

## Stochastic thermodynamics: a brief introduction

CHRISTIAN VAN DEN BROECK <sup>(1)</sup>

<sup>(1)</sup> *Hasselt University, B-3590 Diepenbeek, Belgium.*

**Summary.** — The main purpose of statistical mechanics is to give a microscopic derivation of macroscopic laws, including in particular the celebrated second law of thermodynamics. In recent years, there have in this respect been spectacular developments, including the integral and detailed work fluctuation theorems and the theory of stochastic thermodynamics. We give here a brief introduction to these developments. In a first step, we derive the first and second law of thermodynamics for a Markovian stochastic process at the ensemble level, including two major advances: (1) the theory can be applied to small-scale systems including the effect of fluctuations, (2) the theory is not restricted to near equilibrium dynamics. As an application, we evaluate the efficiency at maximum power of a two-state quantum dot. We also briefly discuss the connection to information-to-work conversion (Landauer principle), and the splitting of the second law into an adiabatic and non-adiabatic component. In a second step we formulate stochastic thermodynamics at the trajectory level, introducing stochastic trajectory dependent quantities such as stochastic entropy, energy, heat, and work. Both first and second law can be formulated at this trajectory level. Concerning the second law, the crucial observation is that the stochastic entropy production can be written as the logarithm of the ratio of path probabilities. This in turn implies a detailed and integral work and fluctuation theorem, linking the probability to observe a given stochastic entropy production, to that of observing minus this change in a reverse experiment. The usual second law, stipulating the increase on average of the stochastic entropy production, follows as a subsidiary consequence.

PACS 05.70.Ln – Nonequilibrium and irreversible thermodynamics.

PACS 05.40.-a – Fluctuation phenomena, random processes, noise, and Brownian motion.

PACS 05.20.-y – Classical statistical mechanics.

### 1. – Preliminaries

**1.1. Introduction.** — The main purpose of statistical mechanics is to give a microscopic derivation of macroscopic laws, including in particular the celebrated second law of thermodynamics. The apparent contradiction between the irreversible behavior, enshrined in the second law, and the reversible microscopic equations of motions has been the object of numerous and sometimes acrimonious debates. In these short notes, we will avoid this

delicate issue by starting with so-called mesoscopic equations of motion, more precisely with a Markovian description of the system under consideration. It is well known that such a description is irreversible from the start. We will however show that one can surmount several other difficulties that have plagued a statistical mechanical interpretation of the second law, notably the application to small systems and to systems far from equilibrium. The basic approach is inspired by the work of Onsager, in the sense that we will incorporate basic properties imposed by the microscopic laws (reversibility, Liouville's theorem, detailed balance) in the irreversible realm, and that of Prigogine since we derive a thermodynamic formalism valid outside of equilibrium. We shall do this at the level of a Markovian description with a thermodynamic description including fluctuations and far from equilibrium states. The most surprising development is the formulation of thermodynamics at the level of single trajectories. It sheds a surprising new light on the traditional version of the second law: the positive average entropy production observed at the ensemble level is the result of the fact that at the trajectory level, realizations with positive entropy production are exponentially more likely than the corresponding realizations with negative entropy production.

**1.2. Nutshell thermodynamics [1, 2, 3].** – We briefly review some basic elements of traditional thermodynamics, in order to compare them with the thermodynamic concepts that we will build for Markov processes. The first observation is that macroscopic systems, when left alone (confined, but otherwise isolated), reach a so-called equilibrium state, which is characterized by a limited set of macroscopic state (conserved) variables. The most basic of these variables is the total (or internal) energy  $E$ . Other variables are the volume  $V$  and possibly the number of particles  $N$ . Second, we note that the energy of a system can be changed by an external perturbation. We distinguish contributions identified as work  $W$  (which can be controlled at the macroscopical level), from a heat contribution  $Q$  (which correspond to uncontrollable energy exchanges via microscopic degrees of freedom). We use the convention that work and heat are positive when given to the system. Conservation of energy (first law) stipulates that:

$$(1) \quad \Delta E = W + Q$$

or, for small changes

$$(2) \quad dE = dW + dQ.$$

Energy is a state variable, but work and heat are not: they depend on the actual way the perturbation is applied to change the state of the system <sup>(1)</sup>. In particular, Joule's famous experiment, establishing the caloric equivalent of heat, corresponds precisely to the two extreme cases, in which the same transition of a system is achieved (e.g., a specific amount of water being heated from a lower to a higher temperature), in one case by only applying work (adiabatic experiment  $\Delta E = W$ ), and in the other case by pure heating ( $\Delta E = Q$ ).

Having identified the equilibrium state of a system, one can raise the question as to the physical nature of system under consideration, and in particular about its interaction

---

<sup>(1)</sup> To stress this fact, one often uses the special notation  $\bar{d}$  for an infinitesimal change of such a variable, but we will not do so for simplicity of notation.

with other systems or with external perturbations. These issues are addressed by the introduction of a new state function and the formulation of the second law <sup>(2)</sup>. The first key assertion is the existence, for systems in a state of equilibrium, of another state variable, called the entropy  $S$ . A (macroscopic) system is thermodynamically fully characterized by the way this entropy depends on its state, via the so-called fundamental relation:  $S = S(E, V, N, \dots)$ . The partial derivative  $\partial_E S = 1/T$  can be identified as the inverse (Kelvin) temperature, which is always positive. Hence one can invert the fundamental relation to obtain the equivalent relation  $E = E(S, V, N, \dots)$ . Of particular interest are so-called quasi-static changes, corresponding to the situation in which the system changes slowly enough so that it is essentially at equilibrium. Since the relation  $E = E(S, V, N, \dots)$  is valid all along such a transformation, one finds by differentiation the so-called Gibbs relation:

$$(3) \quad dE = TdS - PdV + \mu dN.$$

The partial derivatives of  $E$  with respect to  $S$ ,  $V$  and  $N$  are new state variables, namely the temperature  $T$ , minus the pressure  $-P$  and the chemical potential  $\mu$ . Comparing this expression with the first law, one can identify a work contribution  $dW = -PdV + \mu dN$  (sum of mechanical and chemical work) and a heat contribution  $dQ = TdS$ . Since heat can be measured as the deficit of energy minus work, the entropy becomes measurable in a quasi-static experiment (to formally complete the argument, one needs to argue that temperature can be measured, apart from a multiplicative factor, via the efficiency of heat engines). The second ingredient is the additivity of entropy: the entropy of a collection of systems is the sum of separate entropies <sup>(3)</sup>. The final and major ingredient stipulates what happens when constraints are released and/or systems brought in contact with each other. While standard thermodynamics does not describe the details of the ensuing evolution - not surprisingly so since other variables, and possibly a fully microscopic description, are needed to describe what is happening- it nevertheless gives a general prescription for the final equilibrium state that is eventually reached. The equilibrium state is the one with maximum total entropy, compatible with the imposed constraints (e.g., volume, energy or number of particles). In particular the total entropy change (including the entropy changes of all systems that participate in the evolution), being the difference between entropies of final and initial equilibrium states, can never be negative  $\Delta S_{tot} \geq 0$ . This is the celebrated second law of thermodynamics, which has numerous applications in physics (gases, osmotic pressure, blackbody radiation, phase transitions), chemistry (chemical equilibrium) and biology (electro-chemical equilibrium, Nernst relation). It implies that systems that are in thermal contact with each other, must have the same temperature (justifying the use of thermometers). In the same way, systems in direct mechanical and chemical contact have the same pressure and same chemical potential <sup>(4)</sup>.

Of particular interest are idealized systems such as heat baths. A heat bath is a thermodynamic system that is described by a single state variable, its energy. It furthermore

---

<sup>(2)</sup> In some textbooks, one also introduces the zero'th law, stating that two systems at equilibrium with a third one, are also mutually at equilibrium with each other

<sup>(3)</sup> One needs to be more careful when there is a strong interaction between the systems or when for example surface effects are studied.

<sup>(4)</sup> The relation between pressures and chemical potentials can however be more complicated in the presence of specific constraints such as levers or chemical reactions.

maintains its equilibrium state (more precisely, its relaxation time scale is fast enough so that its changes can be considered to be quasi-static), even as it exchanges energy under the form of heat with its surroundings. We refer to these systems as reservoirs and denote their properties with subscript  $r$  <sup>(5)</sup>. For a heat reservoir, one can thus write:

$$(4) \quad dS_r = dE_r/T = dQ_r/T.$$

For a heat and particle reservoir, the energy change has a heat and chemical work component  $dE_r = TdS_r + \mu dN_r = dQ_r + dW_{r,chem}$ , and the entropy change is given by:

$$(5) \quad dS_r = dQ_r/T = (dE_r - \mu dN_r)/T.$$

In the context of stochastic thermodynamics, we will often consider the case of several baths, which we will then identify with a superscript  $(\nu)$ . Furthermore we will assume that these reservoirs are infinitely large, so that their temperature  $T^{(\nu)}$  and chemical potential  $\mu^{(\nu)}$  remain unchanged, even when finite amounts of heat and particles are exchanged.

For a system (entropy  $S$ ) in contact with a single heat bath (entropy  $S_r$ , temperature  $T$ , chemical potential  $\mu$ ), the second law can now be written as follows (remember that  $Q$  is the heat to the system, hence  $Q_r = -Q$  is the heat to the reservoir):

$$(6) \quad \Delta S_{tot} = \Delta S + \Delta S_r \geq 0$$

$$(7) \quad \Delta S \geq -\Delta S_r = Q/T.$$

The equality sign is reached for a reversible process.

The original derivation of the second law was based on the (reasonable) assumption that there exists no perpetuum mobile (of the second kind). Alternative formulations state that heat does not spontaneously flow from a cold to a hot reservoir (Clausius statement), or that heat from a single reservoir cannot, as sole effect, be transformed into work (Kelvin statement). On the basis of such an assumption, Carnot was able to obtain a universal bound for the efficiency of thermal machines, which in turn was used by Clausius to prove the existence of  $S$  as a state function. For further reference, we show in the reverse how the second law limits the efficiency of a thermal machine. Consider a cycle in which an auxiliary system (the thermal engine) takes an amount of heat  $Q_h$  for a hot reservoir at temperature  $T_h$ , dropping an amount of heat  $-Q_c$  in a cold reservoir at temperature  $T_c$ , while returning to its original state at the end of the cycle (hence its entropy also returns to its original value <sup>(6)</sup>). The remainder of the energy is turned into work  $W = -Q_h - Q_c$ . Positivity of the total entropy produced in the cycle  $\Delta S_{tot} = -Q_h/T_h - Q_c/T_c \geq 0$  implies that the efficiency of the heat to work conversion

<sup>(5)</sup> Note that, in this special case, the heat is equal to the internal energy (apart from a constant), hence it is a state variable.

<sup>(6)</sup> In principle the auxiliary system need not be at equilibrium during this transformation, hence its classical thermodynamic entropy is then not defined. One can however argue that, in a steady state operation of a thermal engine, the system returns to its initial state (equilibrium or nonequilibrium) after each cycle and does therefore not contribute to the overall entropy production. As we will see, this statement becomes precise in stochastic thermodynamics: the entropy is a well defined state function, even when the system is out of equilibrium, so its entropy returns to the same value after each cycle.

is bounded by the so-called Carnot efficiency:  $\eta = -W/Q_h \leq \eta_c = 1 - T_c/T_h$ . Note that thermodynamics does not prescribe how the above conversion is achieved. Carnot provided an explicit construction, but by now numerous alternatives are available. It is noteworthy that several of the more recent examples are operating with small scale systems, such that fluctuations or even quantum effects cannot be ignored.

The application of thermodynamics to quasi-static states was extended to spatially distributed systems invoking the so-called local equilibrium assumption (which is basically the quasi-static assumption, not only in time, but also in space) by I. Prigogine. It turns out that both the notation and interpretation of the second law that he formulated on this occasion will be most useful in stochastic thermodynamics. Prigogine introduced the concepts of entropy flow and entropy production. Entropy flow is the contribution to the entropy change due to the (reversible) exchange with the environment. Entropy production is an additional entropy increase due to irreversible processes inside the system. In the above example, we identify the entropy flow to the system as minus the entropy change of the reservoir:  $\Delta_e S = -\Delta S_r$  <sup>(7)</sup>. Furthermore, since the reservoir is assumed to operate quasi-statically, it does not have an internal entropy production. The only irreversible process is taking place in the system and we call it the entropy production  $\Delta_i S = \Delta S_{tot}$ . We can thus rewrite the second law for a non-isolated system, exchanging a reversible entropy flow with its environment, as follows <sup>(8)</sup>:

$$(8) \quad \Delta S = \Delta_i S + \Delta_e S \quad \text{with} \quad \Delta_i S \geq 0$$

$$(9) \quad dS = d_i S + d_e S \quad \text{with} \quad d_i S \geq 0$$

$$(10) \quad \dot{S} = \dot{S}_i + \dot{S}_e \quad \text{with} \quad \dot{S}_i \geq 0.$$

The first line corresponds to the entropy increase upon changing from an initial equilibrium state to a final equilibrium change. Note that the differential and derivative version assume quasi-static changes (or more generally local equilibrium), otherwise the "usual" thermodynamic entropy is not well defined.

We finally present yet another formulation of the second law, which is especially useful if we are interested in the amount of work spent during the transition between two equilibrium states for a system in contact with a heat bath. We introduce the state function the free energy  $F = E - TS$ . For changes in contact with a single heat bath, initial and final temperatures of the system are equal to that of the bath, hence  $\Delta F = \Delta E - T\Delta S$ . We find upon combining the second law  $\Delta_i S = \Delta S - \Delta_e S \geq 0$  with the first law ( $\Delta E = Q + W = T\Delta_e S + W$ ) that:

$$(11) \quad T\Delta_i S = W - \Delta F \geq 0.$$

In words, the amount of work needed for the transition (of the system in contact with a heat bath) is at least equal to the change in system free energy. The equality is reached for a reversible process. If the change of free energy is negative  $\Delta F \leq 0$ , the work can be

---

<sup>(7)</sup> We mention a possible source of confusion: the reservoir entropy is a state function, while we stressed that the entropy exchange is not. This apparent contradiction stems from the fact that when we refer to state variables, we have in mind the state of the system and not the state of the reservoir.

<sup>(8)</sup> Note that Prigogine also writes, for obvious aesthetic reasons, the first law under a similar form, namely  $dE = d_i E + d_e E$  with  $d_i E = 0$ .

negative, i.e. one can derive an amount of work, namely at most  $-\Delta F$ , from the change in the state of the system (which then operates as fuel).

**1'3. Nutshell equilibrium statistical mechanics [4].** – We briefly review some concepts from equilibrium statistical mechanics, which will help us with the proper formulation of stochastic thermodynamics. The system is now described in a fully microscopic way. To make the connection with a Master equation description, it is convenient to take a (semi-classical) quantum view: a micro-state of the system is an energy eigenstate, fully identified by the (set of) parameter(s)  $m$  (for example a complete set of quantum numbers). Each micro-state has a specific energy  $\epsilon_m$  and number of particles  $n_m$ . One of the basic features of equilibrium statistical physics is the description in terms of ensembles, introduced by Gibbs.<sup>(9)</sup> The equilibrium state of the system is characterized by a probability distribution  $p_m$  over these states<sup>(10)</sup>. The specific form of this distribution depends on the situation. For an isolated system, one utilizes the micro-canonical ensemble, with the system's energy lying in a small interval  $I = [E_0, E_0 + \delta E_0]$  (with  $\delta E_0 \ll E_0$ , but still large enough to contain many energy levels). All energy states inside this shell are equally probable. One thus has

$$(12) \quad p_m = p_m^{eq} = 1/\Omega \quad \text{for } \epsilon_m \in I$$

with  $\Omega$  the number of energy states in the shell  $I$ . When the system is in contact with a heat bath (temperature  $T$ ,  $k_B T = \beta^{-1}$  and  $k_B$  is Boltzmann's constant) and a heat or particle reservoir (temperature  $T$ , chemical potential  $\mu$ ), the distributions are canonical and grand-canonical:

$$(13) \quad p_m = p_m^{eq} = e^{-\beta(\epsilon_m - F)}$$

$$(14) \quad p_m = p_m^{eq} = e^{-\beta(\epsilon_m - \mu n_m - G)}$$

where  $F$  and  $G$  are the Helmholtz free energy and the grand potential, respectively<sup>(11)</sup>. Their explicit expression follows from normalization:

$$(15) \quad e^{-\beta F} = \sum_m e^{-\beta \epsilon_m}$$

$$(16) \quad e^{-\beta G} = \sum_m e^{-\beta(\epsilon_m - \mu n_m)}$$

We first turn our attention to the energy of the system, being the following ensemble

<sup>(9)</sup> We mention in passing the connection with the ergodic theorem, which shows the equivalence between the ensemble average considered here and the long-time average of a single trajectory. We also mention that for large systems, fluctuations of macroscopic quantities are exceedingly small, so that the ensemble average coincides with the most probable or typical value.

<sup>(10)</sup> In the full quantum version, we have to use the density matrix  $\rho$ , but off-diagonal elements are anyways zero for equilibrium states in the energy representation.

<sup>(11)</sup> For ideal systems, with the total energy being the sum of single particle energies, the grand potential provides a simple starting point to obtain the famous Fermi-Dirac and Bose-Einstein statistics for the occupation densities of the single particle states.

average:

$$(17) \quad E = \sum_m \epsilon_m p_m.$$

This energy will be modified when the distribution changes and/or when the energy levels move. For small changes one can write:

$$(18) \quad dE = \sum_m (d\epsilon_m p_m + \epsilon_m dp_m) = dW + dQ (+dW_{chem}).$$

We clearly recognize the first law of thermodynamics, with the following interpretation: heat corresponds to instantaneous jumps (transitions) between states of different energy, resulting in a change in occupation probability. In case the number of particles also changes, one has to subtract the chemical energy part to obtain the heat contribution. Work (aside from the chemical work) corresponds to moving an occupied energy level. This can for example be achieved by applying an external field of changing the volume.

We next turn to the definition of entropy. We will use the Shannon expression [6], since it gives rise to a consistent and elegant formulation in stochastic thermodynamics:

$$(19) \quad S = -k_B \sum_m p_m \ln p_m.$$

The above definition of the entropy is, at equilibrium, in agreement with the usual thermodynamic entropy. This can be checked for the three ensembles mentioned above. In particular, it yields the usual thermodynamic relations for Helmholtz free energy  $F = E - TS$  and the grand potential  $G = E - TS - \mu N$ , where:

$$(20) \quad N = \sum_m n_m p_m.$$

Furthermore, the interpretation is compatible with thermodynamics for a quasi-static change. For example, one finds for a quasi-static change (around a reference equilibrium state  $p^{eq}$ ,  $p_m = p_m^{eq} + dp_m$ ) of a system in contact with a single thermal reservoir:

$$(21) \quad dS = -k_B \sum_m dp_m \ln p_m^{eq} = \beta k_B \sum_m \epsilon_m dp_m = \frac{dQ}{T},$$

in agreement with the usual thermodynamic formula.

Finally, we mention difficulty with the above expression as being a thermodynamic entropy for an *isolated system*, which highlights the issue of reversibility versus irreversibility. This argument applies to both classical and quantum description. Liouville's theorem stipulates that  $\rho$ , the density in phase space (classical systems) or the density matrix (quantum mechanics), is constant along the trajectory (i.e., the full time derivative of  $\rho$  is zero). In quantum mechanics, it is a result of the unitarity of the time-evolution operator. Classically, it follows from the Hamiltonian structure of the equations of motion. We start with the evolution equation for the probability density

$\rho$  (this is a conservation equation for the probability or a non-dissipative Fokker Planck equation):

$$(22) \quad \frac{\partial \rho}{\partial t} = - \sum_j \left\{ \frac{\partial}{\partial q_j} \dot{q}_j + \frac{\partial}{\partial p_j} \dot{p}_j \right\} \rho.$$

In combination with:

$$(23) \quad \dot{q}_j = \frac{\partial H}{\partial p_j}$$

$$(24) \quad \dot{p}_j = - \frac{\partial H}{\partial q_j},$$

we find for the full derivative:

$$(25) \quad \frac{d\rho}{dt} = \sum_j \left\{ \frac{\partial \rho}{\partial q_j} \dot{q}_j + \frac{\partial \rho}{\partial p_j} \dot{p}_j \right\} + \frac{\partial \rho}{\partial t} = 0.$$

It easily follows that the following Shannon entropy:

$$(26) \quad S = -k_B \text{Tr} \rho \ln \rho$$

is conserved in time, and does, at first sight, not present a good candidate for the total entropy. We will not discuss this issue further, nor the proposed arguments of resolution (statistical interpretation, coarse graining, projection, chaos, quantum collapse, expansion of universe, nonequilibrium initial condition, canonical typicality).

In the stochastic approach presented below, irreversibility is build in from the start. Furthermore, we do not consider isolated systems, and the relaxation is due to the coupling to reservoirs. The conservation of phase volume has however another fundamental microscopic consequence, which we will need to incorporate in our mesoscopic theory, namely the condition of detailed balance. This property states that it is equally probable, in a system at equilibrium, to observe any kind of transition, as it is to observe its time-reverse. In other words, there is no arrow of time: one cannot distinguish in a movie of a system at equilibrium, whether it is played forward or backward. The proof is most easily given in the microcanonical ensemble. Consider the probability for a transition from a subspace of phase space to another subspace, during a certain time (of measure nonzero). For simplicity we consider that both subspaces are even in the momenta. We note that there is a one-to-one correspondence between every trajectory that makes the transition, and the time-reverse trajectory with reversed momenta. Because of Liouville's theorem, both sets, the one generating the forward and that producing the time-reversed transition, have equal phase volume, and are thus equally probable in a micro-canonical distribution. The property of detailed balance can be inferred from a handwaving yet probably deeper argument using the Kelvin statement of the second law. Indeed, if such a "time-asymmetric" transition would exist in a system at equilibrium, one could extract work from it by building a work-generating device (kind of "waterwheel") driven by these transitions.



**1'4. Nutshell Master equation [5].** – The state of the system is represented by the index  $m$ . We assume Markovian dynamics with transition rates  $W_{m,m'} \geq 0$ , defined as the probability per unit time to make a transition from state  $m'$  to  $m$  ( $m' \neq m$ ) <sup>(12)</sup>. The essence of Markovian dynamics is the assumption that this transition probability, e.g. for a transition from  $m'$  to  $m$ , does not depend on how the former state  $m'$  was reached. As a result, the probability distribution  $p_m(t)$  to be in state  $m$  at time  $t$  obeys a Master equation, which we write in a number of different forms:

$$(27) \quad \dot{p}_m = \sum_{m'} [W_{m,m'} p_{m'} - W_{m',m} p_m]$$

$$(28) \quad = \sum_{m'} J_{m,m'} \quad \text{with} \quad J_{m,m'} = W_{m,m'} p_{m'} - W_{m',m} p_m$$

$$(29) \quad = \sum_{m'} W_{m,m'} p_{m'}$$

In the last line, we introduced, to compactify notation, the "diagonal" element:

$$(30) \quad W_{m,m} = - \sum_{m', m' \neq m} W_{m',m}.$$

Note that as a result, the matrix  $\mathbf{W}$  with elements  $W_{m,m'}$  is a "stochastic" matrix <sup>(13)</sup>, the sum of elements in a column adding up to zero:

$$(31) \quad \sum_m W_{m,m'} = 0.$$

This property guarantees the conservation of probability. Formulated in an alternative way, we note that the matrix  $\mathbf{W}$  has a left eigenvector  $(1, 1, \dots, 1)$  with eigenvalue zero. We call the corresponding right eigenvector the "stationary distribution"  $p_m^{st}$ :

$$(32) \quad \dot{p}_m^{st} = \sum_{m'} W_{m,m'} p_{m'}^{st} = 0.$$

We will assume for simplicity that this distribution is unique <sup>(14)</sup>.

In the sequel, we will consider the possibility of a time-dependent transition matrix  $\mathbf{W} = \mathbf{W}(t)$ . The corresponding distribution is then obviously also time-dependent  $p_m^{st} = p_m^{st}(t)$ . This distribution still satisfies (32), but only at a single instance of time  $t$ , when  $\mathbf{W} = \mathbf{W}(t)$ .  $p^{st}$  is therefore only a genuine stationary distribution when the rate matrix is time-independent. In this case, we can in fact construct a Lyapounov function, showing that any initial distribution relaxes to this stationary distribution. The proof

<sup>(12)</sup> Take care not to confuse the transition rates  $W_{m,m'}$  or the transition matrix  $\mathbf{W}$  with the work  $W$ .

<sup>(13)</sup> "Stochastic" is the name usually reserved for the transition matrix of a discrete time Markov chains, with the elements of each column summing up to 1.

<sup>(14)</sup> Otherwise the state space consists of separate regions.

goes as follows. We introduce the following H-function (terminology borrowed from the H-function introduced by Boltzmann):

$$(33) \quad H = D(p_m || p_m^{st}) = \sum_m p_m \ln \frac{p_m}{p_m^{st}} \geq 0.$$

This quantity is positive and only zero when  $p_m = p_m^{st} \forall m$ . This quantity also appears in information theory, where it is called the Kullback-Leibler distance or relative entropy between the distributions  $p_m$  and  $p_m^{st}$  [6]. Its positivity can easily be shown on the basis of the inequality

$$(34) \quad \ln x \leq x - 1 \quad \text{or} \quad -\ln x \geq 1 - x \quad \forall x \geq 0.$$

Furthermore, one shows using the same inequality that (assuming that  $p_m^{st}$  is time-independent!):

$$(35) \quad \frac{dH}{dt} = \sum_m \frac{dp_m}{dt} \ln \frac{p_m}{p_m^{st}}$$

$$(36) \quad = \sum_{m,m'} W_{m,m'} p_{m'} \ln \frac{p_m}{p_m^{st}}$$

$$(37) \quad = \sum_{m,m'} W_{m,m'} p_{m'} \ln \frac{p_m p_{m'}^{st}}{p_m^{st} p_{m'}}$$

$$(38) \quad = \sum_{m,m'; m \neq m'} W_{m,m'} p_{m'} \ln \frac{p_m p_{m'}^{st}}{p_m^{st} p_{m'}}$$

$$(39) \quad \leq \sum_{m,m'; m \neq m'} W_{m,m'} p_{m'} \left( \frac{p_m p_{m'}^{st}}{p_m^{st} p_{m'}} - 1 \right)$$

$$(40) \quad = \sum_{m,m'} W_{m,m'} p_{m'} \left( \frac{p_m p_{m'}^{st}}{p_m^{st} p_{m'}} - 1 \right) = 0.$$

The H function has properties reminiscent of minus the entropy: it is positive and decreases in time until a minimum is reached at the steady state. There is however, at this stage, no input whatsoever from physics. We will in fact show below that minus the time derivative of the H function corresponds, in an appropriate physical setting, to a contribution to the entropy production (which we will call the non-adiabatic entropy production), namely the one related to the relaxation to the steady state. Hence the H-theorem is not related to the second law proper, but rather to a minimum entropy production theorem.

## 2. – Ensemble stochastic thermodynamics.

**2.1. Ensemble stochastic thermodynamics: first law.** – We now embark on a proper formulation of the first law of thermodynamics for a system obeying a Markovian master equation, proceeding in close analogy with statistical mechanics. We associate to every

state  $m$  of the system an energy  $\epsilon_m$ , and possibly a number of particles  $n_m$ . The average energy and number of particles are given by:

$$E = \sum_m \epsilon_m p_m$$

$$N = \sum_m n_m p_m$$

Note that both  $\epsilon_m$  and  $p_m$  can be time-dependent (while  $n_m$  is time-independent). When the energy levels are shifted, we are performing work on the system via an external agent (which we suppose to be a purely non-dissipative work source, which we need not describe any further). The energy needed to change the probability distribution over the energy levels, i.e. jumps between different states, is coming from heat exchange with reservoirs (plus possibly a chemical work contribution if the number of particles also changes). Hence as in the statistical mechanical description, we can write for the energy flux into the system:

$$\dot{E} = \dot{W} + \dot{Q} (+\dot{W}_{chem})$$

with the work and heat (plus chemical work) flux:

$$\dot{W} = \sum_m \dot{\epsilon}_m p_m$$

$$\dot{Q} (+\dot{W}_{chem}) = \sum_m \epsilon_m \dot{p}_m.$$

Note that we give here the rate of change of the energy because we know the time derivative  $\dot{p}_m$  (it is given by the Master equation) and  $\dot{\epsilon}_m$ . Usually, the time-dependence of the energy level is attributed to an external agent acting on a control variable  $\lambda = \lambda(t)$ , with  $\epsilon_m = \epsilon_m(\lambda)$  (see also discussion further below), hence:  $\dot{\epsilon}_m = \partial \epsilon / \partial \lambda \dot{\lambda}$ . Using the Master equation, the heat and particle rates are given more explicitly by:

$$(41) \quad \dot{Q} (+\dot{W}_{chem}) = \sum_m \epsilon_m \dot{p}_m = \sum_{m,m'} \epsilon_m J_{m,m'} = \frac{1}{2} \sum_{m,m'} \epsilon_{m,m'} J_{m,m'}$$

$$(42) \quad \dot{N} = \sum_m n_m \dot{p}_m = \sum_{m,m'} n_m J_{m,m'} = \frac{1}{2} \sum_{m,m'} n_{m,m'} J_{m,m'}$$

where the net average rate of transitions or flux from  $m'$  to  $m$  (also mentioned above) is given by (note that  $J_{m,m'} = -J_{m',m}$ ):

$$(43) \quad J_{m,m'} = W_{m,m'} p_{m'} - W_{m',m} p_m.$$

For compactness of notation, we also introduced the energy and number of particles flowing into the system upon making the transition from  $m'$  to  $m$ :

$$(44) \quad \epsilon_{m,m'} = \epsilon_m - \epsilon_{m'}$$

$$(45) \quad n_{m,m'} = n_m - n_{m'}.$$

To make the connection with a physical system and to identify amongst other things the chemical work, we need to say more about the transition rates. We will consider the simple situation of a system in contact with a number of heat/particle baths denoted by the superscript  $(\nu)$ . We will assume that each reservoir gives an additive contribution to the transition rate:

$$(46) \quad \mathbf{W} = \sum_{\nu} \mathbf{W}^{(\nu)}.$$

For this reason, we can also separate the fluxes  $J_{m,m'}$ , and hence also heat and particle rates (into the system)  $\dot{Q}$  and  $\dot{N}$ , respectively, into separate contributions coming from exchanges with each of the reservoirs  $\nu$ :

$$(47) \quad J_{m,m'} = \sum_{\nu} J_{m,m'}^{(\nu)}$$

$$(48) \quad J_{m,m'}^{(\nu)} = W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m$$

and (with the obvious convention that the flux  $J^{(\nu)}$  has to be used for the quantities with superscript  $(\nu)$ ):

$$(49) \quad \dot{Q} = \sum_{\nu} \dot{Q}^{(\nu)}$$

$$(50) \quad \dot{N} = \sum_{\nu} \dot{N}^{(\nu)}$$

$$(51) \quad \dot{W}_{chem} = \sum_{\nu} \dot{W}_{chem}^{(\nu)}.$$

We now introduce the main assumption that makes the thermodynamic analysis compatible with microscopic theory. It can be viewed as a "quasi-static" or "local equilibrium assumption", but now at the level of a stochastic description: we assume that each transition rate  $\mathbf{W}^{(\nu)}$  obeys -at each moment- detailed balance with respect to the corresponding instantaneous equilibrium distribution of the system in its contact with the corresponding reservoir  $\nu$ :

$$(52) \quad W_{m,m'}^{(\nu)}(t) p_{m'}^{eq,\nu}(t) = W_{m',m}^{(\nu)}(t) p_m^{eq,\nu}(t).$$

As equilibrium distributions, we consider the canonical case (heat reservoir):

$$(53) \quad p_m^{eq,\nu}(t) = e^{-\beta^{(\nu)}[\epsilon_m(t) - F^{eq,\nu}(t)]}$$

$$(54) \quad e^{-\beta^{(\nu)} F^{eq,\nu}(t)} = \sum_m e^{-\beta^{(\nu)} \epsilon_m(t)}$$

and grand-canonical situation (heat plus particle reservoir):

$$(55) \quad p_m^{eq,\nu}(t) = e^{-\beta^{(\nu)}[\epsilon_m(t) - \mu^{(\nu)} n_m(t) - G^{eq,\nu}(t)]}$$

$$(56) \quad e^{-\beta^{(\nu)} G^{eq,\nu}(t)} = \sum_m e^{-\beta^{(\nu)}[\epsilon_m(t) - \mu^{(\nu)} n_m(t)]}.$$

In the grand-canonical scenario, transitions between states involve particle transport and hence a chemical work contribution. The energy and particle rate of change in the system due to the coupling with reservoir  $\nu$  are obviously given by

$$(57) \quad \dot{E}^{(\nu)} = \frac{1}{2} \sum_{m,m'} \epsilon_{m,m'} J_{m,m'}^{(\nu)}$$

$$(58) \quad \dot{N}^{(\nu)} = \frac{1}{2} \sum_{m,m'} n_{m,m'} J_{m,m'}^{(\nu)}.$$

The corresponding chemical work rate and heat flux read:

$$(59) \quad \dot{W}_{chem}^{(\nu)} = \frac{1}{2} \sum_{m,m'} \mu^{(\nu)} n_{m,m'} J_{m,m'}^{(\nu)}$$

$$(60) \quad = \mu^{(\nu)} \dot{N}^{(\nu)},$$

$$(61) \quad \dot{Q}^{(\nu)} = \frac{1}{2} \sum_{m,m'} q_{m,m'}^{(\nu)} J_{m,m'}^{(\nu)}$$

$$(62) \quad = \dot{E}^{(\nu)} - \mu^{(\nu)} \dot{N}^{(\nu)},$$

with

$$(63) \quad q_{m,m'}^{(\nu)} = \epsilon_{m,m'} - \mu^{(\nu)} n_{m,m'}$$

the heat to the system, coming from reservoir  $(\nu)$  upon making the transition from  $m'$  to  $m$ .

We note in passing the the factor  $1/2$  in all above formula's (and in the formula's that will follow) stems from the fact the we are counting twice the transitions between levels  $m$  and  $m'$ . This can be avoided by replacing the sum with a restricted sum (note that the diagonal contributions  $m = m'$  are zero):

$$(64) \quad \frac{1}{2} \sum_{m,m'} \dots = \sum_{m,m', m > m'} \dots$$

We stress that the above "local equilibrium assumption" deals with the contact between system and reservoir. There is however no assumption whatsoever on the state of the system itself, which can be very far from equilibrium <sup>(15)</sup>. Note also that, according to the above condition, the transition rates will automatically change in time, if the energy levels are shifted. This brings us to the final assumption, namely that the energy, needed for the shift, is provided by an idealized work source. The time-dependence of the energy levels is often represented by introducing a control parameter  $\lambda$ , with  $\epsilon_m = \epsilon_m(\lambda)$ . The idea is that  $\lambda$  represents an external field (e.g. an electric field) or constraint (e.g.

---

<sup>(15)</sup> Even a fully microscopic nonequilibrium dynamics is possible since the Markovian dynamics include deterministic dynamics as a special case.

the volume or a confining potential). A time-dependence of this parameter induces a specific time-dependence of all the energy levels (although there is in principle no principal objections against a time-dependence for each energy level separately).

The above assumptions can be justified in a more detailed analysis by a separation of time scales and by a weak coupling assumption between system and reservoirs. Both assumptions are consistent with a closed description of the system in terms of the autonomous Master equation dynamics (in which the idealized reservoirs and work source do not appear).

We close with an important mathematical implication of our "local equilibrium assumption", which will play a key role in connecting our stochastic analysis with the "usual" thermodynamic formulation. For simplicity of notation, we will, here and in the sequel, often omit the explicit time-dependence "(t)" in the expressions. By combining (13) and (52), we find:

$$(65) \quad \ln \frac{W_{m,m'}^{(\nu)}}{W_{m',m}^{(\nu)}} = \ln \frac{p_m^{eq,\nu}}{p_{m'}^{eq,\nu}} = -\beta^{(\nu)} q_{m,m'} = \beta^{(\nu)} q_{m',m}$$

In other words, the log-ratio of the transition rates (time  $k_B$ ) is equal to minus the heat flow into the system coming from the corresponding reservoir, divided by  $k_B T^{(\nu)}$ .

**2.2. Ensemble stochastic thermodynamics: second law.** – The entropy of the system is formally identical to the definition that we introduced in statistical mechanics section, i.e. we are using the Shannon entropy:

$$(66) \quad S = -k_B \sum_m p_m \ln p_m,$$

but with  $p_m$  now solution of the Master equation (27). Our purpose is to derive an entropy balance equation. One finds:

$$(67) \quad \dot{S} = -k_B \sum_m \dot{p}_m \ln p_m = -k_B \sum_{m,m',\nu} W_{m,m'}^{(\nu)} p_{m'} \ln p_m$$

$$(68) \quad = k_B \frac{1}{2} \sum_{m,m',\nu} (W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m) \ln \frac{p_{m'}}{p_m}$$

$$(69) \quad = k_B \frac{1}{2} \sum_{m,m',\nu} (W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m) \ln \frac{W_{m,m'}^{(\nu)} p_{m'}}{W_{m',m}^{(\nu)} p_m}$$

$$(70) \quad + k_B \frac{1}{2} \sum_{m,m',\nu} (W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m) \ln \frac{W_{m',m}^{(\nu)}}{W_{m,m'}^{(\nu)}}.$$

We can thus write <sup>(16)</sup>

$$(71) \quad \dot{S} = \dot{S}_i + \dot{S}_e$$

with

$$(72) \quad \dot{S}_i = \frac{d_i S}{dt} = k_B \frac{1}{2} \sum_{m,m',\nu} (W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m) \ln \frac{W_{m,m'}^{(\nu)} p_{m'}}{W_{m',m}^{(\nu)} p_m}$$

$$(73) \quad = k_B \sum_{m,m',\nu} W_{m,m'}^{(\nu)} p_{m'} \ln \frac{W_{m,m'}^{(\nu)} p_{m'}}{W_{m',m}^{(\nu)} p_m}$$

and

$$(74) \quad \dot{S}_e = \frac{d_e S}{dt} = k_B \frac{1}{2} \sum_{m,m',\nu} (W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m) \ln \frac{W_{m',m}^{(\nu)}}{W_{m,m'}} p_m$$

$$(75) \quad = k_B \sum_{m,m',\nu} W_{m,m'}^{(\nu)} p_{m'} \ln \frac{W_{m',m}^{(\nu)}}{W_{m,m'}}.$$

We now show that these expressions are exactly what we expect (and deserve). First, we have written the entropy production in a way that its positivity is obvious ( $((x-y)\ln x/y \geq 0)$ ). Second, it has the structure of a sum of fluxes time forces, just like in macroscopic irreversible thermodynamics:

$$(76) \quad \frac{d_i S}{dt} = \frac{1}{2} \sum_{m,m',\nu} J_{m,m'}^{(\nu)} X_{m,m'}^{(\nu)},$$

$$(77) \quad J_{m,m'}^{(\nu)} = W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m$$

$$(78) \quad X_{m,m'}^{(\nu)} = k_B \ln \frac{W_{m,m'}^{(\nu)} p_{m'}}{W_{m',m}^{(\nu)} p_m}.$$

The physical interpretation of these quantities is clear: the "flux"  $J_{m,m'}^{(\nu)}$  is the net average number of transitions per unit time from  $m'$  to  $m$ , and the "force"  $X_{m,m'}^{(\nu)}$  is the log-ratio of the deviation from detailed balance, both with respect to transitions induced by reservoir  $\nu$ . We stress that the entropy production is not only non-negative overall, but it is so in each of its detailed contributions  $J_{m,m'}^{(\nu)} X_{m,m'}^{(\nu)}$ . Every breaking of detailed balance, with respect to any reservoir and/or any pairs of states, gives rises to a separately positive contribution in the entropy production. We also stress that the above expression gives an

---

<sup>(16)</sup> Note (again) that the short hand notation used here  $\dot{S}_i = d_i S/dt$  and  $\dot{S}_e = d_e S/dt$  could be misleading since these are not time derivatives of state functions: there are no such things (state functions) as  $S_i$  and  $S_e$ !



Fig. 1. – Schematic representation of system in contact with two reservoirs.

explicit value of the rate of entropy production, for any state of the system including far from equilibrium states. We leave it as an exercise to show that the entropy production is underestimated if the contributions of separate reservoirs are not identified and one uses for example the total transition matrix  $\mathbf{W}$ :

$$(79) \quad \frac{d_i S}{dt} \geq \frac{1}{2} \sum_{m,m',\nu} J_{m,m'} X_{m,m'}.$$

We finally turn to the entropy flow. Using the crucial property (52), we find:

$$(80) \quad \frac{d_e S}{dt} = k_B \frac{1}{2} \sum_{m,m',\nu} (W_{m,m'}^{(\nu)} p_{m'} - W_{m',m}^{(\nu)} p_m) \ln \frac{W_{m',m}^{(\nu)}}{W_{m,m'}^{(\nu)}}$$

$$(81) \quad = k_B \frac{1}{2} \sum_{m,m',\nu} \beta^{(\nu)} J_{m,m'}^{(\nu)} q_{m,m'}^{(\nu)}$$

$$(82) \quad = \sum_{\nu} \frac{\dot{Q}^{(\nu)}}{T^{(\nu)}}.$$

We conclude that the entropy flow agrees with the standard expression from macroscopic irreversible thermodynamics, being the sum of the heat flows from each reservoir  $\nu$  into the system,  $\dot{Q}^{(\nu)}$ , divided by the temperature of the corresponding reservoir.



**2'3. System in contact with two reservoirs: steady state and strong coupling..** – We consider a system at steady state, in contact with two heat and particle reservoirs, with corresponding temperature and chemical potential,  $T^{(\nu)}$  and  $\mu^{(\nu)}$ ,  $\nu = 1, 2$ , cf. Fig. 1. At this steady state (which also implies the absence of driving, i.e., no work contribution, asides from chemical work) we have  $\dot{E} = \dot{N} = \dot{S} = \dot{W} = 0$ . If the reservoirs have different temperature and/or chemical potential, this steady state is however not an equilibrium state, and we can identify the following heat and particle flows  $\dot{E} = J_E^{(1)} + J_E^{(2)}$ ,  $\dot{N} = J_N^{(1)} + J_N^{(2)}$ :

$$(83) \quad J_E = J_E^{(1)} = \dot{Q}^{(1)} + \mu^{(1)} \dot{N}^{(1)} = -J_E^{(2)} = -\dot{Q}^{(2)} - \mu^{(2)} \dot{N}^{(2)}$$

$$(84) \quad J_N = J_N^{(1)} = \dot{N}^{(1)} = -J_N^{(2)} = -\dot{N}^{(2)}.$$

Furthermore, we find from:

$$(85) \quad \dot{S} = \dot{S}_i + \dot{S}_e = 0$$

$$(86) \quad \dot{S}_e = \frac{\dot{Q}^{(1)}}{T^{(1)}} + \frac{\dot{Q}^{(2)}}{T^{(2)}}$$

that

$$(87) \quad \dot{S}_i = -\dot{S}_e = J_E X_E + J_N X_N \geq 0,$$

with the usual expression of the thermodynamic forces:

$$(88) \quad X_E = \frac{1}{T^{(2)}} - \frac{1}{T^{(1)}}$$

$$(89) \quad X_N = \frac{\mu^{(1)}}{T^{(1)}} - \frac{\mu^{(2)}}{T^{(2)}}.$$

We mention that in the domain of linear irreversible thermodynamics, the fluxes and forces are in linear relation with each other, more precisely:

$$(90) \quad J_E = L_{EE} X_E + L_{EN} X_N$$

$$(91) \quad J_N = L_{NE} X_E + L_{NN} X_N.$$

Positivity of the entropy production requires that the matrix  $\mathbf{L}$  is non-negative. Furthermore, Onsager derived from the reversibility of the microscopic law the symmetry of this matrix:  $L_{EN} = L_{NE}$ .

For the further discussion, we proceed with a constraint, called "strong coupling", that plays a special role for the efficiency of machines both close to equilibrium and at maximum power. The constraint requires that the two fluxes are proportional to each other:  $J_E = \epsilon J_N = J$ . In the region of linear irreversible thermodynamics, this condition is satisfied provided the Onsager matrix has a zero determinant  $\det \mathbf{L} = 0$ . For strong coupling, the entropy production simplifies to:

$$(92) \quad \dot{S}_i = J X \geq 0$$

with the "collapsed" single thermodynamic force:

$$(93) \quad X = X_E + \frac{X_N}{\epsilon} = \frac{x^{(2)} - x^{(1)}}{\epsilon}.$$

with:

$$(94) \quad x^{(\nu)} = \frac{\epsilon - \mu^{(\nu)}}{T^{(\nu)}}.$$

This situation is of special interest because reversibility, corresponding to zero entropy production, can be achieved when  $X = 0$  without requiring that the separate forces  $X_E$  and  $X_N$  be zero. In particular, one does not need that both temperatures and chemical potentials are equal to reach reversibility. Indeed, the condition  $X = 0$  is satisfied whenever  $x^{(1)} = x^{(2)}$ .

It is revealing to evaluate the efficiency of the thermal machine that can be built with the 2 reservoir model. For strong coupling, one finds:

$$(95) \quad J_E^{(1)} = \dot{Q}^{(1)} + \mu^{(1)} \dot{N}^{(1)} = -J_E^{(2)} = -\dot{Q}^{(2)} - \mu^{(2)} \dot{N}^{(2)} = \epsilon \dot{N}^{(1)} = -\epsilon \dot{N}^{(2)},$$

hence

$$(96) \quad \frac{\dot{Q}^{(\nu)}}{T^{(\nu)}} = x^{(\nu)} \dot{N}^{(\nu)},$$

and finally ( $J_N = \dot{N}^{(1)} = -\dot{N}^{(2)}$ , recall also that Carnot efficiency is given by  $\eta_c = 1 - T^{(1)}/T^{(2)}$ , assuming that  $T^{(1)} \leq T^{(2)}$ ):

$$(97) \quad \dot{W}_{chem} = \mu^{(1)} \dot{N}^{(1)} + \mu^{(2)} \dot{N}^{(2)} = -\dot{Q}^{(1)} - \dot{Q}^{(2)}$$

$$(98) \quad = (-T^{(1)}x^{(1)} + T^{(2)}x^{(2)})J_N = T^{(2)}[-(1 - \eta_c)x^{(1)} + x^{(2)}]J_N.$$

We conclude that the efficiency  $\eta$ , being the ratio of the rate of the chemical work produced over heat influx from the hot reservoir, in casu reservoir (2), is given by :

$$(99) \quad \eta = \frac{-\dot{W}_{chem}}{\dot{Q}^{(2)}} = 1 - (1 - \eta_c) \frac{x^{(1)}}{x^{(2)}}.$$

We thus indeed recover Carnot efficiency under the condition of reversibility  $x^{(1)} = x^{(2)}$ . We stress that the present construction is quite different from the original Carnot machine: in order to avoid irreversible heat flows (which imply entropy production and hence make it impossible to attain Carnot efficiency), the original Carnot set-up is running in a cycle of connection and disconnection (with intermediate adiabatic steps to change the temperature). In the present construction, the condition of strong coupling allows to reach reversible operation -hence Carnot efficiency- in a steady state regime where the system is at all times in contact with both reservoirs! The analysis is in fact simplified significantly compared to the original Carnot cycle because it involves a single steady state operation.

**2.4. Two-level system: efficiency at maximum power.** – The previous discussion was based on general thermodynamic arguments. We now switch to a concrete stochastic model. This allows to calculate explicitly the basic quantity that is left unspecified in the preceeding analysis, namely the dependence of the particle or energy flow  $J_N$  and  $J_E$  on the system parameters  $x^{(1)}$  and  $x^{(2)}$ . As model, we consider a quantum dot with a single available energy level at the energy  $\epsilon$  <sup>(17)</sup>, which can exchange an electron with two leads  $\nu$  (temperature  $T^{(\nu)}$ , chemical potential  $\mu^{(\nu)}$ , respectively). The quantum dot has only two states, 1 and 0, corresponding to the energy level filled with one electron, or an empty energy level. The probability per unit time for an electron to jump from lead  $\nu$  into the empty level is given by  $W_{10}^{(\nu)} = a^{(\nu)} f^{(\nu)}$ , where  $a^{(\nu)}$  is a coupling constant, and  $f^{(\nu)}$  the Fermi function:

$$(100) \quad f^{(\nu)} = f(x^{(\nu)}) = \frac{1}{e^{x^{(\nu)}} + 1}.$$

The latter describes the occupancy rates of the energy levels in the lead. The probability for the reverse transition, an electron occupying the energy level of the dot jumping into the lead  $\nu$ , is equal to  $W_{01}^{(\nu)} = a^{(\nu)}(1 - f^{(\nu)})$  (the  $1 - f^{(\nu)}$  factor coming from the fact that the corresponding energy level in the lead has to be empty for such a transition to take place). The steady state distribution for the corresponding Master equation ( $\mathbf{W} = \mathbf{W}^{(1)} + \mathbf{W}^{(2)}$ ):

$$(101) \quad p_0^{st} = \frac{W_{01}}{W_{01} + W_{10}}$$

$$(102) \quad p_1^{st} = \frac{W_{10}}{W_{01} + W_{10}}.$$

Inserting this result into the expression of the particle and energy flow, one finds, after some algebra:

$$(103) \quad J = J(x^{(1)}, x^{(2)}) = J_E = \epsilon J_N = \epsilon \alpha [f^{(1)}(x^{(1)}) - f^{(2)}(x^{(2)})],$$

with

$$(104) \quad \alpha = \frac{a^{(1)} a^{(2)}}{a^{(1)} + a^{(2)}}.$$

The "collapsed thermodynamic force and entropy production read:

$$(105) \quad X = \frac{x^{(2)} - x^{(1)}}{\epsilon}$$

$$(106) \quad \dot{S}_i = \alpha [f^{(1)}(x^{(1)}) - f^{(2)}(x^{(2)})] (x^{(2)} - x^{(1)}) \geq 0$$

We now show how stochastic thermodynamics allows to address a question that goes beyond the usual thermodynamic analysis. From (99) and (96), we find the following

---

<sup>(17)</sup> The other energy levels are supposed to be sufficiently far from the Fermi levels of the reservoir, so that they are always full or empty and do not play a role.

expression for the power  $\mathbb{P}$  of our device:

$$(107) \quad \mathbb{P} = -\dot{W}_{chem} = \frac{T^{(2)}}{\epsilon}(x^{(2)} - (1 - \eta_c)x^{(1)})J(x^{(1)}, x^{(2)}).$$

We raise the following question of interest: for which values of the variables  $x^{(1)}$  and  $x^{(2)}$  (obviously control parameters of our device) will the power reach a maximum? These values  $x^{(1),*}$  and  $x^{(2),*}$  are the solution of the following extremum condition:

$$(108) \quad \frac{\partial \mathbb{P}}{\partial x^{(1)}} = 0$$

$$(109) \quad \frac{\partial \mathbb{P}}{\partial x^{(2)}} = 0.$$

These conditions give rise to a transcendental equation, which can be solved numerically, see [7] for more details. An even more interesting question concerns the efficiency that is reached at maximum power. This efficiency is easily obtained by inserting the values of  $x^{(1),*}$  and  $x^{(2),*}$  into (99). An analytic treatment becomes possible in terms of an expansion in terms of Carnot efficiency  $\eta_C$ . We just cite the final result for the efficiency  $\eta^*$  at maximum power:

$$(110) \quad \eta^* = \frac{\eta_C}{2} + \frac{\eta_C^2}{8} + \frac{7 + \operatorname{csch}^2(a_0/2)}{96}\eta_C^3 + \dots,$$

where  $a_0 \approx 2.39936$  is the solution of  $a_0 = 2 \coth(a_0/2)$ . It turns out that the coefficient  $1/2$  is universal for strong coupling, and is essentially a consequence of Onsager symmetry [8]. The coefficient  $1/8$  is also universal under the additional condition of a left-right symmetry (meaning that the fluxes change sign under inversion of the reservoir values and couplings) [9]. Like Onsager symmetry, this universality can be linked at a deeper level with the reversibility of underlying microscopic laws, and more directly to the fluctuation theorem that we derive below in trajectory stochastic thermodynamics.

### 3. – Ensemble stochastic thermodynamics: more

**3.1. General comments.** – The theory that we developed so far looks consistent and appealing, but it may appear to be tailor-made for a special class of physical systems, described by Markovian dynamics satisfying the condition of local equilibrium (52). It is however possible to show, and this is work in progress, that the theory fits into a much broader scheme. This is not so surprising: it is a typical strength of thermodynamic theories to far exceed the domain application/formulation in which they are originally presented. The Markovian context however allows to easily explore further implications of the theory and to develop new ideas. In this section, we illustrate this with two promising extensions.

**3.2. Landauer principle [10, 11].** – We mentioned one of the formulations of the second law for a system, in contact with a single heat bath, driven from one equilibrium state into another one, namely:

$$(111) \quad T\Delta_i S = W - \Delta F^{eq} \geq 0.$$

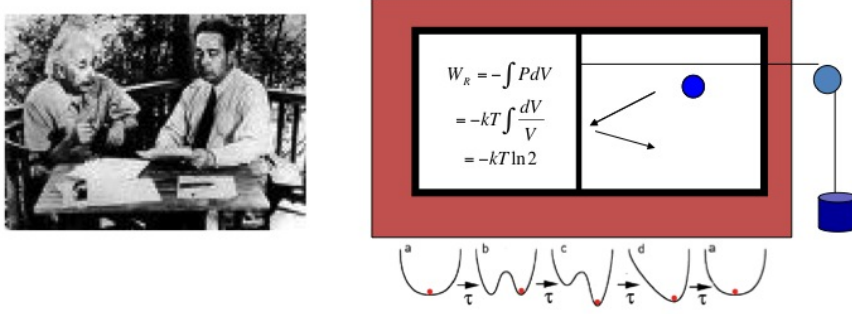


Fig. 2. – Schematic representation of the Szilard engine (with a Brownian variation below), converting one bit of information into  $k_B T \ln 2$  of work. Left: Szilard conversing with Einstein.

We added the superscript *eq* to stress that the free energy is, in conventional thermodynamics, only well defined for equilibrium states, and that the above results only applies to changes between such states. We now show that stochastic thermodynamics not only reproduces this result, but gives a generalization for transitions between any two states, not necessarily at equilibrium. The result is closely related to the so-called Landauer principle, which establishes a relation between thermodynamics and information. We start by rewriting first and second law, and the expression for the entropy flow when in contact with a single heat reservoir (temperature  $T$ ):

$$(112) \quad \dot{W} = \dot{E} - \dot{Q}$$

$$(113) \quad \dot{S}_i = \dot{S} - \dot{S}_e \geq 0$$

$$(114) \quad \dot{Q} = T \dot{S}_e.$$

We now introduce the non-equilibrium free energy:

$$(115) \quad F = E - TS.$$

Combination with the previous formulas leads in a one-line calculation to

$$(116) \quad T \dot{S}_i = \dot{W} - \dot{F} \geq 0$$

which is so to say the "instantaneous" generalization of (111). To make a clearer comparison, it is revealing to integrate this result over an interval of time:

$$(117) \quad T\Delta_i S = W - \Delta F = W - \Delta F^{eq} - T\Delta I \geq 0.$$

This result is valid for any initial and final condition. To compare with equilibrium states, we have introduced the quantity I:

$$(118) \quad F - F^{eq} = TI$$

$$(119) \quad I = k_B D(p_m || p_m^{eq}) = k_B \sum_m p_m \ln \frac{p_m}{p_m^{eq}},$$

which is a measure of the distance between the actual distribution and an equilibrium one. The most important upshot of the new result (117) is that the amount of work  $-W$ , that can be generated by changing the state of a system, is at most equal to the decrease of equilibrium free energy  $-\Delta F^{eq}$  *plus* the decrease in "information content"  $-T\Delta I$ . We give a simple illustration, which at the same time makes the contact with the so-called "Landauer principle", see Fig. 2. We consider a single particle in a box, and identify the states  $m = 0$  and  $m = 1$  as being in the left and right half of the box, respectively. At equilibrium one has  $p_0^{eq} = p_1^{eq} = 1/2$ . We however consider the following nonequilibrium initial state  $p_0 = 1$  and  $p_1 = 0$ . Such an initial condition could have been prepared (by compressing the particle in the left hand side of the box), or by performing a measurement, revealing that the particle is in that half side of the box. This corresponds to the information of 1 bit. In either case, our formula predicts that we can extract work out of this nonequilibrium initial condition, namely (at most)  $-T\Delta I = TI(t = 0) = k_B T \ln 2$  (we use the physically relevant limit " $0 \ln 0$ " = 0). In words one can extract at best  $k_B T \ln 2$  work from erasing one bit. In the same way, one proves that writing one bit cost at least  $k_B T \ln 2$  of work [12].

**3.3. Adiabatic and non-adiabatic entropy.** – Let us return to the explicit expression (72) for entropy production, and in particular to that for the thermodynamic force (78). One easily verifies that the latter can be split into two separate contributions:

$$(120) \quad X_{m,m'}^{(\nu)} = A_{m,m'}^{(\nu)} + N_{m,m'}^{(\nu)}$$

$$(121) \quad A_{m,m'}^{(\nu)} = k_B \ln \frac{W_{m,m'}^{(\nu)} p_{m'}^{st}}{W_{m',m}^{(\nu)} p_m^{st}}$$

$$(122) \quad N_{m,m'} = k_B \ln \frac{p_{m'} p_m^{st}}{p_m p_{m'}^{st}}.$$

This results in a splitting of the entropy production into two contributions that are, and this is somewhat surprising, separately non-negative:

$$(123) \quad \dot{S}_i = \dot{S}_a + \dot{S}_{na} \geq 0$$

$$(124) \quad \dot{S}_a = \frac{1}{2} \sum_{m,m',\nu} J_{m,m'}^{(\nu)} A_{m,m'}^{(\nu)} \geq 0$$

$$(125) \quad \dot{S}_{na} = \frac{1}{2} \sum_{m,m',\nu} J_{m,m'}^{(\nu)} N_{m,m'} = \frac{1}{2} \sum_{m,m'} J_{m,m'} N_{m,m'} \geq 0.$$

The proof again follows from the inequality  $\ln x < 1 - x$ , conservation of probability (31) and the fact that  $p^{st}$  is the instantaneous "steady state", cf. (32). One can give the following interpretation: the so-called adiabatic contribution  $\dot{S}_a$  to the entropy production is the one that survives when one takes the "adiabatic" limit in which the probability distribution is at all times equal to the (instantaneous) steady state. It is in particular equal to the full entropy production when operating at a steady state (time-independent rates). Note that this component will be only zero when operating at full equilibrium. At nonequilibrium steady states it has a constant non-zero value, expressing the amount of irreversible dissipation needed to maintain this state.

The contribution  $\dot{S}_{na}$  is a "relaxational" entropy production, internal to the system. It only depends on the total transition matrix  $\mathbf{W}$ , and can be rewritten under the following way

$$(126) \quad \dot{S}_{na} = -k_B \sum_m \dot{p}_m \ln \frac{p_m}{p_m^{st}} \geq 0.$$

In the special case of constant transition matrix (so that  $p^{st}$  is a time-independent quantity), one verifies that  $\dot{S}_{na} = -k_B \dot{H}$ . This gives a physical meaning to the H function: its time derivative is minus the non-adiabatic entropy production. Only in the special case of an equilibrium steady state does it correspond to minus the (full) irreversible entropy production.

**3.4. Other extensions.** – We will be very brief and give an haphazard list of other developments. One can include driving in the above discussed example of a quantum dot, by considering a time-dependent energy  $\epsilon$ . The system can then also operate via a traditional Carnot cycle (system in contact with only one of the reservoirs at any given time), and one can show that both Carnot efficiency and efficiency at maximum power are reproduced. One can also discuss energy injection in a steady state by considering a random perturbation of the energy level. Again all the "familiar" thermodynamic features are reproduced, including also the issue of work to work conversion engines (the driving can be used to pump particles up a chemical gradient). Universal features, similar to those for thermal machines, can be derived [13, 14]. Several variants of systems with two quantum dots have been studied, including a photo-electric cell [15] and photo-electric cooling [16]. Another model that was studied in the context of efficiency at maximum power is a maser model [9]. One can relax the condition of "local equilibrium" for the transition rates. In this case a new contribution appears in the entropy production, which can be interpreted in terms of a "Maxwell demon" that breaks the detailed balance of the transition rates [17]. Using Markovian partitions, a connection can be established between the entropy production discussed here and the concept of Kolmogorov-Sinai entropy in dynamical systems [18]. In an early paper [19], it is shown that the steady states close to equilibrium are the states of minimum entropy production. A large section of the literature deals with stochastic thermodynamics for Langevin equations [20, 21, 22, 23]. Note however that the formulation for Master equations includes, as a particular case, the continuous Markov processes described by Fokker Planck and Langevin equation, since they can be obtained -via an appropriate limiting procedure- from a Master equation. As an historic note, we mention that the "early steps" in the development of ensemble stochastic thermodynamics were in fact taken at the level of a Master equation description [24, 25, 19, 26], with (nonequilibrium) chemical reactions as prototypical example, followed more than a decade later by similar and further developments in the context of

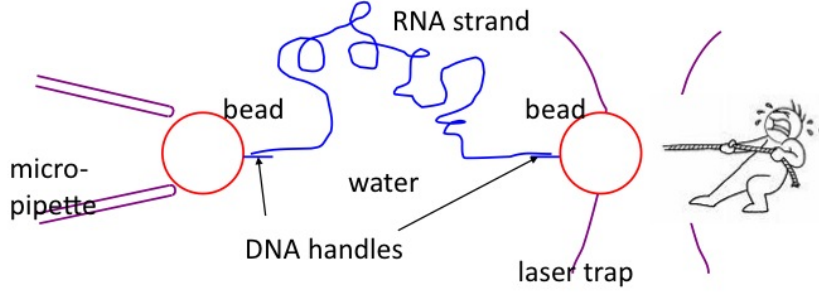


Fig. 3. – The work  $w$  needed to stretch a RNA strand with optical tweezers is a random variable.

soft condensed matter, with (driven) overdamped Brownian motion as workhorse [21, 22]. The Langevin version of the adiabatic and non-adiabatic entropy production is derived in [27]. For a further review of the theory and applications in the context of Langevin and Fokker Planck equations, see [28, 29].

#### 4. – Trajectory stochastic thermodynamics

**4.1. Motivation.** – We discussed on several occasions one of the traditional formulations of the second law, namely  $T\Delta_i S = W - \Delta F^{eq} \geq 0$ , giving a bound for the work on a system undergoing a change between two equilibrium states, while in contact with a heat bath. We stress that classical thermodynamics does not specify the value of  $W$ , it only gives a lower bound. This bound is reached for a reversible (and in particular infinitely slow) process. As example, consider the expansion of an ideal gas (temperature  $T$ , number of particles  $N$ ) from initial volume  $V_i$  to final volume  $V_f$ . We can extract an amount of work  $-W \leq -\Delta F^{eq} = T\Delta S^{eq} = Nk_B T \ln V_f/V_i = \int_{V_i}^{V_f} P dV$  ( $\Delta E^{eq} = 0$  for isothermal change in an ideal gas). The limit is reached for a quasi-static isothermal expansion. For any other (e.g., faster) scenario, the extracted work will be less. Note however that the same amount of work will be needed when one repeats the experiment in the same way, i.e.,  $W$  is a self-averaging quantity in such a macroscopic experiment. Consider now a similar experiment but on a small (non-macroscopic) scale, for example the elongation of a polymer (e.g., RNA strand) with optical tweezers from an initial to a final equilibrium position, cf. Fig.3. The amount of work can be obtained from force versus elongation curves (work being force time displacement). We now observe that



this quantity will be different in one run from another, because the system is subject to fluctuations <sup>(18)</sup>. We denote it by  $w$ , using a lower script to stress that the quantity depends on the particular trajectory  $\Pi$  that the system happens to follow in the given run,  $w = w^\Pi$ . The question now arises concerning the connection with the second law. One could argue that the second law only applies to macroscopic systems. Hence one should do the experiment with a macroscopic number  $N$  of independent RNA strands. By the law of large numbers, the work per strand will converge to its average value, and the second law becomes:  $N \langle w \rangle - \Delta F^{eq} \geq 0$  (where the free energy difference  $\Delta F^{eq}$  refers to that for a collection of  $N$  RNA strands). This may look, at first, like a satisfactory explanation. However, by repeating the above experiment, one can construct the probability distribution  $P(w)$ . It looks odd that the second law of thermodynamics, being one of the most fundamental laws in nature, just prescribes an upper bound for the first moment of this distribution. We now proceed to show that one obtains a much deeper formulation of the second law as a symmetry property of this probability distribution, which implies in particular the above inequality for its first moment. We will derive this symmetry property in the context of stochastic thermodynamics, but we stress that it has -in our opinion- a much deeper validity, as documented in the literature in several other specific or general settings (thermostated systems, classical and quantum dynamics, relativity and quantum field theory).

**4.2. First law: trajectory thermodynamics [28].** – Let us return to our stochastic description of a system with states  $m$  and probability distribution  $p_m$ , obeying a Markovian Master equation. For simplicity (and because of lack of space and time), we will in the sequel assume that there is no particle transport involved (so we need not worry about the change of particles upon jumping between levels and the associated chemical work). We will now focus on various properties of the system, not at the ensemble level, but at the trajectory level. A trajectory, generically denoted by  $\Pi$ , corresponds to the specification of the actual state in the time interval under consideration, i.e.,  $m(t), t \in [t_i, t_f]$ . In view of the discrete nature of the state, one can alternatively specify the initial state  $m_i = m_1 = m(t_i)$ , the jumps from  $m_j$  to  $m_{j+1}$  at specific instances of time  $t_{j+1,j}$ ,  $j = 1, \dots, N-1$  where  $N-1$  is the total number of jumps, and  $m_f = m_N = m(t_f)$  being the final state at time  $t_f$ . To stress that we are dealing with trajectory dependent quantities, we will use a lower script, e.g.,  $\Delta e$  for energy difference,  $w$  for work,  $q$  for heat (and  $s$  for entropy, to be defined in the next section). Most of the time, we suppress for simplicity of notation the reference to the particular trajectory under consideration ( $\Delta e = \Delta e^\Pi$ ,  $w = w^\Pi$ ,  $q = q^\Pi$ , etc.).

The energy is well defined, even at the level of trajectories: the energy at time  $t$  is the energy of the particular state  $m(t)$  in which the system resides at that time in the trajectory under consideration:

$$(127) \quad e = e^\Pi(t) = \epsilon_{m(t)}(t).$$

The energy is in fact a state function, but the state is now the actual micro-state of the system (compare with the ensemble picture, where  $E$  is also a state variable, but

---

<sup>(18)</sup> The only and notable exception is an infinitely slow process, in which the work is always the same and equal to the (equilibrium) free energy difference. We will see below that the probability distribution for  $w$  then indeed reduces to a delta function.

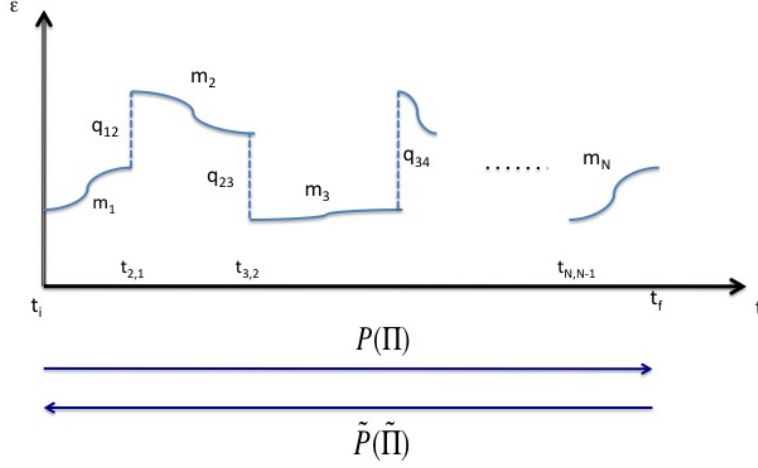


Fig. 4. – Schematic representation of the first law along a trajectory.

expressed in terms of the statistical state, i.e. the probability distribution over the energy levels). In particular the energy  $e(t)$  at time  $t$  for a trajectory  $\Pi$  depends only on the state of the system at that time, and not on the remainder of the trajectory. For the same reason the energy difference  $\Delta e$  only depends on final and initial states: the change  $\Delta e$  between any initial and final times  $t_i$  and  $t_f$  is given by:

$$(128) \quad \Delta e = e_f - e_i = \epsilon_{m_f}(t_f) - \epsilon_{m_i}(t_i).$$

Conservation of energy is of course valid trajectory-wise, so one can write the first law of thermodynamics trajectory-wise (i.e. valid for any trajectory  $\Pi$ ) :

$$(129) \quad \Delta e = w + q.$$

As in the ensemble picture, heat and work are not state functions but depend on the actual trajectory that the system has followed (in addition to the dependence on the way the perturbation is applied). They are related, respectively, to the jumps between energy levels and the shift in energy level, as they occur along the trajectory under consideration. Explicitly, one has for the trajectory  $\Pi$ :

$$\begin{aligned} w &= [\epsilon_{m_1}(t_{2,1}) - \epsilon_{m_1}(t_i)] + [\epsilon_{m_2}(t_{3,2}) - \epsilon_{m_2}(t_{2,1})] + \dots + [\epsilon_{m_N}(t_f) - \epsilon_{m_N}(t_{N,N-1})] \\ q &= \sum_{jumps} q_{j+1,j} \quad q_{j+1,j} = \epsilon_{m_{j+1}}(t_{j+1,j}) - \epsilon_{m_j}(t_{j+1,j}). \end{aligned}$$

In case of different thermal reservoirs  $\nu$ , a trajectory  $\Pi$  needs also to specify which reservoir is responsible for which transition, so that one can further specify the subdivision of the heat flow into contributions due to the different reservoirs:

$$(130) \quad q = \sum_{\nu} q^{(\nu)},$$

where  $q^{(\nu)}$  is the sum of those energy jumps, for which the heat comes from reservoir  $\nu$ .

It is instructive to reproduce the first law in its differential form. To do so, we rewrite the expression (127) for the energy as follows:

$$(131) \quad e(t) = \epsilon_{m(t)}(t) = \sum_m \epsilon_m(t) \delta_{m,m(t)}^{Kr},$$

so that the two contributions, work rate and heat rate, appear quite naturally as before from the modulation of the energy level and from the change in state (the "jumps"), respectively:

$$(132) \quad \dot{e} = \dot{w} + \dot{q}$$

$$(133) \quad \dot{w} = \sum_m \dot{\epsilon}_m(t) \delta_{m,m(t)}^{Kr}$$

$$(134) \quad \dot{q} = \sum_m \epsilon_m(t) \dot{\delta}_{m,m(t)}^{Kr}.$$

One easily verifies the agreement between the integral and differential formulation of the first law <sup>(19)</sup>.

**4.3. Second law: trajectory thermodynamics.** – A main hurdle is to define entropy at the trajectory level. This may appear, at first, to be an oxymoron since, as argued so forcefully by Boltzmann in his historic debate about the second law, entropy is property of the ensemble. One can however attach an entropy to an event taking place in a sampling of a random variable. This is routinely done in information theory, where one quantifies the concept of surprise as  $-\ln p_m$  upon observing the outcome  $m$  when its probability is  $p_m$  [6]. There is no surprise when  $p_m = 1$  and the surprise becomes increasingly large when  $p_m \rightarrow 0$ . Upon repeating the experiment, we find that the average surprise is equal to the entropy  $S = -\sum_m p_m \ln p_m$ . We can of course use the same concept when both  $p$  and  $m$  are time-dependent and thus define the stochastic or trajectory entropy as follows:

$$(135) \quad s = s^{\Pi}(t) = -k_B \ln p_{m(t)}(t).$$

In other words, the entropy of the system in a specific trajectory is, at each time, minus the logarithm of the probability, at that time, to be in the observed state. While being,

---

<sup>(19)</sup> To find the time-derivative of the Kronecker delta, note that  $\delta_{m,m(t)}^{Kr}$  goes from zero to one, and from one to zero, when  $m(t)$  jumps into, or out of state  $m$ , respectively. Hence the time-derivative consists of a sum of delta functions, with weights  $+1$  and  $-1$ , centered at the time of the jumps.

like the energy, a "micro-state" variable, function of  $m(t)$ , it retains an "ensemble quality", since its value is also determined in terms of the probability distribution  $p_m$  (at the same time  $t$ ). This definition of the stochastic entropy was introduced by U. Seifert [29].

We proceed to show how the above definition of stochastic entropy leads to a pleasing formulation of the second law at the trajectory level, and even more importantly will result in a profound reassessment of the second law itself. Being a micro-state function, we find that the change of stochastic system entropy over a finite time interval  $[t_i, t_f]$  is given by:

$$(136) \quad \Delta s = -k_B \ln p_{m_f}(t_f) + k_B \ln p_{m_i}(t_i).$$

In analogy with the second law, we would like to split this system entropy change into an entropy flow and an entropy production term. At the ensemble level, the entropy flow is average heat flow divided by temperature (of the corresponding reservoir). Heat flow is however equally well defined at the trajectory level, as we discussed in the previous section. Recalling that  $q_{j+1,j}^{(\nu)}$  is the heat taken from reservoir  $(\nu)$  upon the jump from  $m_j$  to  $m_{j+1}$ , we can immediately write the trajectory version of the entropy flow:

$$(137) \quad \Delta_e s = \sum_{jumps} \frac{q_{j+1,j}^{(\nu)}}{T^{(\nu)}}.$$

It will be usefull, when discussing the entropy production, to rewrite this expression using the basic property (65) as follows:

$$(138) \quad \Delta_e s = -k_B \sum_{jumps} \ln \frac{W_{j+1,j}^{(\nu)}}{W_{j,j+1}^{(\nu)}}.$$

By combining Eqs. (136) and (138), we obtain the following expression for the trajectory entropy production:

$$(139) \quad \Delta_i s = \Delta s - \Delta_e s = -k_B \ln p_{m_f}(t_f) + k_B \ln p_{m_i}(t_i) + k_B \sum_{jumps} \ln \frac{W_{j+1,j}^{(\nu)}}{W_{j,j+1}^{(\nu)}}.$$

Note that this quantity can have any sign. We will in fact show below that  $\Delta_i s$  can not always be non-negative, i.e., there must exist trajectories for which it is negative. But before rewriting the above not so beautiful expression into a form, that will allow us to make such sweeping statements, we make a first simple "test". Let us consider the experiment that we mentioned before as one motivation for trajectory thermodynamics: a small scale system is brought from one equilibrium state into another one, under injection of an amount of work  $w$ . When the experiment is repeated, the detailed trajectory that the system will follow is different and hence the work will also change. It would be very pleasing if one finds that the above introduced entropy production is related to this work, in a way similar to the macroscopic counterparts, cf. (111) and (117). We therefore consider the system in contact with a heat bath at temperature  $T$ , and introduce the stochastic free energy :

$$(140) \quad f = e - Ts,$$

which is obviously also a micro-state function.

Combination of the stochastic second law, cf. (137) and (139), with the stochastic first law (129) leads to:

$$(141) \quad T\Delta_i s = w - \Delta f,$$

which is the stochastic analogue of (117).

We now identify the expressions for the stochastic entropy and free energy when the probability distribution  $p_m$  has an equilibrium form. For a canonical distribution (13) one finds (instating the subscript  $eq$  to stress that we are dealing with the equilibrium distribution):

$$(142) \quad s^{eq} = \frac{e - F^{eq}}{T},$$

hence

$$(143) \quad f^{eq} = F^{eq}.$$

At equilibrium, the stochastic free energy reduces to the ensemble averaged free energy, and is independent of the actual micro-state  $m$ ! In particular, if initial and final conditions are at equilibrium, we find from (141) that:

$$(144) \quad T\Delta_i s = w - \Delta F^{eq}.$$

This result is of particular interest since the statistical properties of the random variables  $\Delta_i s$  and  $w$  are now essentially the same ( $\Delta F^{eq}$  being a given fixed amount). As in the ensemble average case, we would like to differentiate this result from the situation where initial and final distributions are not at equilibrium. We define, in analogy to (118):

$$(145) \quad f - f^{eq} = Ti$$

$$(146) \quad i = k_B \ln \frac{p_m}{p_m^{eq}},$$

so that we can rewrite (141) as follows

$$(147) \quad T\Delta_i s = w - \Delta F^{eq} - T\Delta i.$$

We finally turn to an alternative expression of the stochastic entropy production  $\Delta_i s$ , which will allow to derive a deep symmetry relation concerning its stochastic properties. We start by defining a "forward" experiment by applying a specific time-dependence of the transition rates  $\mathbf{W}(t)$ , in the interval  $[t_i, t_f]$  starting from a given initial distribution  $p_m(t_i)$  at the initial time  $t_i$ . In this experiment, one can identify the probability  $\mathcal{P}(II)$  to observe a specific trajectory  $II$ . We now define a time-reversed "tilde" experiment. The initial probability distribution is the final distribution of the forward experiment. The rates  $\tilde{\mathbf{W}}$  are the rates  $\mathbf{W}$ , but being ran backward in time. We denote by  $\tilde{\mathcal{P}}(\tilde{II})$  the probability to observe the time-reversed trajectory  $\tilde{II}$  in this time-reversed experiment

<sup>(20)</sup>. We now write what we believe to be the single most important expression in stochastic thermodynamics:

$$(148) \quad \Delta_i s = k_B \ln \frac{\mathcal{P}(\Pi)}{\tilde{\mathcal{P}}(\tilde{\Pi})}.$$

The proof goes as follows. The probability  $\mathcal{P}(\Pi)$  to observe the specific trajectory  $\Pi$ , cf. Fig. 4, is equal to the probability  $p_{m_i}(t_i)$  to start in the state  $m_i$  times the probability to stay in this state until the first jump, times the probability to make this jump, and so on for the other jumps, with a final factor expressing that the system does not leave its final state  $m_f$ . The probabilities (per unit time) to make the jumps are of course well known, namely

$$(149) \quad W_{j+1,j}^{(\nu)}.$$

The probability for not making a jump while in state  $m$  during an interval of time  $[t, t']$  is given by  $(t_i = t + idt$  with  $dt = (t' - t)/n$ ):

$$(150) \quad \lim_{n \rightarrow \infty} \prod_{i=1}^n [1 - \sum_{m', m' \neq m} W_{m',m}(t_i) dt] = \lim_{n \rightarrow \infty} \prod_{i=1}^n [1 + W_{m,m}(t_i) dt] = e^{\int_t^{t'} W_{m,m}(\tau) d\tau}$$

Turning to the probability of the reverse trajectory, we make the crucial observation that the latter contributions are exactly the same: the probability for not making transitions are identical in forward and backward trajectories. The probability for making (the backward) jumps on the other hand are obviously given by

$$(151) \quad W_{j,j+1}^{(\nu)}.$$

The probability for the starting state  $m_f$  of the reverse trajectory is, by assumption, given by  $p_{m_f}(t_f)$ . We thus conclude that:

$$(152) \quad \ln \frac{\mathcal{P}(\Pi)}{\tilde{\mathcal{P}}(\tilde{\Pi})} = \ln p_{m_i}(t_i) - \ln p_{m_f}(t_f) + \sum_{jumps} \ln \frac{W_{j+1,j}^{(\nu)}}{W_{j,j+1}^{(\nu)}},$$

which is indeed identical to  $\Delta_i s/k_B$ . One should give credit to G. Crooks, who realized the above cancelation (in his phd thesis [31]) and applied it to the heat flux (which is in fact the entropy flow):

$$(153) \quad \Delta_e s = -k_B \ln \frac{\mathcal{P}_0(\Pi)}{\tilde{\mathcal{P}}_0(\tilde{\Pi})} = -k_B \sum_{jumps} \ln \frac{W_{j+1,j}^{(\nu)}}{W_{j,j+1}^{(\nu)}}.$$

---

<sup>(20)</sup> Note that we are in fact dealing here with functional probability densities for paths. Note further that we assume the variables  $m$  to be even function of the momenta, and that there is no magnetic field.

Here  $\mathcal{P}_0$  and  $\tilde{\mathcal{P}}_0$  are the probabilities for the trajectory  $\Pi$  and  $\tilde{\Pi}$  disregarding the contribution for the starting probabilities  $p_{m_i}(t_i)$  and  $p_{m_f}(t_f)$ . In most earlier works, this contribution, which is in fact equal to  $\Delta s$ , was referred to as "the boundary term" whose physical significance was not fully realized until the work of Seifert.

Before turning to the "dramatic" implications of (144), we close the loop by returning to the ensemble expression for the entropy production. As  $\Delta_i s$  is the entropy production for a specific trajectory  $\Pi$ , which occurs with probability  $\mathcal{P}(\Pi)$ , the average entropy production reads:

$$(154) \quad \Delta_i S = \langle \Delta_i s \rangle = k_B \sum_{\Pi} \mathcal{P}(\Pi) \ln \frac{\mathcal{P}(\Pi)}{\tilde{\mathcal{P}}(\tilde{\Pi})} = k_B D(\mathcal{P}||\tilde{\mathcal{P}}) \geq 0.$$

We immediately recognize, with contentedness and satisfaction, that this is indeed a non-negative quantity. One can also verify with relief that it corresponds to the time integrated version of the ensemble entropy production  $\dot{S}_i$  given in (72),  $\Delta_i S = \int_{t_i}^{t_f} \dot{S}_i dt$ .

As if all this was not pleasing enough, we close with another bonus of the above result. It was derived from a Master equation description, but the expression for the stochastic entropy production is expressed in terms of probability for paths, without explicit reference to the transition matrix. Since Langevin/Fokker Planck equations can always be obtained via a limiting procedure for a Master equation, the same result applies for this description, but the probabilities of the paths now refer to Brownian paths <sup>(21)</sup>. The conclusions that we will derive in the next section do not depend on the detailed form of the trajectories and therefore apply equally well to any Markovian process, be it a jump process, a continuous process or a combination of both.

**4.4. Integral and detailed fluctuation theorem..** – We are now ready to "move to the top". We will start with the so-called integral fluctuation theorem. Instead of looking at the "usual" ensemble entropy production  $\Delta_i S$ , the average of the stochastic entropy production  $\Delta_i s$ , let us consider the following average:

$$(155) \quad \langle e^{-\Delta_i s/k_B} \rangle = \langle \frac{\tilde{\mathcal{P}}}{\mathcal{P}} \rangle = \sum_{\Pi} \mathcal{P} \frac{\tilde{\mathcal{P}}}{\mathcal{P}} = 1,$$

where we used the fact that  $\tilde{\mathcal{P}}$  is a normalized probability (and the sum over all forward paths a sum implies over all backward paths <sup>(22)</sup>). The above expression is called the integral fluctuation theorem. Note that it holds for any initial probability distribution (and any perturbation in the sense of time-dependent transition rates). It implies, by Jensen's inequality [6], the "usual" second law:

$$(156) \quad \Delta_i S = \langle \Delta_i s \rangle \geq 0.$$

For the special case that the transition is between equilibrium states at the same temperature, we know that  $T\Delta_i s = w - \Delta F^{eq}$ , and the above expression reduces to

<sup>(21)</sup> Fokker Planck equations describe so-called continuous Markov processes with realizations that are continuous, but nowhere differentiable.

<sup>(22)</sup> To be more precise, we need to show that the Jacobian for the transformation of forward to backward paths is one. This property in fact derives at the most fundamental level from Liouville's theorem.

the celebrated Jarzynski equality (originally derived in the context of a microscopic Hamiltonian [32], and later for a mesoscopic Markovian description [33]):

$$(157) \quad \langle e^{-\beta w} \rangle = e^{-\beta \Delta F^{eq}}.$$

This result is quite remarkable since it applies independently of the type of perturbation and the intermediate departure of the system from equilibrium, while it incorporates via Jensen's inequality the "traditional" second law information  $\langle w \rangle \geq \Delta F^{eq}$ .

For transitions between nonequilibrium states one obtains, using (147), a generalized Jarzynski equality:

$$(158) \quad \langle e^{-\beta(w-T\Delta i)} \rangle = e^{-\beta \Delta F^{eq}},$$

which by Jensen's inequality implies the earlier discussed Landauer principle, cf. (117).

The above integral fluctuation theorems can be derived from an even more "detailed" property, which is appropriately called a detailed fluctuation theorem. We ask the following question: given an experimental setting (initial condition and driving), what is the probability  $P(\Delta_i s)$  to observe a change in the stochastic entropy equal to  $\Delta_i s$ ? Obviously, this probability can be calculated as follows

$$(159) \quad P(\Delta_i s) = \sum_{\Pi} \mathcal{P}(\Pi) \delta(\Delta_i s - k_B \ln \frac{\mathcal{P}(\Pi)}{\tilde{\mathcal{P}}(\tilde{\Pi})})$$

$$(160) \quad = e^{\Delta_i s / k_B} \sum_{\Pi} \mathcal{P}(\tilde{\Pi}) \delta(\Delta_i s - k_B \ln \frac{\mathcal{P}(\Pi)}{\tilde{\mathcal{P}}(\tilde{\Pi})})$$

$$(161) \quad = e^{\Delta_i s / k_B} \sum_{\tilde{\Pi}} \mathcal{P}(\tilde{\Pi}) \delta(-\Delta_i s - k_B \ln \frac{\tilde{\mathcal{P}}(\tilde{\Pi})}{\mathcal{P}(\Pi)})$$

$$(162) \quad = e^{\Delta_i s / k_B} \tilde{P}(-\Delta_i s),$$

where

$$(163) \quad \tilde{P}(-\Delta_i s) = \sum_{\tilde{\Pi}} \mathcal{P}(\tilde{\Pi}) \delta(-\Delta_i s - k_B \ln \frac{\tilde{\mathcal{P}}(\tilde{\Pi})}{\mathcal{P}(\Pi)}).$$

We are thus lead to the famous fluctuation theorem:

$$(164) \quad \frac{P(\Delta_i s)}{\tilde{P}(-\Delta_i s)} = e^{\Delta_i s / k_B}.$$

In words: it is exponentially more likely to see a stochastic entropy increase  $\Delta_i s$  in an experiment, than to see a corresponding decrease  $-\Delta_i s$  in the time-reverse experiment. Before proceeding to a further discussion and illustration of this amazing result, we need to address a possible source of confusion in the notation and subtlety in the definition (163):  $-\Delta_i s$  is clearly minus the entropy production in the forward path, but how is it related to the entropy change in the backward path? It turns out that  $-\Delta_i s$  is indeed the entropy production in the backward path  $\tilde{\Pi}$  under the special condition that both initial



and final conditions of the trajectory are stationary states. Indeed we can apply the general result to find the entropy production  $\Delta_i \tilde{s}$  of a path  $\tilde{I}$  in the backward protocol:

$$(165) \quad \Delta_i \tilde{s} = k_B \ln \frac{\tilde{\mathcal{P}}(\tilde{I})}{\tilde{\mathcal{P}}(\tilde{I})}.$$

It is obvious that  $\tilde{I} = I$ . However  $\tilde{\mathcal{P}} = \mathcal{P}$  only if the initial and final distribution match: the final distribution of the backward scenario has to be the initial distribution of the forward trajectory. This will in general only be the case if the initial and final distributions are stationary (which in an experiment means that we have to stop the driving and wait until the steady state is reached). Under this condition one concludes that  $\Delta_i \tilde{s} = -\Delta_i s$ , and the fluctuation theorem takes on the additional meaning that one compares the entropy productions in forward and backward experiments. A simple and important application are so-called the nonequilibrium steady states. In this case, we have no driving so that furthermore  $\tilde{\mathcal{P}} = \mathcal{P}$ . Hence it is, in this case, exponentially more likely to see a stochastic entropy increase  $\Delta_i s$  than to see a corresponding decrease  $-\Delta_i s$  in the same experiment.

We close with some comments on the solution of (144), which we write now as a mathematical condition on a probability density  $P(x)$  and its twin  $\tilde{P}(x)$  ( $x = \Delta_i s/k_B$ ):

$$(166) \quad \frac{P(x)}{\tilde{P}(-x)} = e^x.$$

We mention the interest of the cumulant generating function:

$$(167) \quad G(\lambda) = \int dx P(x) e^{-\lambda x},$$

and a similar definition for  $\tilde{G}$  in terms of  $\tilde{P}$ . One easily verifies that the detailed fluctuation theorem Eq. (166) is equivalent with the following symmetry property:

$$(168) \quad G(\lambda) = \tilde{G}(1 - \lambda).$$

The calculation of the cumulant generating function is in most cases easier than that of the probability distribution. Furthermore, the detailed fluctuation theorem can often be proven without an explicit calculation by showing that the equation for the cumulant generating function possesses the above symmetry [34, 35]. Furthermore, the cumulant generating function gives direct access to the cumulants of the corresponding quantities, which can often be evaluated exactly in a large time limit (large deviation function).

Considering the simple case,  $P = \tilde{P}$ , one can try as solution a Gaussian probability distribution (with average  $\langle x \rangle$  and dispersion  $\sigma^2$ ), to find that it is a solution provided the dispersion is twice the average:

$$(169) \quad P_G(x) = \frac{e^{-\frac{(x - \langle x \rangle)^2}{4\langle x \rangle}}}{\sqrt{4\pi\langle x \rangle}}.$$

One concludes that the general solution of (166) is thus given by this Gaussian times any non-negative even function (with proportionality factor guaranteeing normalization):

$$(170) \quad P(x) = P_G(x)f(x)$$

$$(171) \quad f(x) = f(-x) \geq 0$$

$$(172) \quad \int_{-\infty}^{\infty} dx P_G(x)f(x) = 1.$$

Of special interest in the case of a Gaussian distribution with vanishing mean: one finds  $P(x) = \delta(x)$ . This corresponds to equilibrium with the stochastic entropy production being always zero. Hence at equilibrium there is no entropy production even trajectory-wise. When the system is not at equilibrium, the distribution will have a finite width. Consider again a nonequilibrium steady state (so that  $P = \tilde{P}$ ). Note the somewhat surprising implication now of (166): in order to have trajectories with positive stochastic entropy production, there must also be trajectories with a corresponding negative entropy production, even though the latter are exponentially unlikely compared to the former.

Finally we again note that in transitions between equilibrium states (temperature  $T$ ), one can identify the entropy with work via  $T\Delta_i s = w - \Delta F^{eq}$ , and obtain the famous Crooks' relation [36]:

$$(173) \quad \frac{P(w)}{\tilde{P}(-w)} = e^{\beta(w - \Delta F^{eq})}.$$

There are by now many illustrations of this beautiful relation. We cite in particular the early experimental verification for the work upon opening and closing of an RNA hairpin [37], the computer simulations of a Joule experiment of dragging a triangle through an ideal gas [38], and the thought experiment of a photon exchange between black bodies at equilibrium at a different temperature [39]. Note on the other hand that the verification of the above relation requires working on an energy scale of the order of  $k_B T$ .

## 5. – Perspectives

The above discussion is only the beginning of what can be done with trajectory thermodynamics [40, 41, 42, 43, 44, 45, 46, 47] see also [29, 48, 49, 50]. All the additional features and problems that we discussed at the ensemble level can be reconsidered at the trajectory level, in particular the splitting of the stochastic entropy into an adiabatic and a non-adiabatic component, the identification of a stochastic contribution for information processing, the discussion of various models, etc.. There are furthermore questions specific to the trajectory picture, notably the so called Feynman Kac formula [51], which in its origin considers functionals of Brownian motion, and shows how these are related to the solution of a differential equation (in particular the Schrodinger equation). The quantities we are dealing with here are functionals of more general Markov processes, but analogous techniques can be developed for this case. These results allow to rederive Onsager symmetry and beyond [52], to obtain the famous fluctuation dissipation theorem, linking response properties to equilibrium correlation functions, and beyond [53, 54, 55], and even to discuss response when perturbing a nonequilibrium steady state or even a general time-dependent reference state [56]. The fluctuation and work theorem have also

been proven in various other contexts, notably for microscopic classical and quantum Hamiltonian dynamics, for thermostated systems, and for non-Markovian processes. A lot of work has also gone into the study of the large deviation properties for trajectory dependent quantities in nonequilibrium steady states, such as the (heat or particle) fluxes to the reservoirs (since these are in principle more easily accessible). The best studied model in this context is probably the asymmetric exclusion model [57]. It may, at first sight, appear difficult to verify experimentally the predictions of trajectory thermodynamics. Yet a number of beautiful experiments have recently been carried out, in which a very good agreement is obtained with the theoretical predictions [37, 58, 59, 60, 61].

We end with a sweeping conclusion. Thermodynamics is probably the only branch of physics that has found applications in almost all fields of science. Providing a novel and extended framework for thermodynamics is therefore expected to have very productive and possibly also very deep implications. It remains to be seen how many of the above ideas presented above supersede the framework in which they were formulated. It is encouraging to see that the fluctuation theorems remain valid (with appropriate interpretation) for quantum and relativistic dynamics. Furthermore the quantum case raises very interesting new questions dealing with typical quantum features [62, 63, 64], such as interaction between system and reservoir, energy uncertainty principle, the measurement process, the quanta of transport, entanglement, Bell inequalities and quantum computation. It is also tempting to speculate that these new insights can be used profitably to make more efficient machines at the small scale. Many novel constructions for such thermal engines and refrigerators have indeed recently been proposed in the literature.

## REFERENCES

- [1] CALLEN H.B., *Thermodynamics and an Introduction to Thermostatistics*, (Wiley) 1985.
- [2] KONDEPUDI D. and PRIGOGINE I., *Modern thermodynamics*, (Wiley) 1998.
- [3] DE GROOT S. R. and MAZUR P., *Non-equilibrium thermodynamics*, (Dover) 1984.
- [4] FERMI E., *Thermodynamics*, (Dover) 1956.
- [5] VAN KAMPEN N.G., *Stochastic processes in physics and chemistry*, (Elsevier) 2007.
- [6] COVER T. M. and THOMAS J. A., *Elements of information theory*, (Wiley) 2006.
- [7] ESPOSITO M., LINDENBERG K. and VAN DEN BROECK C., *EPL*, **85** (2009) 60010.
- [8] VAN DEN BROECK C., *Phys. Rev. Lett.*, **95** (2005) 190602.
- [9] ESPOSITO M., KAWAI R., LINDENBERG K. and VAN DEN BROECK C., *Phys. Rev. Lett.*, **102** (2009) 130602.
- [10] LANDAUER R., *IBM Journal of Research and Development*, **5** (1961) 183.
- [11] ESPOSITO M. and VAN DEN BROECK C., *EPL*, **95** (2011) 40004.
- [12] VAN DEN BROECK C., *Nature Physics*, **6** (2010) 937.
- [13] ESPOSITO M., KUMAR N., LINDENBERG K. and VAN DEN BROECK C., *Phys. Rev.E*, **85** (2012) 031117.
- [14] CLEUREN B., RUTTEN B. and VAN DEN BROECK C., *Phys. Rev. Lett.*, **108** (2012) 120603.
- [15] RUTTEN B., ESPOSITO M. and CLEUREN B., *Phys. Rev.B*, **80** (2009) 235122.
- [16] CLEUREN B., RUTTEN B. and VAN DEN BROECK C., *Phys. Rev. Lett.*, **108** (2012) 120603.
- [17] ESPOSITO M. and SCHALLER G., *EPL*, (2012) .
- [18] GASPARD P., *J. Stat. Phys.*, **117** (2004) 599.
- [19] LUO J.L. VAN DEN BROECK, C. and NICOLIS, G., *Z. Phys. B*, **56** (1984) 165.
- [20] OONO Y. and PANICONI M., *Prog. Theor. Phys. Suppl.*, **130** (1998) 29.
- [21] SEKIMOTO K., *Prog. Theor. Phys. Suppl.*, **130** (1998) 17.
- [22] PARRONDO J.M.R. and ESPAGNOL P., *Am. J. Phys.*, **64** (1996) 1125.
- [23] HATANO T. and SASA S. I., *Phys. Rev. Lett.*, **86** (2001) 3463.
- [24] KLEIN M. J. AND MEIJER P.H.E., *Phys. Rev.*, **96** (1954) 250.

- [25] SCHNAKENBERG, *Rev. Mod. Phys.*, **48** (1976) 571.
- [26] VAN DEN BROECK C., *Selforganization by Nonlinear Irreversible Processes*, (Springer) 1986.
- [27] VAN DEN BROECK C. and ESPOSITO M., *Phys. Rev. E*, **82** (2010) 011144.
- [28] SEKIMOTO K., *Stochastic Energetics*, (Springer) 2010.
- [29] SEIFERT U., *Eur. Phys. J. B*, **64** (2008) 423.
- [30] SEIFERT U., *Phys. Rev. Lett.*, **95** (2005) 040602.
- [31] CROOKS G. E., *Excursions in statistical dynamics*, (Ph.D. thesis, University of California, Berkeley) 1999.
- [32] JARZYNSKI C., *Phys. Rev. Lett.*, **78** (1997) 2690.
- [33] JARZYNSKI C., *J. Stat. Phys.*, **96** (1999) 415.
- [34] LEBOWITZ J. L. and SPOHN H., *J. Stat. Phys.*, **95** (1999) 333.
- [35] PELITI L., *Phys. Rev. Lett.*, **101** (2008) 098903.
- [36] CROOKS G. E., *Phys. Rev. E*, **61** (2000) 2361.
- [37] BUSTAMANTE C., LIPHARDT J. and RITORT F., *Physics Today*, **58** (2005) 43.
- [38] CLEUREN B., VAN DEN BROECK C. and KAWAI R., *Phys. Rev. Lett.*, **96** (2006) 050601.
- [39] CLEUREN B. and VAN DEN BROECK C., *EPL*, **79** (2007) 30001.
- [40] BOCHKOV G. N. and KUZOVLEV Y. E., *Physica A*, **106** (1981) 443.
- [41] EVANS D.J., COHEN E.G.D. and MORRIS G.P., *Physical Review Letters*, **71** (1993) 2401.
- [42] GALLAVOTTI G. and COHEN E. G. D., *Phys. Rev. Lett.*, **74** (1995) 2694 .
- [43] MAES C., *J. Stat. Phys.*, **95** (1999) 367.
- [44] KURCHAN J., *J. Phys. A*, **31** (1998) 3719.
- [45] RITORT F., *Semin. Poincare*, **2** (2003) 195.
- [46] KAWAI R., PARRONDO J.M.R. and VAN DEN BROECK C., *Phys. Rev. Lett.*, **98** (2007) 080602.
- [47] ESPOSITO M. and VAN DEN BROECK C., *Phys. Rev. Lett.*, **104** (2010) 090601.
- [48] VAN DEN BROECK C., *J. Stat. Phys.*, (2010) P10009.
- [49] CHERNYAK V.Y., CHERTKOV M. and JARZYNSKI C., *J. Stat. Mech.*, (2006) P08001.
- [50] HARRIS R. J. and SCHUTZ G. M., *J. Stat. Mech.*, (2007) P07020.
- [51] HUMMER G. and SZABO A., *Proc Natl Acad Sci*, **98** (2001) 3658.
- [52] ANDRIEUX D. and GASPARD P., *J. Stat. Phys.*, **127** (2007) 107.
- [53] PROST J., JOANNY J.F. and PARRONDO J.M.R., *Phys. Rev. Lett.*, **103** (2009) 090601.
- [54] BAIESI M., MAES C. and WYNANTS B., *Phys. Rev. Lett.*, **103** (2009) 010602.
- [55] SEIFERT U. and SPECK T., *EPL*, **89** (2010) 10007.
- [56] VERLEY G., CHETRITE R. and LACOSTE D., *Phys. Rev. Lett.*, **108** (2012) 120601.
- [57] BODINEAU Y. and DERRIDA B., *J. Stat. Phys.*, **123** (2006) 277.
- [58] SPECK T., BLICKLE V., BECHINGER C. and SEIFERT U., *EPL*, **79** (2007) 30002.
- [59] TOYABE S., SAGAWA T., UEDA M., MUNAYUKI E. and SANO M., *Nature Physics*, **6** (2010) 988.
- [60] BRUT A., ARAKELYAN A., PETROSYAN A., CILIBERTO S., DILLENSCHNEIDER R. and ERIC LUTZ, *Nature*, **483** (2012) 187.
- [61] BECHINGER C. and BLICKLE V., *Nature Physics*, **8** (2012) 143.
- [62] MARUYAMA K., NORI F. and VEDRAL V., *Rev. Mod. Phys.*, **81** (2009) 1.
- [63] ESPOSITO M., HARBOLA U. and MUKAMEL S., *Rev. Mod. Phys.*, **81** (2009) 1665.
- [64] CAMPISI M., HANGGI P. and TALKNER P., *Rev. Mod. Phys.*, **83** (2011) 771.