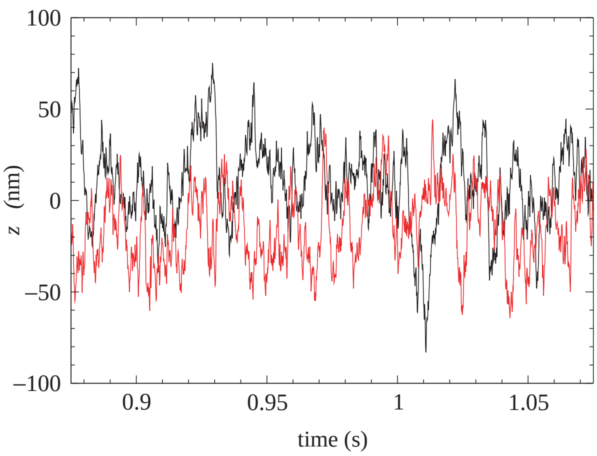

FIG. 1: Time series of typical paths $z(t)$ for the Brownian particle in the optical trap moving at the velocity u for the forward process and $-u$ for the reversed process with $u = 4.24\ 10^{-6} m/s$.

In order to test experimentally Eq. (9), we have analyzed for a specific value of $|u|$ a pair of time series up to $5\ 10^7$ points each, one corresponding to the forward process and the other corresponding to the reversed process, having discarded first the transient evolution. Figure 1 depicts examples of paths $z(t)$ for the Brownian particle in a moving optical trap.

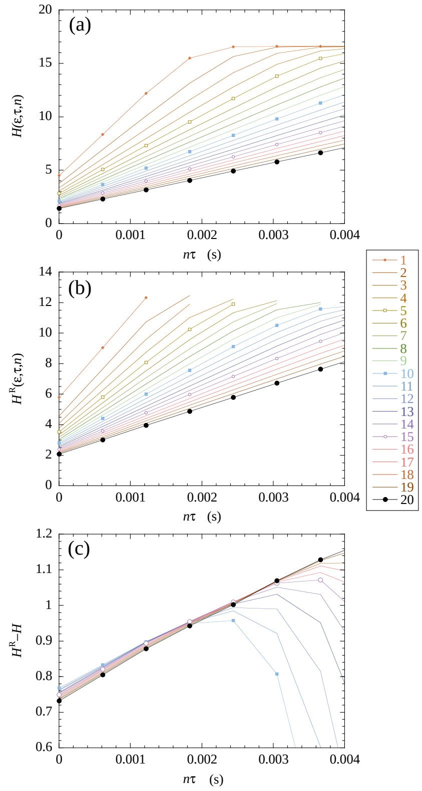

FIG. 2: (a) Entropy production of the Brownian particle versus the driving speed u. The solid line is given by Eq. (5). (b) Entropy production of the RC electric circuit versus the injected current I. The solid line is the Joule law, $d_{\mathrm{i}}S/dt = RI^2/T$. The dots are the results of Eq. (9).

For different values of ϵ between 5.6-11.2 nm, the mean pattern entropy (7) is calculated with the distance defined by taking the maximum among the deviations $|Z(t) - Z_m(t)|$ with respect to some reference path $\boldsymbol{Z}_m$ for the times $t = 0, \tau, \ldots (n-1)\tau$. The forward entropy per unit time $h(\epsilon, \tau)$ is evaluated from the linear growth of the mean pattern entropy (7) with the time $n\tau$. The backward entropy per unit time $h^{\mathrm{R}}(\epsilon, \tau)$ is obtained similarly from the time-reversed pattern entropy (8). The difference of the two dynamical entropies gives the entropy production depicted in Fig. 2a for different driving speeds u. We get a good agreement with the theoretical prediction (5).

On the other hand, we have analyzed by the same method the time series of the RC electric circuit. We see in Fig. 2b that the entropy production obtained from the time series analysis of the RC circuit agrees very well with the known Joule law, which is a further confirmation of Eq. (9).

We also tested the possibility to extract the heat (4) dissipated along a single stochastic path by searching for the recurrences in the time series according to Eq. (6).

A randomly selected path as well as the corresponding heat dissipated are plotted in Fig. 3. We find a very good agreement so that the relation (6) is also verified at the level of single paths. At this level, the heat exchanged between the particle and the surrounding fluid can be positive or negative because of the molecular fluctuations. It is only by averaging over the forward process that the dissipated heat takes the positive value depicted in Fig. 2.

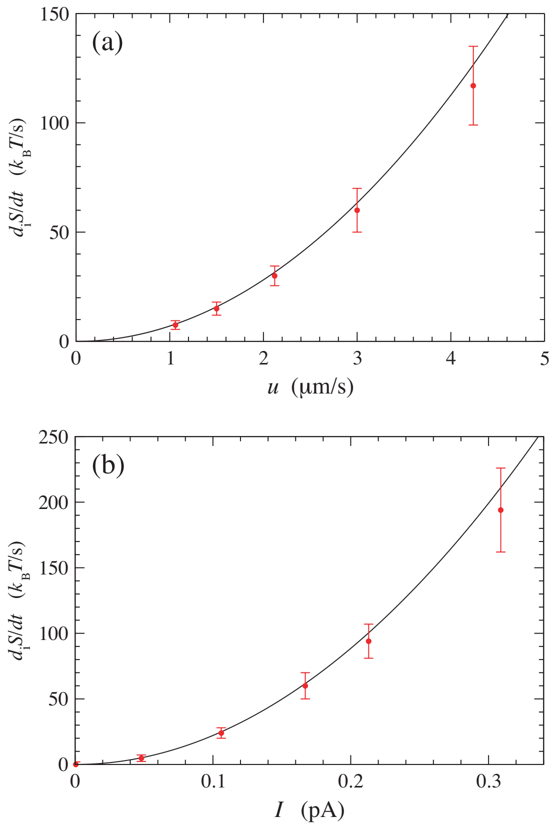

FIG. 3: Measure of the heat dissipated by the Brownian particle along the forward and reversed paths of Fig. 1. The trap velocities are $\pm u$ with $u = 4.24\ 10^{-6} m/s$. We are searching for recurrences between the two processes. (a) Inset: A randomly selected trajectory in the time series. The probabilities of the corresponding forward (black) and the backward (red) paths for $\epsilon = 8.4$ nm. These probabilities present an exponential decrease modulated by the fluctuations. (b) The dissipated heat given by the logarithm of the ratio of the forward and backward probabilities according to Eq. (6) for different values of $\epsilon = k \times 0.558$ nm with $k = 11, \ldots, 20$ in the range 6.1-11.2 nm. They are compared with the theoretical value (squares) calculated from Eq. (4). For small values of ϵ, the agreement is quite good for short time and within experimental errors for larger time.

In conclusion, we measured the entropy production by searching the recurrences of trajectories in the fluctuating dynamics of two nonequilibrium processes. The experiments we performed consisted in the recording of two long time series. The first one corresponds to a forward experiment while the other is measured from the same experimental setup except that the sign of the constraint driving the system out of equilibrium has been reversed. From these two time series, we are able to compute two dynamical entropies, the difference of which gives the entropy production. Moreover, we tested the possibility to extract the dissipated heat along a single random path. This shows that the entropy production arises from the breaking of the time-reversal symmetry in the probability distribution of the statistical description of the nonequilibrium steady state. Since the decay rates of the multitime probabilities of the forward and reversed paths characterize their dynamical randomness, the present results show that the thermodynamic entropy production finds its origin in the time asymmetry of the dynamical randomness.

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