



ELSEVIER

Contents lists available at ScienceDirect

Comptes Rendus Physique

www.sciencedirect.com



Prix Jaffé 2018 de l'Académie des sciences

From space-time chaos to stochastic thermodynamics

Du chaos de l'espace-temps à la thermodynamique stochastique

Sergio Ciliberto

Université de Lyon, CNRS, Laboratoire de physique, École normale supérieure de Lyon (UMR 5672), 46, allée d'Italie, 69364 Lyon cedex 07, France



ARTICLE INFO

Article history:

Available online 19 September 2019

Keywords:

Stochastic thermodynamics
Out of equilibrium
Thermal noise
Information
Chaotic dynamics

Mots-clés :

Thermodynamique stochastique
Hors équilibre
Bruit thermique
Information
Dynamique chaotique

ABSTRACT

We summarize the results of several experiments that show the evolution of some scientific interests and goals of the statistical and nonlinear physics community in the last 40 years. Specifically, we present how the ideas of extending concepts of equilibrium statistical physics to out-of-equilibrium physics have been developed to characterize various phenomena such as, for example, transition to space-time chaos and glass aging. We then discuss the applications of this out-of-equilibrium thermodynamics to microsystems driven out of equilibrium either by external forces or by temperature gradients. We show that in these systems thermal fluctuations play a role and that all thermodynamics quantities, such as work, heat, and entropy fluctuate. We recall general concepts such as fluctuation theorems and fluctuation dissipation relations used to characterize the statistical properties of these small systems. We describe experiments where all these concepts have been applied and tested with high accuracy. Finally, we show how these theoretical concepts and the experiments allowed us to improve our knowledge on the connection between information and thermodynamics.

© 2019 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

R É S U M É

Nous résumons plusieurs expériences qui montrent l'évolution de certains intérêts et objectifs scientifiques de la physique statistique au cours des quarante dernières années. En particulier, nous présentons de quelle façon les idées sur les fluctuations d'énergie dans les systèmes hors équilibre se sont développées aux niveaux théorique et expérimental, en partant des études sur le chaos spatio-temporel. Ces idées ont été appliquées aux systèmes microscopiques dans lesquels le rôle des fluctuations thermiques ne peut pas être négligé. Dans ce contexte, nous décrivons quelques expériences dans lesquelles les propriétés statistiques des fluctuations du travail, de la chaleur et de l'entropie ont été mesurées. Enfin, nous montrons comment ces mesures nous ont permis de mieux comprendre le lien entre information et thermodynamique.

© 2019 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

E-mail address: sergio.ciliberto@ens-lyon.fr.

<https://doi.org/10.1016/j.crhy.2019.09.001>

1631-0705/© 2019 Académie des sciences. Published by Elsevier Masson SAS. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Thermodynamical equilibrium is an idealized situation that occurs very rarely in nature, being out of equilibrium the most common case. Physical systems can indeed be out of equilibrium either because they are submitted to external forces and temperature gradients or because they are slowly relaxing towards equilibrium. In both cases there will be a balance between the injected and dissipated energies, which in general are fluctuating quantities. For example, let us consider the motion of a Brownian particle subjected to a constant external force; because of thermal fluctuations, the work performed on the particle by this force per unit time, i.e. the injected power, fluctuates and the smaller is the force, the larger will be the importance of power fluctuations. Indeed thermal fluctuations become important when the size of the system is decreased and in macroscopic systems one does not care about them. However, the injected and dissipated energies may fluctuate also in macroscopic systems if the dynamics is chaotic. For instance, think of a motor used to stir a fluid strongly. The motor can be driven by imposing a constant velocity. Because of the turbulent motion of the fluid, the power needed to keep the velocity constant fluctuates [1,2]. This simple example shows that fluctuations of the injected and dissipated power may be relevant not only in microscopic but also in macroscopic systems such as hydrodynamic flows [2], granular media [3–6], mechanical systems [7], and more recently on self-propelling particles [8,9]. The main difference is that, in macroscopic systems, fluctuations are produced by the dynamics and are sustained by a constant energy flux, whereas in small systems they are either of thermal or quantum nature. As in this article we will discuss classical systems, it is useful to divide the fluctuations in out-of-equilibrium systems into two classes: one where thermal fluctuations play a significant role (thermal systems) and another where the fluctuations are produced by chaotic flows or fluctuating driving forces (athermal chaotic systems).

In the last fifteen years, we have experimentally studied the properties of energy fluctuations in macroscopic and microscopic systems, such as turbulent flows, electronic circuits, Brownian particles, and micro actuators. However, before discussing the kind of questions we analyzed within the framework of the so-called stochastic thermodynamic, we would like to discuss how our interest in these problems developed.

Indeed, around the years 1980–1990, the chaotic dynamics in highly confined systems have been widely experimentally studied to characterize the dynamics in terms of the route to chaos, the Lyapunov exponents, and the attractors properties. In the same period based on the work of Y. Pomeau [10], P. Manneville [11], and other theoreticians, we started to investigate the transition to space-time chaos in systems whose size was much larger than the instability wavelength. The experiments showed that the transition presented features of a second-order phase transition and that several analogies with thermodynamics can be done for the fluctuations of global variables characterizing the disorder of these systems [12, 13]. For example, P. Hohenberg and B. Shraiman [14] proposed that, for these chaotic systems, thermodynamics relations among the observables might be constructed and an effective temperature might be defined using Fluctuations Dissipation Relation (FDR), i.e. extending the fluctuation dissipation theorem out of equilibrium and defining the temperature as the correlation–response ratio (see section 3). Using an experiment of thermal convection, we showed that, in some specific cases, these ideas can be applied to real systems [15], although many questions have been raised about the general validity of these experimental results. Performing these experiments, we realize that similar questions have been asked in the study of other problems, such as, for example, the aging of amorphous materials. Specifically, L. Cugliandolo and J. Kurchan [16,17] proposed the use of FDR in order to define an effective temperature of these aging materials, which are systems weakly but durably out of equilibrium. We performed experiments on this problem trying to measure FDR in these slowly relaxing material and to find effective temperatures for their dynamics. For performing these measurements, we set up very precise apparatus that allowed us to study not only the thermal fluctuations in aging glasses but also in out-of-equilibrium systems in which the role of thermal fluctuations cannot be neglected. In parallel, we continued our studies on hydrodynamic instabilities and turbulence where we analyzed the statistical properties of fluctuating injected and dissipated power.

In the following, we will shortly summarize our experimental results on thermal systems, because the results of experiments on macroscopic systems are far to be universal and still present a lot of open questions. The main problem that we want to discuss is the role of fluctuations in out-of-equilibrium systems where the energies injected or dissipated are smaller than $100k_B T$ (k_B being the Boltzmann constant and T the temperature). This limit is relevant for example in biological, nano and micro systems, where thermal fluctuations cannot be neglected. We will discuss the role of fluctuations in these systems and how one can gain some information by measuring them. In order to clarify the kind of questions that we analyze, let us consider the simplest and most basic out-of-equilibrium system, that is, a thermal conductor whose extremities are connected to two heat baths at different temperatures, as sketched in Fig. 1. The second law of thermodynamics imposes that in average the heat flows from the hot to the cold reservoir (from H to C in Fig. 1). However, the second law does not say anything about fluctuations and in principle one can observe for a short time a heat current in the opposite direction, which corresponds to an instantaneous negative entropy production rate.

These rare events of negative entropy production rate (in which the heat flows in the opposite direction of the mean) can be observed in other systems connected to a single heat bath, such as the above-mentioned example of the Brownian particle or electric circuits. In these systems, we can ask what is the probability that the particle moves in the direction opposite to the force and the electric current flows in the wrong direction inside the electric circuit. Let us consider an electrical conductor connected to a potential difference $V = V_A - V_B$ and kept at temperature T by a heat bath as depicted in Fig. 1(b). Unlike the previous example, the electrical conductor is in contact with a single heat bath and the out-of-equilibrium regime is imposed by the external potential difference V . If the mean current $\bar{I} = V/R$ (R being the electrical

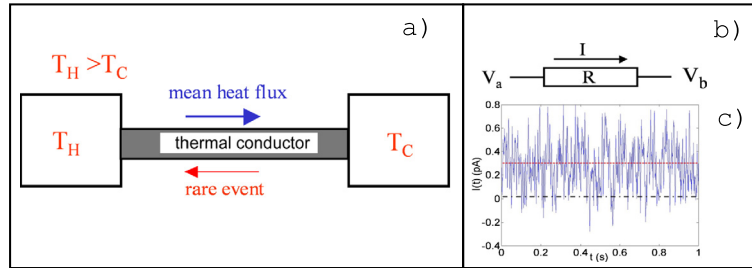


Fig. 1. (a) Schematic representation of a conductor whose extremities are in contact with two heat baths at temperatures T_H and T_C with $T_H > T_C$. (b) Electrical analogy: a potential difference $V = V_a - V_b$ is applied to a conductor of electrical resistance R and kept at a temperature T . (c) Instantaneous current I flowing into the resistance using $R = 10 \text{ M}\Omega$, $T = 300 \text{ K}$, and $\tau_0 = 2 \text{ ms}$ (see [18]).

resistance of the conductor) is of the order of 10^{-13} A and the injected power is about $100 k_B T / s \simeq 10^{-19} \text{ J/s}$, then the instantaneous current inside the resistance is subject to fluctuations produced by the Nyquist thermal noise, whose amplitude is comparable to the mean, as shown in Fig. 1(c). The variance of these fluctuations is $\delta I^2 \simeq k_B T / (R \tau_0)$, where τ_0 is the characteristic time constant of the electrical circuit. In the specific case of Fig. 1(c), the current is several times opposed to its mean value. Taking into account that $V \cdot I$ is the power dissipated by a conductor, this means that, during this rare event, the conductor produces power instead of dissipating it, i.e. the conductor is extracting energy from a single heat bath. The probability of having those negative currents has been studied both theoretically and experimentally in [18,19] within the context of stochastic thermodynamics and the fluctuation theorem (FT).

These negative extreme events are clearly very important, because in small systems they can in principle stop the mechanisms and, in other cases, they can contribute to reducing the mean dissipated power [20]. Furthermore, FT has not only a theoretical interest, but can actually be useful for applications [21]. As these negative events are extremely rare, the large deviation theory plays an important role in this context.

2. Stochastic thermodynamics and fluctuation theorems

2.1. Fluctuation theorem

What is the probability of observing these rare events? The answer to this question can be found within the framework of stochastic thermodynamics [22] and fluctuations theorems (FTs) [23–31].

A fluctuation theorem (FT) fixes the symmetry around 0 of the probability density function (pdf) $P(X_\tau)$ of a quantity X_τ , which can be either the work performed on the system by external forces or the heat exchanged with the heat bath in a time τ . The FT compares the probability of a positive event ($X_\tau = +x$) versus the probability of a negative event ($X_\tau = -x$). When the system is in contact with a single heat bath, the FT takes the form

$$\ln \frac{P(X_\tau)}{P(-X_\tau)} = \Psi(\tau) \frac{X_\tau}{k_B T} \quad (1)$$

where $\Psi(\tau)$ takes into account the finite-time corrections. In a non-equilibrium steady state (NESS), one has $\lim_{\tau \rightarrow \infty} \Psi(\tau) = 1$. In contrast, $\Psi(\tau) = 1, \forall \tau$ when the system is driven in the time τ from an equilibrium state to non-equilibrium. If X_τ is the heat exchanged with the heat bath Q_τ , then Q_τ/T in Eq. (1) can be easily identified as the entropy production during the time τ . However, it has to be noticed that for the heat Eq. (1) holds only for $Q_\tau / \langle Q_\tau \rangle \leq 1$, being $\langle Q_\tau \rangle >$ the mean value of Q_τ . The difference between the FT for work and heat has been first understood in refs. [19,32] and then tested in many experiments.

2.2. Trajectory-dependent entropy and the total entropy

Another quantity, useful to characterize the dynamical properties of energy fluctuations, is the trajectory-dependent entropy difference $\Delta S_s(t, \tau) = -k_B \ln[P(\vec{r}(t + \tau), \lambda) / P(\vec{r}(t), \lambda)]$, where $P(\vec{r}(t), \lambda)$ is the probability of finding the system in the position $\vec{r}(t)$ of the phase space at a value λ of the control parameter. Thus the total entropy difference on the time τ is: $\Delta S_{\text{tot}}(t, \tau) = \Delta S_s(t, \tau) + Q_\tau(t)/T$ [30,31], i.e. the sum of the trajectory-dependent entropy change and the entropy change in the reservoirs due to energy flow. The mean total entropy difference is equal to the entropy production rate, i.e. $\langle \Delta S_{\text{tot}}(t, \tau) \rangle = \langle Q_\tau(t)/T \rangle$, which is zero in equilibrium because in average no heat is exchanged with the heat bath. It is important to notice that at equilibrium $\Delta S_{\text{tot}}(t, \tau)$ has not only a zero mean, but also has no fluctuations and its probability distribution is a delta function. In other words, $\langle \Delta S_{\text{tot}}(t, \tau) \rangle$ is a good quantity to characterize the statistical properties of the out-of-equilibrium dynamics, because in equilibrium it is rigorously zero. The fluctuations of this quantity impose several constraints on time reversibility, which is a central result of stochastic thermodynamics [30,33–35] and has been tested experimentally [36]. The FT for the ΔS_{tot} in a NESS implies $\Sigma(\tau) = 1$ for any τ , i.e. the FT has not an asymptotic validity, but is valid for any τ . This is certainly a useful property in an experiment because one has not to look for very long

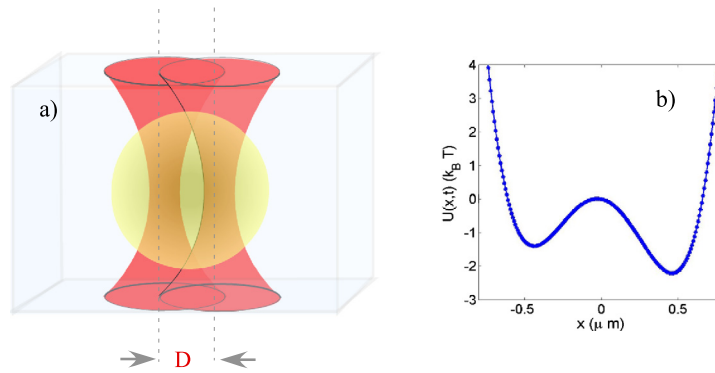


Fig. 2. (a) Drawing of the polystyrene particle trapped by two laser beams whose axis distance is about the radius of the bead. (b) Potential felt by the bead trapped by the two laser beams. The barrier height between the two wells is about $2k_B T$.

asymptotic behavior. However the calculation of S_{tot} in experiments is not easy and a lot of care must be taken in order to correctly estimate this quantity [37,38].

2.3. Jarzynski and Crooks equalities

The knowledge of out-of-equilibrium fluctuations is actually very useful in experiments to extract fundamental information on the equilibrium and out-of-equilibrium properties of a specific system. Typical examples are the Jarzynski and Crook equalities [33,39,40], which estimate the equilibrium properties starting from non-equilibrium measurements.

Specifically, when a system parameter $\lambda(t)$ is varied from an initial value $\lambda(0)$ to the final value $\lambda(t_s)$, Jarzynski defines for one realization of the “switching process” from the initial to the final state the work performed on the system as

$$W = \int_0^{t_s} \dot{\lambda} \frac{\partial H_\lambda[z(t)]}{\partial \lambda} dt \quad (2)$$

where z denotes the phase-space point of the system and H_λ its λ -parametrized Hamiltonian. One can consider an ensemble of realizations of this “switching process” with initial conditions all starting within the equilibrium distribution. Then $W(t_s)$, because of thermal fluctuations, will have a different value for each realization of the ensemble. The Jarzynski equality (JE) states that [39,40]

$$\exp\left(-\frac{\Delta F}{k_B T}\right) = \langle \exp\left(-\frac{W}{k_B T}\right) \rangle \quad (3)$$

In other words, $\langle \exp[-\beta W_{\text{diss}}] \rangle = 1$, since we can always write $W = \Delta F + W_{\text{diss}}$, where W_{diss} is the dissipated work. Thus it is easy to see that there must exist some paths γ such that $W_{\text{diss}} \leq 0$. Moreover, the inequality $\langle \exp x \rangle \geq \exp \langle x \rangle$ allows us to recover the second principle, namely $\langle W_{\text{diss}} \rangle \geq 0$, i.e. $\langle W \rangle \geq \Delta F$.

Eq. (3) turns out to be a very useful tool to experimentally estimate the free energy in small systems (see [21] for more details).

2.4. Experimental tests

2.4.1. Brownian particle in a non-linear potential

As an example of the experimental measurements that we performed, we present an experiment in which the work pdfs are highly not Gaussian. In this example, we measure the fluctuations of a Brownian particle trapped in a non-linear potential produced by two laser beams, as shown in Fig. 2 [41]. It is very well known that a particle of small radius $R \simeq 2 \mu\text{m}$ can be trapped by a focused laser beam, which produces a harmonic potential, thereby confining the Brownian particle motion to the potential well. When two laser beams are focused at a distance $D \simeq R$, as shown in Fig. 2(a) the particle has two equilibrium positions, i.e. the foci of the two beams. Thermal fluctuations allow the particle to hop from one to the other. The particle feels an equilibrium potential $U_0(x) = ax^4 - bx^2 - dx$, shown in Fig. 2(b), where a , b and d are determined by the laser intensity and by the distance of the two focal points. This potential has been computed from the measured equilibrium distribution of the particle $P(x) \propto \exp(U_0(x))$ (see [41] for more experimental details). To drive the system out of equilibrium, we periodically modulate the intensity of the two beams at low frequency ω . Thus the potential felt by the bead has the following profile: $U(x, t) = U_0(x) + U_p(x, t) = U_0 + cx \sin(\omega t)$.

The x position of the particle can be described by an overdamped Langevin equation:

$$\nu \frac{dx}{dt} = -\frac{\partial U(x, t)}{\partial x} + \eta \quad (4)$$

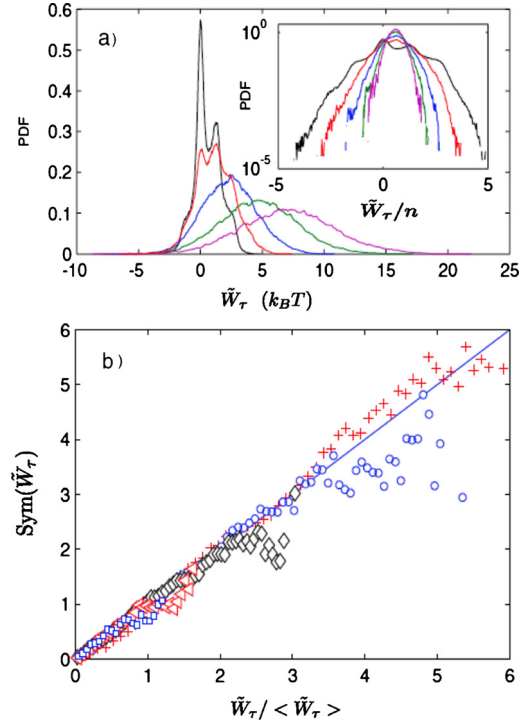


Fig. 3. (a) Distribution of classical work \tilde{W}_τ for different numbers of period $n = 1, 2, 4, 8$ and 12 ($\omega = 4.71$ rad/s). Inset: Same data in lin-log. (b) Normalized symmetry function as a function of the normalized work for $n = 1$ (+), 2 (o), 4 (◇), 8 (△), 12 (□).

with ν the friction coefficient and η the thermal noise delta correlated in time. When $c \neq 0$, the particle can experience a stochastic resonance [42–44] when the forcing frequency is close to the Kramers rate [41]. One can compute the work

$$\tilde{W}_\tau = \int_t^{t+\tau} f(t') \dot{x}(t') dt' \quad (5)$$

of the external force $f(t) = -c \sin(\omega t)$ on the time interval $[t, t + \tau]$, where $\tau = \frac{2\pi m}{\omega}$ is a multiple of the forcing period [41]. We consider the pdf $P(\tilde{W}_\tau)$, which is plotted in Fig. 3(a). Notice that, for $n = 1, 2$, the distributions have two peaks and a very complex shape. They tend to a Gaussian for large n (inset of Fig. 3(a)). In Fig. 3(b), we plot the normalized symmetry function

$$\text{Sym}(\tilde{W}_\tau) = \frac{k_B T}{\tilde{W}_\tau} \ln \left[\frac{P(\tilde{W}_\tau)}{P(-\tilde{W}_\tau)} \right]$$

as a function of $\tilde{W}_\tau / \langle \tilde{W}_\tau \rangle$. We can see that the curves are close to the line of slope 1. For high values of the work, the dispersion of the data increases due to the lack of events. The slope tends toward 1, as expected by the FT in Eq. (1). In spite of the fact that FT for NESS is asymptotic, the convergence of $\text{Sym}(\tilde{W}_\tau)$ towards the asymptotic behavior is very fast. Indeed, a straight line of slope 1 is obtained even at $n = 1$, although the corresponding distribution $P(\tilde{W}_\tau)$ presents a very complex and unusual shape (see Fig. 3(a)). The very fast convergence to the asymptotic value is rather striking because the convergence of FT for work is not universal, and other systems need very large values of τ in order to reach the asymptotic value. These measurements are in full agreement with a realistic model based on the Fokker–Planck equation, where the measured values of $U(x, t)$ have been inserted [45]. This example shows the application of the FT in a non-linear case where the distributions are strongly non-Gaussian.

2.4.2. Two heat baths

In the introduction, we discussed the case of heat conduction. In order to measure the main properties of the energy fluxes systems driven out of equilibrium by a temperature gradient, we studied both experimentally and theoretically the statistical properties of the energy exchanged by two conductors kept at different temperatures, as illustrated in Fig. 4(a), which has a mechanical analogy shown in Fig. 4(b) [46,47]. The specificity of this system is that the heat flux is sustained only by the thermal fluctuations, which are larger in the hot resistance than in the cold one. In these two articles, we measured the trajectory-dependent entropy based on the measure of V_1 and V_2 .

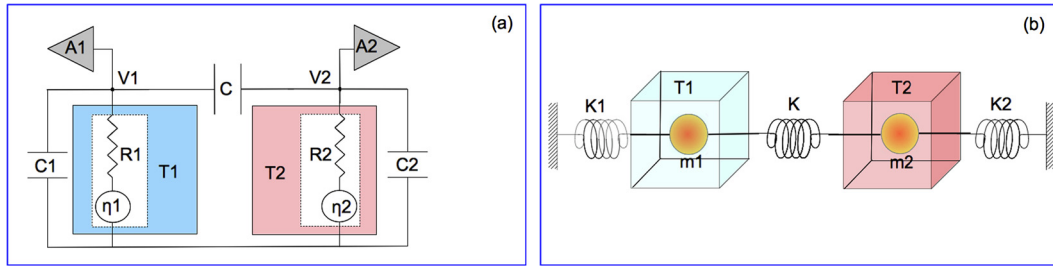


Fig. 4. (a) Diagram of the circuit. The resistances R_1 and R_2 are kept at temperatures T_1 and $T_2 = 296$ K, respectively. T_1 can be fixed in the interval 88–296 K. They are coupled via the capacitance C . The capacitances C_1 and C_2 schematize the capacitances of the cables and of the amplifier inputs. The voltages V_1 and V_2 are amplified by the two low-noise amplifiers A_1 and A_2 . The other relevant parameters are q_m ($m = 1, 2$), i.e. the charges that have flowed through the resistances R_m , and the instantaneous current flowing through them, i.e. $i_m = \frac{dq_m}{dt}$. The two baths are coupled via the thermal noise of each conductor, indicated by η_1 and η_2 in the diagram. (b) The circuit in (a) is equivalent to two Brownian particles (m_1 and m_2) moving inside two different heat baths at T_1 and T_2 . The two particles are trapped by two elastic potentials of stiffness values K_1 and K_2 and coupled by a spring of stiffness K . The analogy is straightforward by considering q_m the displacement of the particle m , i_m its velocity, $K_m = C_m/X$ (with $m \neq m'$) the stiffness of the spring m , and $K = C/X$ the coupling spring, where $X = C_2 C_1 + C(C_1 + C_2)$.

$$\Delta S_{s,\tau} = -k_B \ln \left[\frac{P(V_1(t+\tau), V_2(t+\tau))}{P(V_1(t), V_2(t))} \right]$$

and the total entropy

$$\Delta S_{\text{tot},\tau} = Q_\tau \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \Delta S_{s,\tau}$$

where Q_τ is the heat flowing in the two resistances because of the electric coupling. For this quantity, the FT takes the form

$$\ln \frac{P(\Delta S_{\text{tot}})}{P(-\Delta S_{\text{tot}})} = \frac{\Delta S_{\text{tot}}}{k_B}, \quad \forall \tau \quad (6)$$

3. Fluctuation dissipation relations for NESSs

As we have seen in the previous section, current theoretical developments in nonequilibrium statistical mechanics have led to significant progress in the study of systems around states far from thermal equilibrium. Systems in nonequilibrium steady states (NESSs) are the simplest examples, because the dynamics of their degrees of freedom x under fixed control parameters λ can be statistically described by time-independent probability densities $\rho_0(x, \lambda)$. NESSs naturally occur in mesoscopic systems such as colloidal particles dragged by optical tweezers, Brownian ratchets and molecular motors because of the presence of nonconservative or time-dependent forces [48]. At these length scales, fluctuations are important, so it is essential to establish a quantitative link between the statistical properties of the NESS fluctuations and the response of the system to external perturbations. Around thermal equilibrium, this link is provided by the fluctuation–dissipation theorem [49].

As we already discussed in the § ‘Introduction’, the validity of the fluctuation–dissipation theorem (FDR) in systems out of thermal equilibrium has been the subject of intensive study since 1985, when it has been proposed to be used as a method to define an effective temperature of dynamical instabilities and space-time chaos. For a system in equilibrium with a thermal bath at temperature T , the FDT establishes a simple relation between the two-times correlation function $C(t, s) = \langle O(t)O(s) \rangle$ of an observable $O(t)$ and the linear response function $R(t, s) = \delta O(t)/\delta h(s)$ of this observable to a weak external perturbation of its conjugate variable h . At equilibrium, FDT takes the form:

$$\partial_s C(t, s) = k_B T R(t, s) \quad (7)$$

where in equilibrium $C(t, s)$ and $R(t, s)$ depend only on the time difference $(t - s)$. However, Eq. (7) is not necessarily fulfilled out of equilibrium and violations are observed in a variety of systems such as glassy materials [50–56], granular matter [57], biological systems [58], and resonators [59].

This motivated a theoretical and experimental work devoted to a search of a general framework describing fluctuation–dissipation relations (FDR) (see the review [49]). The generalization of the fluctuation–dissipation theorem around NESS for systems with Markovian dynamics has been achieved from different theoretical approaches [60–72]. The different generalized formulations of FDR link correlation functions of the fluctuations of the observable of interest $O(x)$ in the unperturbed NESS with the linear response function of $O(x)$ due to a small external time-dependent perturbation around the NESS. However, several approaches require the measure of other “auxiliary” observables (such as local currents and entropy), whereas

other theoretical formulations are based on a non-linear transformation of the observables. Let us consider the simple example of a Brownian particle confined in a periodic potential $U(x)$ and driven in a NESS by a constant external force that pushes the particle at a velocity $v_o(t)$. It can be shown that any function $O(x)$ of the particle position verifies:

$$\partial_s C(t, s) - \langle O(t)v_o(s)O(s) \rangle = k_B TR(t, s) \quad (8)$$

This example (tested experimentally in [73]) shows that in this case the equilibrium FDT (Eq. (7)) is modified, in the NESS (Eq. (8)), by an extra correlation function of the observable with the local velocity. The FDR is useful in experiments and simulations to determine $R(t, s)$ in the NESS using only the measure of fluctuations, i.e. by computing the correlations in the left term of Eq. (8). However, not all the variables have the same experimental accessibility and the existence of various formulations of FDR for NESS allows one to choose those that are the best for a particular system [73,74]. Hence, before implementing the different fluctuation–response formulas in real situations, it is important to test their experimental validity under very well controlled conditions and to assess the influence of finite data analysis. The experimental test of some fluctuation–dissipation relations has been done in [73–76] for colloidal particles in toroidal optical traps and in systems subjected to thermal gradients [77,78]. We will not describe here specific experimental results that have been already widely discussed in the above-mentioned articles (see also [35,49,79]). What is important to recall is that in all of formulations the corrections to equilibrium relations are related to the out-of-equilibrium current of the system, which is proportional to the mean total entropy production for a NESS.

4. Thermodynamics, information, and the Maxwell demons

It is worth to say that the study of stochastic thermodynamics has allowed us to bring more insight on the connection between information and thermodynamics. Specifically, the study of the energy fluctuations in small systems has transformed gedanken experiments, as the Maxwell demon, in experiments that may actually be performed thanks to new technologies such as optical/electrical traps and single electron devices. The relationship between stochastic thermodynamics and information has nowadays an increasing importance, both theoretically and experimentally. This relationship is related to the famous paradox of the Maxwell demon (see Fig. 5), who is an intelligent creature able to monitor individual molecules of a gas contained in two neighboring chambers [80,81]. Initially, the two chambers are at the same temperature, defined by the mean kinetic energy of the molecules and proportional to their mean-square velocity. Some of the particles, however, travel faster than others. By opening and closing a molecule sized trapdoor in the partitioning wall, the demon can collect the faster molecules in one chamber and the slower ones in the other. The two chambers then contain gases with different temperatures, and that temperature difference may be used to power a heat engine and produce mechanical work. By gathering information about the particles positions and velocities and using that knowledge to sort them, the demon is able to decrease the entropy of the system and convert information into energy. Assuming the trapdoor is frictionless, the demon is able to do all that without performing any work himself, in an apparent violation of the second law of thermodynamics. This paradox has stimulated a long debate on the connection between information and thermodynamics. A solution to the problem was proposed in 1929 by Leo Szilard, who used a simplified one-particle engine to explain it. Modern technologies allow us to realize this gedanken experiment related to the Maxwell demon original idea [80].

4.1. The Szilard engine

For example, a Szilard engine has been realized in 2010 [82] by using a single microscopic Brownian particle in a fluid and confined to a spiral-staircase-like potential. This has been the first example of a device that converts information into energy for a system coupled with a single thermal environment. However, there is not a contradiction with the second law,

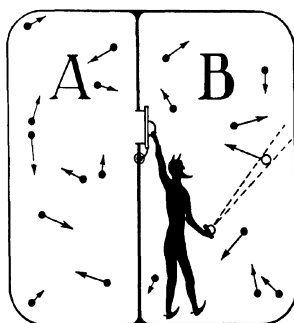


Fig. 5. Maxwell's demon. By detecting the positions and velocities of gas molecules in two neighboring chambers and using that information to time the opening and closing of a trapdoor that separates them, a tiny, intelligent being could, in theory, sort molecules by velocity. By doing so, it could create a temperature difference across the chambers that could be used to perform mechanical work. If the trapdoor is frictionless, the sorting requires no work from the demon himself, which is able to produce work starting from a single heat reservoir, violating in this way the second principle of thermodynamics. (See text for details.)

because Sagawa and Ueda [83] formalized the idea that information gained through microlevel measurements can be used to extract added work from a heat engine. Their formula for the maximum extractable work is:

$$W_{\max} = -\Delta F + k_B T \langle I \rangle \quad (9)$$

where ΔF is the free energy difference between the final and initial state and the extra term represents the so-called mutual information I . In the absence of measurement errors, the quantity I reduces to the Shannon entropy H , i.e. $I = H = -\sum_k P(\Gamma_k) \ln[P(\Gamma_k)]$, where $P(\Gamma_k)$ is the probability of finding the system in the state Γ_k .

In this context, the Jarzynski equality discussed in section 2.3 also contains this extra term and becomes:

$$\langle \exp(-\beta W + I) \rangle = \exp(-\beta \Delta F) \quad (10)$$

which leads to

$$\langle W \rangle \geq \Delta F - k_B T \langle I \rangle \quad (11)$$

Eqs. (10) and (11) generalize the second law of thermodynamics, taking into account the amount of information introduced into the system [81,84]. Indeed, Eq. (11) indicates that, thanks to information, the work performed on the system to drive it between an initial and a final equilibrium state can be smaller than the free energy difference between the two states.

Eq. (10) has been directly tested in a single-electron transistor [85].

Box 1: Landauer's erasure principle

Landauer's principle can be seen as a direct consequence of the second law of thermodynamics. Consider a system (SYS) coupled with a reservoir (RES) at temperature T . According to the second law, the total entropy change for system and reservoir is positive: $S_{\text{tot}} = S_{\text{sys}} + S_{\text{res}} \geq 0$. Since the reservoir is always at equilibrium, owing to its very large size, we have, following Clausius, $\Delta S_{\text{res}} = Q_{\text{res}}/T$. In other words, the heat absorbed by the reservoir satisfies $Q_{\text{res}} \geq T \Delta S_{\text{sys}}$. For a two-state system that stores one bit of information, there are initially two possible states that can be occupied with probability one half, and the initial Shannon entropy is $H_i = \ln(2)$. After erasure, the system is with unit probability in one of the states and the final Shannon entropy vanishes $H_f = 0$. The change of information entropy is thus $\Delta H = -\ln(2)$. During this erasure process, the ability of the system to store information has been modified. By further using the (assumed) equivalence between thermodynamic entropy S and information entropy H , we can write $\Delta S_{\text{sys}} = k_B H = k_B \ln(2)$. We hence obtain $Q_{\text{res}} \geq k_B T \ln(2)$, showing that the heat dissipated into the reservoir during the erasure of one bit of information is always larger than $k_B T \ln(2)$.

4.2. Energy cost of information erasure

Eq. (9) shows that one can extract work from information. In the rest of this section, we will discuss the reverse process, i.e. the energy needed to process information. By applying the second law of thermodynamics, Landauer demonstrated that information erasure is necessarily a dissipative process: the erasure of one bit of information is accompanied by the production of at least $k_B T \ln(2)$ of heat into the environment. This result is known as Landauer's erasure principle.

It emphasizes the fundamental difference between the process of writing and erasing information. Writing is akin to copying information from one device to another: state left is mapped to left and state right is mapped to right, for example. This one-to-one mapping can be realized in principle without dissipating any heat (in statistical mechanics, one would say that it conserves the volume in phase space). By contrast, erasing information is a two-to-one transformation: states left and right are mapped onto one single state, say right (this process does not conserve the volume in phase space and is thus dissipative).

Landauer's original thought experiment has been realized [20,86] for the first time in a real system in 2011 using a colloidal Brownian particle in a fluid trapped in a double-well potential produced by two strongly focused laser beams [20]. This system has two distinct states (particle in the right or left well) and may thus be used to store one bit of information. The erasure principle has been verified by implementing a protocol proposed by Bennett and illustrated in Fig. 6(a). At the beginning of the erasure process, the colloidal particle may be either in the left or right well, with equal probability of one half. The erasure protocol is composed of the following steps: (1) the barrier height is first decreased by varying the laser intensity, (2) the particle is then pushed to the right by gently inclining the potential, and (3) the potential is brought back to its initial shape. At the end of the process, the particle is in the right well with unit probability, irrespective of its departure position. As in the previous experiment, the position of the particle is recorded with the help of a camera. For a full erasure cycle, the average heat dissipated into the environment is equal to the average work needed to modulate the form of the double-well potential. This quantity (plotted as a function of time in Fig. 6(b)) was evaluated from the measured trajectory and shown to be always larger than Landauer's bound, which is asymptotically approached in the limit of long erasure times. However, in order to reach the bound, the protocol must be accurately chosen because, as discussed in [20] and shown experimentally [87], there are protocols that are intrinsically irreversible, no matter how slow are performed. The way in which a protocol can be optimized has been theoretically solved in [88], but the optimal protocol is not often easy to apply in an experiment

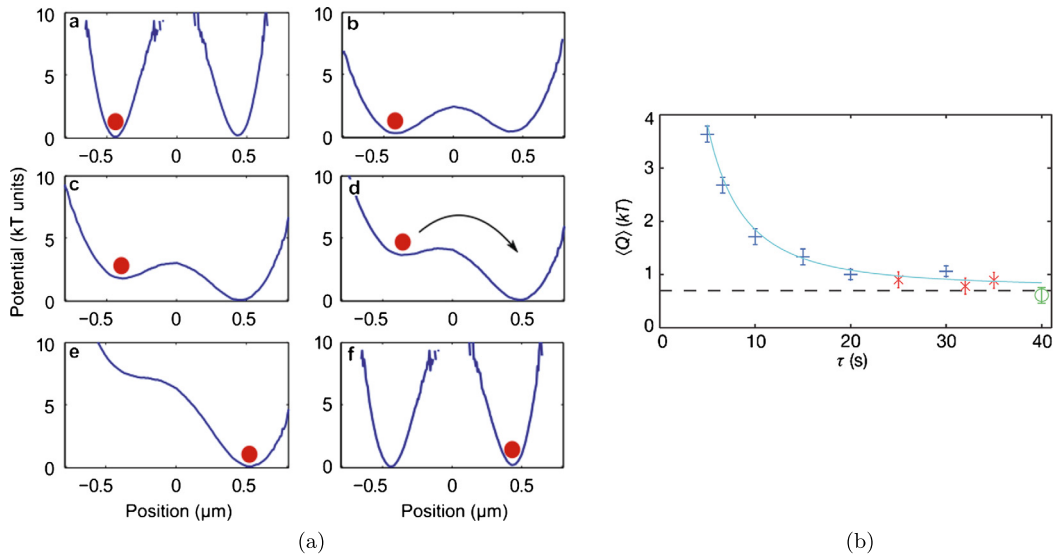


Fig. 6. Experimental verification of Landauer's erasure principle. A colloidal particle is initially confined in one of two wells of a double-well potential with probability one half. This configuration stores one bit of information. By modulating the height of the barrier and applying a tilt, the particle can be brought to the well on the right with probability one, irrespective of the initial position. (b) In the limit of long erasure cycles, the heat dissipated during the erasure process (plotted as a function of time in b) can approach, but not exceed, the Landauer bound indicated by the dashed line (see [20] for details).

4.3. Other examples on the connection between information and energy

By having successfully turned gedanken into real experiments, the above-mentioned results provide a firm empirical foundation to the physics of information and to the intimate connection existing between information and energy. This connection is reinforced by the relationship between the generalized Jarzinsky equality [89] and Landauer's bound, which has been proved and tested on experimental data in [86]. A number of additional experiments have been performed on this subject [90–94], confirming the initial experimental observation. It is worth to mention experiments where the Landauer's bound has been reached in nano devices [90,93]. These experiments open the way to insightful applications for future developments of information technology.

Finally, the connection between thermodynamics and information plays a very important role in the understanding of biological systems [95,96]. The summary of this section is that information can be used to produce energy, but information processing needs more energy than what is produced, so that the second principle is not violated by a Maxwell demon.

5. Conclusions

The purpose of this article was to write a short overview of the historical development of the study of the energy fluctuations in out-of-equilibrium systems, mainly focusing on the experimental tests that we developed in the past. We started from the first ideas on FDR applied to space-time chaos till the application of stochastic thermodynamics in small systems and to the energetics of information. Many aspects have been only sketched, because more detailed reviews have been written on the subject [21]. We did not discuss the energy fluctuations of macroscopic systems, as the connection with theoretical predictions is in general more complex and as it will be difficult to summarize it in a short review [38].

References

- [1] R. Labbé, F.J. Pinton, S. Fauve, *J. Phys. II* 6 (1996) 1099.
- [2] S. Ciliberto, N. Garnier, S. Hernandez, C. Lacpatia, F.J. Pinton, G. Ruiz Chavarria, *Physica A* 340 (2004) 240.
- [3] K. Feitosa, N. Menon, *Phys. Rev. Lett.* 92 (2004) 164301.
- [4] N. Kumar, S. Ramaswamy, K.A. Sood, *Phys. Rev. Lett.* 106 (2011) 118001.
- [5] A. Mounier, A. Naert, *Europhys. Lett.* 100 (2012), <https://doi.org/10.1209/0295-5075/100/30002>.
- [6] A. Naert, *Europhys. Lett.* 97 (2012), <https://doi.org/10.1209/0295-5075/97/20010>.
- [7] O. Cadot, A. Boudaoud, C. Touzé, *Eur. Phys. J. B* 66 (2008) 399.
- [8] A. Argun, A.-R. Moradi, E. Pince, G.B. Bagci, G. Volpe, arXiv:1601.01123, 2017.
- [9] S. Krishnamurthy, S. Ghosh, D. Chatterji, R. Ganapathy, A.K. Sood, *Nat. Phys.* 12 (2016) 1134.
- [10] Y. Pomeau, *Physica D* 23 (1986) 3.
- [11] H. Chaté, P. Manneville, *Phys. Rev. Lett.* 54 (1987) 112.
- [12] S. Ciliberto, P. Bigazzi, *Phys. Rev. Lett.* 60 (1988) 286.
- [13] M. Caponeri, S. Ciliberto, *Phys. Rev. Lett.* 64 (1990) 2775.

- [14] P. Hohenberg, B. Shraiman, *Physica D* 37 (1989) 109.
- [15] M. Caponeri, S. Ciliberto, *Physica D* 58 (1992) 365.
- [16] L. Cugliandolo, J. Kurchan, *Phys. Rev. Lett.* 71 (1993) 173.
- [17] L.F. Cugliandolo, J. Kurchan, L. Peliti, *Phys. Rev. E* 55 (1997) 3898.
- [18] N. Garnier, S. Ciliberto, *Phys. Rev. E* 71 (2005) 060101.
- [19] R. van Zon, S. Ciliberto, E.G.D. Cohen, *Phys. Rev. Lett.* 92 (2004) 130601.
- [20] A. Bérut, A. Arakelyan, A. Petrosyan, S. Ciliberto, R. Dillenschneider, E. Lutz, *Nature* 483 (2012) 187.
- [21] S. Ciliberto, *Phys. Rev. X* 6 (2017) 021051.
- [22] K. Sekimoto, *Prog. Theor. Phys. Suppl.* 130 (1998) 17.
- [23] D.J. Evans, E.G.D. Cohen, G.P. Morriss, *Phys. Rev. Lett.* 71 (1993) 2401.
- [24] D.J. Evans, D.J. Searles, *Adv. Phys.* 51 (2002) 1529.
- [25] G. Gallavotti, E.G.D. Cohen, *Phys. Rev. Lett.* 74 (1995) 2694.
- [26] J.L. Lebowitz, H. Spohn, *J. Stat. Phys.* 95 (1999) 333.
- [27] J. Kurchan, *J. Phys. A, Math. Gen.* 31 (1998) 3719.
- [28] J.D.J.D. Searles, L. Rondoni, J.D. Evans, *J. Stat. Phys.* 128 (2007) 1337.
- [29] D.J. Evans, D.J. Searles, S.R. Williams, *J. Chem. Phys.* 128 (2008) 014504.
- [30] U. Seifert, *Phys. Rev. Lett.* 95 (2005) 040602.
- [31] L. Puglisi, A. Rondoni, A. Vulpiani, *J. Stat. Mech.* (2006) P08010.
- [32] R. van Zon, E.G.D. Cohen, *Phys. Rev. Lett.* 91 (2003) 110601.
- [33] G.E. Crooks, *J. Stat. Phys.* 90 (1998) 1481.
- [34] P. Gaspard, *J. Stat. Phys.* 117 (2004) 599.
- [35] U. Seifert, *Rep. Prog. Phys.* 75 (2012) 126001.
- [36] D. Andrieux, P. Gaspard, S. Ciliberto, S. Garnier, S. Joubaud, S. Petrosyan, *J. Stat. Mech. Theory Exp.* 2008 (2008) P01002.
- [37] S. Joubaud, B.N. Garnier, S. Ciliberto, *Europhys. Lett.* 82 (2008) 30007.
- [38] S. Ciliberto, S. Joubaud, A. Petrosian, *J. Stat. Mech.* (2010) P12003.
- [39] C. Jarzynski, *Phys. Rev. Lett.* 78 (1997) 2690.
- [40] C. Jarzynski, *Phys. Rev. E* 56 (1997) 5018.
- [41] P. Jop, A. Petrosyan, S. Ciliberto, *Europhys. Lett.* 81 (2008) 50005.
- [42] R. Benzi, G. Parisi, A. Suter, A. Vulpiani, *SIAM J. Appl. Math.* 43 (1983) 565.
- [43] L. Gammaitoni, F. Marchesoni, S. Santucci, *Phys. Rev. Lett.* 74 (1995) 1052.
- [44] C. Schmitt, B.B. Dybiec, P. Hänggi, C. Bechinger, *Phys. Rev. Lett.* 74 (2006) 937.
- [45] A. Imparato, P. Jop, A. Petrosyan, S. Ciliberto, *J. Stat. Mech. Theory Exp.* 2008 (2008) P10017.
- [46] S. Ciliberto, A. Imparato, A. Naert, M. Tanase, *Phys. Rev. Lett.* 110 (2013) 180601.
- [47] S. Ciliberto, A. Imparato, A. Naert, M. Tanase, *J. Stat. Mech. Theory Exp.* 2013 (2013) P12014.
- [48] P. Reimann, C.V. den Broeck, H. Linke, P. Hänggi, J.M. Rubi, A. Pérez-Madrid, *Phys. Rev. Lett.* 87 (2001) 010602.
- [49] U. Marini Bettolo Marconi, A. Puglisi, L. Rondoni, A. Vulpiani, *Phys. Rep.* 461 (2008) 111.
- [50] L.F. Cugliandolo, *J. Phys. A, Math. Gen.* 44 (2011) 483001.
- [51] T.S. Grigera, N.E. Israeloff, *Phys. Rev. Lett.* 83 (1999) 5038.
- [52] L. Bellon, S. Ciliberto, C. Laroche, *Europhys. Lett.* 53 (2001) 511.
- [53] D. Herisson, M. Ocio, *Phys. Rev. Lett.* 88 (2002) 257202.
- [54] L. Berthier, J.-L. Barrat, *Phys. Rev. Lett.* 89 (2002) 095702.
- [55] A. Crisanti, J. Ritort, *J. Phys. A, Math. Gen.* 36 (2003) R181.
- [56] P. Calabrese, A. Gambassi, *J. Phys. A, Math. Gen.* 38 (2005) R133.
- [57] A. Barrat, V. Colizza, V. Loreto, *Phys. Rev. E* 66 (2002) 011310.
- [58] K. Hayashi, M. Takano, *Biophys. J.* 93 (2007) 895.
- [59] L. Conti, et al., *Phys. Rev. E* 85 (2012) 066605.
- [60] P. Hänggi, H. Thomas, *Z. Phys.* 22 (1975) 295.
- [61] T. Harada, S.-i. Sasa, *Phys. Rev. Lett.* 95 (2005) 130602.
- [62] E. Lippiello, F. Corberi, M. Zannetti, *Phys. Rev. E* 71 (2005) 036104.
- [63] T. Speck, U. Seifert, *Europhys. Lett.* 74 (2006) 391.
- [64] R. Chetrite, G. Falkovich, K. Gawędzki, *J. Stat. Mech.* (2008) P08005.
- [65] J. Prost, J.-F. Joanny, J.M. Parrondo, *Phys. Rev. Lett.* 103 (2009) 090601.
- [66] R. Chetrite, S. Gupta, *J. Stat. Phys.* 143 (2011) 543.
- [67] M. Baiesi, C. Maes, B. Wynants, *Phys. Rev. Lett.* 103 (2009) 010602.
- [68] M. Baiesi, C. Maes, B. Wynants, *J. Stat. Phys.* 137 (2009) 1094.
- [69] U. Seifert, T. Speck, *Europhys. Lett.* 89 (2010) 10007.
- [70] K. Hayashi, S. Sasa, *Phys. Rev. E* 69 (2004) 066119.
- [71] T. Sakaue, T. Ohta, *Phys. Rev. E* 77 (2008) 050102R.
- [72] B. Altaner, M. Polettini, M. Esposito, *Phys. Rev. Lett.* 117 (2016) 180601.
- [73] R. Gomez-Solano, A. Petrosyan, S. Ciliberto, R. Chetrite, K. Gawędzki, *Phys. Rev. Lett.* 103 (2009) 040601.
- [74] J. Mehli, V. Blickle, U. Seifert, C. Bechinger, *Phys. Rev. E* 82 (2010) 032401.
- [75] V. Blickle, T. Speck, C. Lutz, U. Seifert, C. Bechinger, *Phys. Rev. Lett.* 98 (2007) 210601.
- [76] R. Gomez-Solano, A. Petrosyan, S. Ciliberto, C. Maes, *J. Stat. Mech.* (2011) P01008.
- [77] M. Baiesi, S. Ciliberto, G. Falasco, C. Yolcu, *Phys. Rev. E* 94 (2016) 022144.
- [78] C. Yolcu, A. Bérut, G. Falasco, A. Petrosyan, S. Ciliberto, M. Baiesi, *J. Stat. Phys.* 167 (2017) 29.
- [79] S. Ciliberto, R. Gomez-Solano, A. Petrosyan, *Annu. Rev. Condens. Matter Phys.* 4 (2013) 235.
- [80] E. Lutz, S. Ciliberto, *Phys. Today* 68 (2015) 30.
- [81] J.M.R. Parrondo, J.M. Horowitz, T. Sagawa, *Nat. Phys.* 11 (2015) 131.
- [82] S. Toyabe, T. Sagawa, M. Ueda, M. Muneyuki, M. Sano, *Nat. Phys.* 6 (2010) 988.
- [83] T. Sagawa, M. Ueda, *Phys. Rev. Lett.* 104 (2010) 090602.
- [84] T. Sagawa, M. Ueda, *Phys. Rev. Lett.* 102 (2009) 250602.
- [85] J.V. Koski, V.F. Maisi, T. Sagawa, J. Pekola, *Phys. Rev. Lett.* 113 (2014) 030601.
- [86] A. Bérut, A. Petrosyan, S. Ciliberto, *Europhys. Lett.* 103 (2013) 60002.
- [87] M. Gavrilov, J. Bechhoefer, *Europhys. Lett.* 114 (2016) 50002.

- [88] E. Aurell, K. Gawedzki, C. Meja-Monasterio, R. Mohayaei, P. Muratore-Ginanneschi, *J. Stat. Phys.* 147 (2012) 487.
- [89] S. Vaikuntanathan, C. Jarzynski, *Europhys. Lett.* 87 (2009) 60005.
- [90] J.V. Koski, V.F. Maisi, J. Pekola, D. Averin, *Proc. Natl. Acad. Sci.* 111 (2014) 13786.
- [91] E. Roldàn, I. Martínez, J. Parrondo, D. Petrov, *Nat. Phys.* 10 (2014) 457.
- [92] Y. Jun, M. Gavrilov, J. Bechhoefer, *Phys. Rev. Lett.* 113 (2014) 190601.
- [93] J. Hong, B. Lambson, S. Dhuey, J. Bokor, *Sci. Adv.* 2 (2016) e1501492.
- [94] M. Gavrilov, J. Bechhoefer, *Phys. Rev. Lett.* 117 (2016) 200601.
- [95] A.C. Barato, D. Hartich, U. Seifert, *New J. Phys.* 16 (2014) 103024.
- [96] S. Ito, T. Sagawa, *Nat. Commun.* 6 (2015) 7498.