ELSEVIER

Physica A 305 (2002) 445–466

PHYSICA A

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Entropy, extropy and information potential in stochastic systems far from equilibrium

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Received 28 May 2001

Abstract

The relations between information, entropy and energy, which are well known in equilibrium thermodynamics, are not clear far from equilibrium. Moreover, the usual expression of the classical thermodynamic potentials is only valid near equilibrium. In previous publications, we showed for a chemical system maintained far from equilibrium, that a new thermodynamic potential, the information potential, can be defined by using the stochastic formalism of the Master Equation. Here, we extend this theory to a completely general discrete stochastic system. For this purpose, we use the concept of extropy, which is defined in classical thermodynamics as the total entropy produced in a system and in the reservoirs during their equilibration. We show that the statistical equivalent of the thermodynamic extropy is the relative information. If a coarse-grained description by means of the thermodynamic extensive variables is available (which is the case for many macroscopic systems) the coarse-grained statistical extropy allows one to define the information potential in the thermodynamic limit. Using this potential, we study the evolution of such systems towards a non-equilibrium stationary state. We derive a general thermodynamic inequality between energy dissipation and information dissipation, which sharpens the law of the maximum available work for non-equilibrium systems. © 2002 Published by Elsevier Science B.V.

1. Introduction

The relations existing between information, entropy and energy are well known in equilibrium thermodynamics and in the corresponding stochastic systems [1], thanks

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[1] Partially supported by the National Scientific Research Program, Hungary, no. T025475.

PII: S0378-4371(01)00502-7

to the information definition of entropy [2]—although different definitions of entropy have been given [3], and their comparison remains a matter of discussion [3,4]. In fact, near equilibrium, the classical thermodynamic potentials provide convenient tools for studying the system evolution, energy dissipation and entropy production. However, the usual expressions of these potentials in terms of macroscopic variables break down far from equilibrium. Since most phenomena of theoretical and practical importance correspond to non-equilibrium situations, much work has been devoted to extending the thermodynamic definitions and to studying the behavior of entropy far from equilibrium [1,5–8]. In previous publications [9], we addressed these important questions in the specific case of chemical systems maintained far from equilibrium by external constraints. In particular, we showed that a new thermodynamic potential, called information potential, can be defined for them using the stochastic formalism of the Master Equation and its Hamilton–Jacobi approximation. This information potential allows one to study the evolution towards a non-equilibrium stationary state, and yield interesting comparisons between energy and information dissipations.

In the present article, our main purpose is to extend this method and to define the information potential in the general case of a system whose microscopic evolution is described by a jump process. In order to define the thermodynamic quantities far from equilibrium, we assume that in a mesoscopic, coarse-grained description, the system can be characterized by stochastic, extensive variables obeying a Master Equation. This method, however, makes necessary to define the information content of the system properly both on the microscopic and mesoscopic scales, and to relate it to thermodynamic quantities. This will be done by using the relative information and its physical counterpart, the statistical extropy of a stochastic system.

Relative information, which is just the negative of Kullback entropy [3], plays an important role in studying the evolution of non-isolated systems towards a stationary distribution [3–8]. However, its physical meaning is not completely clear for open systems maintained far from equilibrium by external constraints that are frequently considered in physico-chemistry. For this reason, we prefer to use the concept of extropy, which is defined [10,11] as the total entropy produced by the system and the reservoirs when they evolve up to equilibrium. This quantity is mainly used in thermodynamics and in mathematical economics. It is clearly related to other thermodynamic potentials, such as free energy, but it is more general since, for instance, it does not give a special role to energy, and does not supposes the existence of a temperature. We shall show that relative information can be interpreted as statistical extropy, and that it is possible to relate the statistical extropy of a microscopic system to the similar quantity in a coarse-grained description, and to the thermodynamic extropy. This method will allow the general definition of the information potential [9,12]. In particular, thanks to the information potential, it will be proved that the rate of energy dissipation is always larger than the rate of information dissipation (up to temperature) during the evolution to a non-equilibrium stationary state.

In the next section, we define and study statistical extropy, and we compare it with thermodynamic extropy, especially for systems in quasi-equilibrium. The third and main section of this paper addresses the case of open systems maintained out of equilibrium by external constraints. The information potential of such systems is defined in relation to statistical extropy. Its main properties are studied in a general way: they imply that the information potential is a thermodynamic potential appropriate for studying far from equilibrium systems.

2. Relative information and statistical extropy

This section summarizes some well known results concerning entropy and related quantities that were obtained or discussed by a number of authors [1,3–8]. It also emphazises the similarities and differences between the statistical, or microscopic, and the thermodynamic, or macroscopic points of views, which is necessary for Section 3.

2.1. Relative information of a stochastic system

Let us consider a discrete stochastic system. Its states are denoted by $\{i\}_{i=1,\dots,N}$. We will call these states "microscopic states", or "microstates", although they are not necessarily the ultimate description of matter: they just represent the most detailed description of the system which is available in the frame of a given study. Let $p_i(t)$ be the probability to find it in state i at time t. We assume that $p_i(t)$ satisfies the Master Equation:

$$\frac{\mathrm{d}}{\mathrm{d}t} p_i = \sum_{i'} (W_{ii'} p_{i'} - W_{i'i} p_i) \equiv \boldsymbol{L}(\{p_i\}) , \tag{1}$$

where $W_{ii'}$ is the transition rate for jumping from i' to i. It is independent of t for a time homogeneous process, which will be assumed from now on. Following Shannon [2] we define the information entropy $S(\{p_i\})$ by

$$S(\{p_i\}) = -\sum_i p_i \ln p_i . \tag{2}$$

According to Shannon, $-\ln p_i$ is the amount of information gained when the system is observed in state i, if the a priori probability of i is p_i. Thus, $\ln p_i$ measures the disorder associated to state i by the distribution $\{p_i\}$, and $S(\{p_i\})$ is the average disorder of $\{p_i\}$.

If the states i are actually microscopic in the physical sense, $S(\{p_i\})$ is generally considered [4] to be equal (up to the Boltzmann factor, which will be taken equal to 1) to the thermodynamic entropy when the system is in thermodynamic equilibrium. The same assumption is made if the system is in a quasi-equilibrium state such that the macroscopic properties of the system are completely described by the macroscopic values of the thermodynamic variables. It is an important question to know if this property is conserved when the states i are not physically microscopic, but result from some coarse-grained description. This point will be partially addressed below, although its complete discussion remains outside the scope of the present paper.

We now consider two probability distributions $\{p_i\}$ and $\{q_i\}$ obeying the Master Equation (1). Let us define the *relative information* of $\{p_i\}$ with respect to $\{q_i\}$ as

$$S(\{p_i\}/\{q_i\}) = \sum_i p_i \ln p_i/q_i \tag{3}$$

$S(\{p_i\}/\{q_i\})$, which is just the opposite of the relative entropy, or Kullback entropy [3], is the average disorder created by replacing $\{p_i\}$ by $\{q_i\}$, the average being taken on the initial distribution. It is also the average information lost when $\{p_i\}$ is replaced by $\{q_i\}$.

It is remarkable and well known [3,4,7–9,13] that this relative information is a non-negative, non-increasing function of time for the evolution defined by the Master Equation (1)

$$\begin{aligned} &S(\{p_i\}/\{q_i\}) \geqslant 0\,, \\ &\frac{\mathrm{d}}{\mathrm{d}t} S(\{p_i\}/\{q_i\}) \leqslant 0 \end{aligned} \tag{4}$$

the equality holding, in both cases, if and only if $p_i = q_i$ for any i (with the condition, for the second inequality, that the system is irreducible: any state i can be reached from any other state in a finite number of jumps). Thanks to these properties, relative entropy or relative information have been used in many articles [4–8,14,15] to study the asymptotic evolution of stochastic systems for large times. We shall assume now on that the Master Equation (1) is *irreducible*, which implies that there is one unique stationary distribution $\{p_i^0\}$. Then, inequalities (4) hold, in particular, if $\{q_i\}$ is this stationary distribution, and any solution of the Master Equation tends asymptotically to $\{p_i^0\}$.

The relative information $S(\{p_i\}/\{p_i^0\})$ can be considered as *the effective information contained in distribution* $\{p_i\}$. In fact, the stationary distribution $\{p_i^0\}$, which is asymptotically realized for any initial configuration of the system, can be taken as the lowest possible level of information. Then $\ln p_i/p_i^0$ is the information gained when we learn that the probability of state i is p_i, and $S(\{p_i\}/\{p_i^0\})$ is the average information obtained when we know that the actual probability distribution is $\{p_i\}$, rather than the standard, stationary distribution $\{p_i^0\}$. In the next section, it is shown that if $\{p_i^0\}$ is an equilibrium distribution, the relative information $S(\{p_i\}/\{p_i^0\})$ is the microscopic counterpart of the thermodynamic extropy, as remarked by different authors [4,7–9,13].

2.2. Equilibrium system and statistical extropy

Let us assume that a homogeneous system is in contact with reservoirs, exchanging with them the extensive quantities X_α, $\alpha = 0, 1, \ldots, n$. Then, its equilibrium distribution is $\{p_i^e\}$

$$p_i^e = \frac{1}{Z^e} \exp\left(-\sum_\alpha \gamma_\alpha^R X_{ai}\right)\,. \tag{5}$$

Here γ_α^R is the reservoir intensive variable corresponding to the extensive quantity X_α, and $X_{\alpha i}$ is the value of the extensive quantity X_α of the system when it is in state i (in general, state i is not completely defined by the $\{X_{\alpha i}\}$, and many states may correspond to the same values $\{X_{\alpha i}\}$). The partition function Z^e, which is defined from the normalization of $\{p_i^e\}$, is a function of $\{\gamma_\alpha^R\}$.

The thermodynamic quantities are connected to the statistical description of the system by classical relations. The macroscopic value of X_α is its average $\langle X_\alpha\rangle$, which is, at equilibrium

$$\langle X_\alpha\rangle^e = -\frac{\partial \ln Z^e}{\partial \gamma_\alpha^R} \,. \tag{6}$$

If the energy E plays a special role for the system under study, we give it the label 0 among the extensive variables X_α: $E = X_0$, and $T^R = l/\gamma_0^R$ is the reservoir temperature. Then the non-equilibrium (generalized) free energy F can be defined as

$$F = \langle E\rangle - T^R S + \sum_{\alpha>0} T^R \gamma_\alpha^R \langle X_\alpha\rangle \tag{7}$$

and its equilibrium value F^e is

$$F^e = -T^R \ln Z^e \,. \tag{8}$$

The second principle implies that the maximum work that can be produced by the system during its evolution to equilibrium is the opposite of the corresponding variation of F. The relations between energy and entropy, which are evoked by this result, were the object of deep discussions by a number of authors [4–8]. However, energy is not necessarily defined for the systems considered here, and rather than the variation of F, we shall generally prefer using the variation of S, which is extropy.

In fact, the thermodynamic extropy Π is [10,11] the total entropy produced by the system and the reservoirs when they evolve up to equilibrium. The initial macroscopic state of the system is characterized by the respective values γ_α and $\langle X_\alpha\rangle$ of its intensive and extensive variables α. The thermodynamic equilibrium is determined by the reservoir intensive variables γ_α^R, and it is shown [10] that the thermodynamic extropy is in the quasi-equilibrium approximation (see Section 2.3.)

$$\Pi = \sum_\alpha (\gamma_\alpha^R - \gamma_\alpha)\langle X_\alpha\rangle \,. \tag{9}$$

In similarity with the definition of thermodynamic extropy, the *statistical, or microscopic extropy* $\Pi(\{p_i\}/\{p_i^e\})$ can be defined as the total entropy change of the system and of the reservoirs when the system distribution evolves from $\{p_i\}$ to the equilibrium distribution $\{p_i^e\}$

$$\Pi(\{p_i\}/\{p_i^e\}) = -\sum_i p_i^e \ln p_i^e + \sum_i p_i \ln p_i + \sum_\alpha \gamma_\alpha^R (\langle X_\alpha^R\rangle^e - \langle X_\alpha^R\rangle) \,. \tag{10}$$

The last sum in the right-hand side of (10) is the entropy change of the reservoirs, $\langle X_\alpha^R \rangle^e$ and $\langle X_\alpha^R \rangle$ being, respectively, the equilibrium and initial average values of X_α in the reservoir. According to the definition of a thermodynamic reservoir, the intensive quantities γ_α^R are maintained to fixed values for any evolution of the reservoirs.

In this section, we assume that all extensive quantities X_α are conservative, i.e., for all α the total value of X_α in the system and in the reservoirs is constant during the exchanges, so that

$$\langle X_\alpha^R \rangle^e - \langle X_\alpha^R \rangle = \langle X_\alpha \rangle - \langle X_\alpha \rangle^e \, . \tag{11}$$

Using expression (5) of p_i^e and the previous conservation laws, we get

$$\begin{aligned} \Pi(\{p_i\})/\{p_i^e\}) &= \ln Z^e + \sum_\alpha \gamma_\alpha^R \langle X_\alpha \rangle + \sum_i p_i \ln p_i \\ &= \sum_i p_i \ln p_i/p_i^e = S(\{p_i\}/\{p_i^e\}) \, . \end{aligned} \tag{12}$$

Thus, the statistical extropy $\Pi(\{p_i\}/\{p_i^e\})$ is the relative information of $\{p_i\}$ with respect to $\{p_i^e\}$, i.e., it is the effective information of the initial distribution $\{p_i\}$, according to the final remark of Section 2.1. It remains to connect it with thermodynamic, macroscopic extropy.

2.3. *Statistical interpretation of thermodynamic extropy*

An important difference between thermodynamic and statistical extropies is that the latter one is defined for any initial distribution $\{p_i\}$, whereas thermodynamic extropy only makes sense if the initial state is completely determined by the non-equilibrium values of the macroscopic variables $\langle X_\alpha \rangle$, at least for a homogeneous medium. In practice, this condition is often approximately realized, and this justifies the use of non-equilibrium classical thermodynamics for many systems. The macroscopic variables of these systems evolve very slowly compared with the microscopic degrees of freedom, so that at any time t, the distribution $\{p_i\}$ is practically the quasi-equilibrium distribution $\{p_i^*\}$ corresponding to the average values $\langle X_\alpha \rangle(t)$ at time t: this is the adiabatic, or *quasi-equilibrium approximation*. The distribution $\{p_i^*\}$ maximizes the entropy, or minimizes the relative entropy, under the constraints of given values $\langle X_\alpha \rangle(t)$. Then the instantaneous intensive variables $\gamma_\alpha(t)$ of the system can be defined as the Lagrange multipliers corresponding to these constraints, and we have

$$p_i^*(t) = \frac{1}{Z(t)} \exp\left(- \sum_\alpha \gamma_\alpha(t) X_{\alpha i} \right) \tag{13}$$

$Z(t) = Z(\{\gamma_\alpha(t)\})$ being determined by the normalization of $\{p_i^*\}$, and $\{\gamma_\alpha(t)\}$ by

$$\langle X_\alpha \rangle(t) = -\frac{\partial}{\partial \gamma_\alpha} \ln Z_\alpha(t) \, . \tag{14}$$

We now show that the thermodynamic extropy Π coincides with the statistical extropy when the quasi-equilibrium approximation applies

$$\Pi = \Pi(\{p_i^*\}/\{p_i^e\}) \equiv S(\{p_i^*\}/\{p_i^e\}) . \tag{15}$$

As a matter of fact, inserting (13) into (12) yields

$$S(\{p_i^*\}/\{p_i^e\}) = \ln Z^e - \ln Z + \sum_\alpha (\gamma_\alpha^R - \gamma_\alpha)\langle X_\alpha \rangle . \tag{16}$$

Now, if the set of extensive variables $\{X_\alpha\}$ is *complete* in the sense that the set of accessible states i of the system is completely defined by the $\{X_\alpha\}$, $\ln Z$ can be expressed in terms of the intensive variables only. Since it should also be an extensive quantity, it should vanish and we obtain

$$S(\{p_i^*\}/\{p_i^e\}) = \sum_\alpha (\gamma_\alpha^R - \gamma_\alpha)\langle X_\alpha \rangle \tag{17}$$

which is the thermodynamic extropy Π as given by (9).

In principle, the previous considerations should only apply for systems that remain homogeneous during all their evolution, which would strongly limit their validity. However, it will be seen in Section 2.5 that they can be extended to inhomogeneous systems in the frame of the local equilibrium approximation.

2.4. General comparison of statistical and thermodynamic extropies

Let us now consider a non-equilibrium distribution $\{p_i(t)\}$ and the quasi-equilibrium distribution $\{p_i^*(t)\}$ corresponding to *the same average values* $\langle X_\alpha \rangle(t)$ as $\{p_i(t)\}$, given by expression (12). The difference between the statistical and thermodynamic extropies is

$$S(\{p_i\}/\{p_i^e\}) - S(\{p_i^*\}/\{p_i^e\}) = -\sum_i p_i \ln \frac{p_i^*}{p_i} + \sum_i (p_i - p_i^*) \ln \frac{p_i^*}{p_i^e} . \tag{18}$$

However, the last sum in the right-hand side of (18) vanishes [10] because $\langle X^\alpha \rangle$ has the same value when it is computed with $\{p_i(t)\}$ and with $\{p_i^*(t)\}$. Then

$$S(\{p_i\}/\{p_i^e\}) - S(\{p_i^*\}/\{p_i^e\}) = -\sum_i p_i \ln \frac{p_i^*}{p_i} \geqslant 0 \tag{19}$$

the equality holding only if $p_i = p_i^*$ for all i. Thus, the statistical extropy is always larger than the thermodynamic extropy, except if the quasi-equilibrium distribution is exactly realized: then, statistical and thermodynamic extropies coincide, but this is generally not true.

Now, in order that the adiabatic approximation be valid during the whole approach to equilibrium (except, perhaps, during a transitory regime) it is necessary that $\{p_i^*(t)\}$ be an approximate solution of the Master Equation (7). As a consequence, according to properties (4) of relative information, we have (at least approximately)

$$-\frac{\mathrm{d}}{\mathrm{d}t} S(\{p_i^*\}/\{p_i^e\}) \geqslant 0 . \tag{20}$$

Furthermore, it can be shown that under appropriate assumptions the rate of statistical entropy production is always larger than the rate of thermodynamic entropy production

$$-\frac{\mathrm{d}}{\mathrm{d}t}S(\{p_i\}/\{p_i^e\}) \geqslant -\frac{\mathrm{d}}{\mathrm{d}t}S(\{p_i^*\}/\{p_i^e\}) \geqslant 0 . \tag{21}$$

Relations (20) and (21) seem quite reasonable, since the quasi-equilibrium distribution clearly contains less information, and fewer sources of disorder than the exact, non-equilibrium distribution. However, inequalities (21) are not straightforward consequences of our basic equations, because their validity requires non-trivial assumptions that will be discussed elsewhere. Similar inequalities will be derived in Section 3 when the system is described by means of its extensive variables, which represents another case of reducing the information contents in its description.

2.5. Inhomogeneous systems

In the case of an inhomogeneous, spatially extended system, we assume that it is divided into N cells, and the values of the macroscopic variables are given *in each cell*. The cells are chosen to be much smaller than the total system, in order to be approximately homogeneous, but still large enough to be considered as macroscopic. Each extensive quantity in each cell can be exchanged with other cells and with the reservoir, the total value of an extensive quantity being the sum of the values in each cell and in the reservoirs. For energy, if defined, this assumption implies that the energy interactions between cells can be neglected, as it is usually admitted in the multivariate Master Equation describing reaction–diffusion systems [1]. It is convenient to consider that a macroscopic variable has different labels for different cells. We will adopt this convention from now on.

With the previous conventions, the adiabatic approximation described in Section 2.3 corresponds to the *local equilibrium hypothesis* [1,16]. This widely used hypothesis considers that each cell is at a thermodynamic equilibrium, even if it is not equilibrated with the other cells. Then, all cells are homogeneous but the intensive variables can have different values in different cells. In these conditions, most of the foregoing formulas hold, provided that at equilibrium each intensive variable corresponding to a given physical quantity has the same value in all cells.

The local equilibrium approximation, introduced by Jaynes [16], does not take into account time correlations [16–18], which may be important on a molecular time scale. Nevertheless, it can be used on a macroscopic time scale [7] in many cases of great practical importance. In particular, it is currently adopted as a first approximation in the kinetic theory of gases or in mechanics of continuous media. A similar but more general hypothesis will allow us to extend the previous interpretation of relative information to systems which can be described (at least approximately) in terms of stochastic thermodynamic variables, when they are submitted to constraints that prevent them to reach an equilibrium state. This is the purpose of next section.

3. Non-equilibrium stationary state

3.1. Detailed balance

Let us assume that the distribution $\{p_i^e(t)\}$ is *an equilibrium solution* of the Master Equation (1). As it was shown [15],[2] this implies that all possible processes given by the transition rates $W_{i'i}$ should be equilibrated, which is the well-known detailed balance condition

$$W_{i'i}\, p_i^e = W_{ii'}\, p_{i'}^e \,. \tag{22}$$

This dynamic definition of equilibrium implies stationarity, but it is obviously much stronger. It is generally admitted, on the basis of the microscopic time reversibility of physical laws, that detailed balance holds for elementary physical processes. However, it imposes strong requirements on the transition rates, which may not be satisfied for stochastic processes representing complex phenomena. In this case, the stationary distribution $\{p_i^0\}$ is a *non-equilibrium stationary distribution*. Such a non-equilibrium stationary distribution can also exist in open physical systems, maintained far from their natural equilibrium state by constraints imposed by the environment. We will now study such systems, for which our previous calculations in general do not hold.

3.2. General interpretation of non-equilibrium relative information

The relative information, $S(\{p_i\}/\{p_i^0\})$ can be defined for any stationary distribution $\{p_i^0\}$, and it is a positive, decreasing function of time according to the general inequalities (4). It results from Section 2 that $S(\{p_i\}/\{p_i^e\})$ is the statistical extropy of the system if $\{p_i^0\}$ is the equilibrium distribution $\{p_i^e\}$ given by expression (5). Now, if we consider *a non-equilibrium stationary distribution* $\{p_i^0\}$ the derivation of Section 2.2 does not apply any more. However, it is shown in Appendix A that if the reservoirs are supposed to remain in a quasi-equilibrium state when the system evolves, the non-equilibrium relative information $S(\{p_i\}/\{p_i^0\})$ again coincides with the statistical extropy $\Pi(\{p_i\}/\{p_i^0\})$ of the system, i.e., it is the total entropy produced during the evolution towards the stationary state

$$\Pi(\{p_i\}/\{p_i^0\}) = S(\{p_i\}/\{p_i^0\})\,. \tag{23}$$

The quasi-equilibrium hypothesis for the reservoirs, commented in Appendix A, assumes that the internal equilibrium of the reservoirs is established very rapidly in comparison with the characteristic evolution time of the system. This assumption will be adopted here, as it is currently made in thermodynamics. It should be pointed out that, contrarily to the simple calculations of Section 2.2, the derivation of Eq. (23) presented in Appendix A does not suppose that the extensive quantities are conservative.

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[2] See also Ref. [15] (J. Math. Phys. 39 (1998) 1517) for application to non-equilibrium first order transitions.

3.3. Master equation in terms of macroscopic variables

In practice, it is only possible to observe the macrovariables X_α, rather than the microscopic states i. Thus one should study the "coarse-grained" probabilities

$$p(\boldsymbol{x},t) = \sum_{X_i=\boldsymbol{x}} p_i(t)\,, \tag{24}$$

where $\boldsymbol{x} = x_0, x_1, \ldots, x_N$ represent given values of the macrovariables. It was already pointed out that $\boldsymbol{x}$ generally does not determine a microscopic state completely. Thus, in Eq. (24) the sum runs on all microstates i such that the corresponding macroscopic variables X_i have the value $\boldsymbol{x}$.

It is known that, in general, the stochastic process $\boldsymbol{x}$ is not Markovian [19]. However, it can happen that $p(\boldsymbol{x},t)$ satisfies a new Master Equation that will be called *the coarse-grained Master Equation*

$$\frac{\mathrm{d}}{\mathrm{d}t} p(\boldsymbol{x}) = \sum_{\boldsymbol{x}'} [w(\boldsymbol{x}/\boldsymbol{x}')p(\boldsymbol{x}') - w(\boldsymbol{x}'/\boldsymbol{x})p(\boldsymbol{x})]\,, \tag{25}$$

where $w(\boldsymbol{x}'/\boldsymbol{x})$ is the "coarse-grained" transition rate from $\boldsymbol{x}'$ to $\boldsymbol{x}$.

Such a coarse-grained Master Equation only holds in special circumstances. It is of great interest to study the conditions which ensure its validity, and to relate the coarse-grained Master Equation to the microscopic Master Equation: in this case only the description of the system in term of the macrovariables $\boldsymbol{x}$ is self-consistent and can be really useful. However, we will not address this problem here (see e.g. Refs. [17–22] for discussion). From now on, we suppose that the coarse-grained Master Equation (25) is at least approximately valid. Equivalent hypotheses are currently made for the stochastic descriptions in terms of macrovariables (see for instance Ref. [1]).

Furthermore, if (1) admits a stationary solution p_i^0, we suppose that the coarse-grained Master Equation (25) has the stationary solution $p^0(\boldsymbol{x})$

$$p^0(\boldsymbol{x}) = \sum_{X_i=x} p^0 i\,. \tag{26}$$

Let us first consider the case when $p_i(\boldsymbol{x},t)$ tends to the equilibrium solution (12). Then $p(\boldsymbol{x})$ tends to

$$p^e(\boldsymbol{x}) = \frac{\Gamma(\boldsymbol{x})}{Z^e} \exp\left(-\sum_\alpha \gamma_\alpha^R x_\alpha\right) \tag{27}$$

$\Gamma(\boldsymbol{x})$ being the number of microstates corresponding to the same value of $\boldsymbol{x}$.

Using the *microcanonical entropy* $S(\boldsymbol{x}) = \ln\Gamma(\boldsymbol{x})$, defined for any value of $\boldsymbol{x}$, and the equilibrium entropy S^e obtained by applying expression (2) to the equilibrium distribution (12), we can define the *microcanonical extropy* $\Pi(\boldsymbol{x})$ in analogy with (10)

$$\Pi(\boldsymbol{x}) = S^e - S(\boldsymbol{x}) + \sum_\alpha \gamma_\alpha^R (x_\alpha - \langle x_\alpha\rangle^e)\,. \tag{28}$$

Then the equilibrium solution (27) can easily be written under the Einstein form

$$p^e(\boldsymbol{x}) = \exp(-\Pi(\boldsymbol{x})) \tag{29}$$

with $\Pi(\langle \boldsymbol{x}\rangle^e) \cong 0$. If energy exists, the microcanonical free energy $F(\boldsymbol{x})$ is defined in analogy with (7) and satisfies the relation

$$T^R \Pi(\boldsymbol{x}) = F(\boldsymbol{x}) - F^e\,.$$

This is the maximum work that the system can deliver when it returns to equilibrium, starting from an initial state characterized by the values $\boldsymbol{x} = \{x_\alpha\}$ of the extensive variables.

Further on, however, we shall consider systems which are maintained out of equilibrium by external constraints, assuming that Eq. (25) holds (at least approximately) and has a *non-equilibrium stationary solution* $\{p^0(\boldsymbol{x})\}$.

3.4. Quasi-stationary hypothesis, coarse-grained extropy

(i) *Conditional entropy.* We introduce the conditional probability

$$p_{i/\boldsymbol{x}} = p_i/p(\boldsymbol{x}) \quad \text{for } X_i = \boldsymbol{x} \tag{30}$$

and the conditional entropy

$$S(\{p_{i/\boldsymbol{x}}\}) = -\sum_{i, X_i = \boldsymbol{x}} p_{i/\boldsymbol{x}} \ln p_{i/\boldsymbol{x}}\,. \tag{31}$$

It is easily verified [2] that

$$S(\{p_i\}) = -\sum_{\boldsymbol{x}} p(\boldsymbol{x}) \ln p(\boldsymbol{x}) + \sum_{\boldsymbol{x}} p(\boldsymbol{x}) S(\{p_{i/\boldsymbol{x}}\})\,. \tag{32}$$

It will now be shown that under the quasi-stationary hypothesis, which is discussed below and holds in most practical cases, the entropy $S(\{p_i\})$ of the actual system is much larger than the similar coarse-grained quantity $-\sum_{\boldsymbol{x}} p(\boldsymbol{x}) \ln p(\boldsymbol{x})$, so that the second term in the right-hand side of Eq. (32) is predominating.

(ii) *Quasi-stationary hypothesis.* At equilibrium the conditional probability is by (27)

$$p^e_{i/\boldsymbol{x}} = 1/\Gamma(\boldsymbol{x})\,.$$

We will now assume that, even if the system is maintained out of equilibrium by external constraints, its conditional probability $p_{i/\boldsymbol{x}}$ tends to the same stationary value. Furthermore, we suppose that this relaxation *is much faster* than the relaxation of $p(\boldsymbol{x}, t)$ to $p^0(\boldsymbol{x}, t)$. We call these assumptions the *quasi-stationary hypothesis.*

The quasi-stationary hypothesis means that the external constraints can only temporarily affect the equiprobability of the microstates corresponding to a given $\boldsymbol{x}$, which holds at equilibrium. Clearly, it should be justified for each particular system using its specific description. However, it is reasonable if the system allows of a significant macroscopic, stochastic description. As a matter of fact, the macrovariables can be considered as *the slow variables of the system*: once all the macrovariables are determined, the definition of the microstate i is achieved by giving the values of internal microscopic variables whose evolution is much faster than the evolution of the macroscopic quantities. Then the uniform conditional distribution maximizes the conditional entropy for the given values of the macrovariables. Similar hypotheses are generally adopted in the thermodynamics of macroscopic systems, and they seem necessary for obtaining general conclusions from a stochastic description in term of macrovariables.

If $p(\boldsymbol{x},t)$ is a solution of the coarse-grained Master Equation (25), we can define another probability distribution $\{q_i\}$ on the microstates i by

$$q_i(t) = p(X_i,t)/\Gamma(X_i)\,. \tag{33}$$

This quasi-stationary hypothesis implies that, at large times, $\{q_i(t)\}$ is an approximate solution of the microscopic Master Equation. In particular, there is a non-equilibrium stationary distribution

$$p_i^0 = p^0(X_i)/\Gamma(X_i)\,. \tag{34}$$

Furthermore, in this hypothesis the conditional entropy $S(\{p_{i/\boldsymbol{x}}\})$ is approximately equal to the microcanonical entropy used in Section 3.3

$$S(\{p_{i/x}\}) \cong \ln \Gamma(\boldsymbol{x})$$

and the entropy of the microscopic system is

$$S(\{p_i\}) \cong -\sum_{\boldsymbol{x}} p(\boldsymbol{x}) \ln p(\boldsymbol{x}) + \sum_{\boldsymbol{x}} p(\boldsymbol{x}) \ln \Gamma(\boldsymbol{x}) \cong \sum_{\boldsymbol{x}} p(\boldsymbol{x}) \ln \Gamma(\boldsymbol{x})\,. \tag{35}$$

In fact, for a system of volume V with d variables x_α, the number of possible values of $\boldsymbol{x}$ is of order V^d and $-\sum_x p(\boldsymbol{x}) \ln p(\boldsymbol{x}) \leqslant \ln V^d$, whereas $\ln \Gamma(\boldsymbol{x})$ is generally of order V, so that the approximation (35) certainly holds for large volumes V. In case, the probability distribution p is sharply peaked on state $\boldsymbol{x}$, the entropy $S(\{p_i\})$ coincides with the microcanonical entropy $S(\boldsymbol{x})$, as it should be.

(iii) *Coarse-grained extropy*. We now introduce the "coarse-grained extropy", or "coarse-gained relative information"

$$\Pi(\{p(\boldsymbol{x})\}/\{p^0(\boldsymbol{x})\}) = S(\{p(\boldsymbol{x})\}/\{p^0(\boldsymbol{x})\}) \equiv \sum_x p(\boldsymbol{x}) \ln \frac{p(\boldsymbol{x})}{p^0(\boldsymbol{x})}\,. \tag{36}$$

As for Eq. (32), we can write

$$S(\{p_i\}/\{p_i^0\}) = S(\{p(\boldsymbol{x})\}/\{p^0(\boldsymbol{x})\}) + \sum \boldsymbol{x} p(\boldsymbol{x}) \sum_{i, X_i=\boldsymbol{x}} p_{i/x} \ln \frac{p_{i/x}}{p^0_{i/x}} \tag{37}$$

which shows that the microscopic extropy is larger than or equal to the coarse-grained extropy

$$S(\{p_i\}/\{p_i^0\}) \geqslant S(\{p(\boldsymbol{x})\}/\{p^0(\boldsymbol{x})\})\,. \tag{38}$$

Furthermore, it is shown in Appendix B.1 that the entropy production is larger in the microscopic description than in the coarse-grained description

$$-\frac{\mathrm{d}}{\mathrm{d}t} S(\{p_i\}/\{p_i^0\}) \geqslant -\frac{\mathrm{d}}{\mathrm{d}t} S(\{p(\boldsymbol{x})\}/\{p_i^0(\boldsymbol{x})\})\,. \tag{39}$$

If the quasi-equilibrium approximation holds, however, it is clear from (37) that both extropies are practically equal at large times. Thus, the coarse-grained extropy of the system is essentially the extropy of the microscopic system, whereas the "proper" entropy of the coarse-grained system $-\sum_{\boldsymbol{x}} p(\boldsymbol{x}) \ln p(\boldsymbol{x})$, being much smaller than the entropy of the actual, microscopic system, has no special interest in general.

These points are further discussed in Appendix B.

3.5. Large systems: thermodynamic approximation

We now consider that the size of the system is characterized by a parameter V, usually the volume (or the volume of each cell, in the multivariate formalism [1] defined in Section 2.5). Furthermore, we assume that the possible jumps result from local phenomena: the probability transitions are the sums of local probability transitions, each one concerning one geometrical point of the system and its neighborhood. These local transitions allow small jumps only, and depend on the local values of $\boldsymbol{x}$. Then it can be assumed [1,9,22,23] that the transition rates have the form

$$w(\boldsymbol{x}/\boldsymbol{x}') \cong V\widehat{w}(\boldsymbol{x}' - \boldsymbol{x}; \boldsymbol{x}/V) \tag{40}$$

$\hat{w}$ being some finite function of the jump $\boldsymbol{x}' - \boldsymbol{x}$ and of $\hat{\boldsymbol{x}} = \boldsymbol{x}/V$. This is clear if, for instance, $\hat{w}$ is the reaction rate in a chemical system described by the numbers of molecules $x_1, x_2, \dots, x_n$ of the different reactive species [1]. Then, x_α/V is the concentration of species α.

Following Kubo and other authors [22,23,9], we look for a probability distribution in the form

$$p(\boldsymbol{x}, t) \propto \exp(-V\Phi(\widehat{\boldsymbol{x}}, t)), \tag{41}$$

where Φ is some finite function of $\widehat{\boldsymbol{x}}, t$, so that for large V, the distribution is strongly peaked on the value $\widehat{\boldsymbol{x}}$ for which Φ vanishes, which should be the average $\langle\widehat{\boldsymbol{x}}\rangle = \langle\boldsymbol{x}\rangle/V$.

With this hypothesis, which is reasonable for most macroscopic systems and in particular for reaction–diffusion systems [1], it can easily be shown [23,9] that, in the large volume limit, Φ approximately satisfies the following Hamilton–Jacobi equation:

$$\frac{\partial}{\partial t}\Phi = \sum_{\boldsymbol{h}} \widehat{w}(\boldsymbol{h}; \widehat{\boldsymbol{x}}) \left(\exp\left(\boldsymbol{h} \cdot \frac{\partial \Phi}{\partial \widehat{\boldsymbol{x}}} \right) - 1 \right) \tag{42}$$

the neglected terms being of order $1/V$. Here, the x_α/V are considered as continuous variables. The summation is on all possible transition $\boldsymbol{h} = \boldsymbol{x}' - \boldsymbol{x}$ allowed in Eq. (40), and we use the vector notation

$$\boldsymbol{h} \cdot \frac{\partial \Phi}{\partial \widehat{\boldsymbol{x}}} = \sum_{\alpha} h_\alpha \frac{\partial \Phi}{\partial \widehat{\boldsymbol{x}}_\alpha} .$$

Eq. (42), in the multidimensional case, can be solved explicitly in a few exceptional examples only [13]. Nevertheless, it is very useful for studying the non-equilibrium thermodynamic properties of the system, as it will be seen below.

3.6. Information potential

Let us consider some possible value $\boldsymbol{a}$ of $\boldsymbol{x}$, and suppose that at some time t, the system is exactly in state $\boldsymbol{a}$:

$$p(\boldsymbol{x},t)=\delta_{\boldsymbol{x},\boldsymbol{a}}$$

δ being the Kronecker symbol. Then its statistical extropy is

$$S(\{\delta_{\boldsymbol{x},\boldsymbol{a}}\}/\{p^0(\boldsymbol{x})\})=\ln p^0(\boldsymbol{a}) \tag{43}$$

and we define the information potential of the system $\Phi^\circ(\widehat{\boldsymbol{a}})$ as [9]

$$\Phi^\circ(\widehat{\boldsymbol{a}})=\lim_{V\to\infty}-(\ln p^0(\boldsymbol{a}))/V\,, \tag{44}$$

where $\widehat{\boldsymbol{a}}=\boldsymbol{a}/V$. Then Φ° is the asymptotic value, for $t\to\infty$, of the function Φ defined in Section 3.5. Formula (44) shows that Φ° is, in the thermodynamic limit, the amount of information per unit volume lost when the system evolves from state $\widehat{\boldsymbol{a}}$ to its stationary distribution.

Φ° has the properties of a thermodynamic potential. In fact, Φ° is clearly non-negative. Furthermore, the information potential of a macroscopic system, computed at its time-dependent average state $\langle\widehat{\boldsymbol{x}}\rangle(t)$, decreases with time

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi^\circ(\langle\widehat{\boldsymbol{x}}\rangle(t))\leqslant 0\,. \tag{45}$$

This inequality is derived in Appendix B.2. However, it can be understood by remarking that for large V, the probability distribution of a macroscopic variable should be sharply peaked on the average state $\langle\boldsymbol{x}\rangle(t)$, so that $p(\langle\boldsymbol{x}\rangle(t))$ is of the order of 1, and

$$S(\{p(\boldsymbol{x},t)\}/\{p^0(\boldsymbol{x})\})\cong-\ln p^0(\langle\boldsymbol{x}\rangle(t))\equiv V\Phi^\circ(\langle\widehat{\boldsymbol{x}}\rangle(t))\,. \tag{46}$$

Thus, the information potential is just the coarse-grained extropy, per unit volume, in the large volume approximation. Since $p(\boldsymbol{x},t)$ is a solution of the Master Equation, the relative information decreases with t, as well as the information potential.

Because of inequality (45), the information potential can be considered as a new thermodynamic potential. As usual, it depends not only on the system, but also on its environment, this dependence being expressed by the parameters implicitly contained in the transition rates w.

3.7. System with constrained variables

We now consider the case of a system maintained out of equilibrium by external constraints on the macroscopic variables. More precisely, we assume that, apart from the free variables $\boldsymbol{x}$, the system depends on some variables $\{a_\beta\}_{\beta=1,\ldots,m}=\boldsymbol{a}$ which are maintained at constant values by a convenient external action. Although such a compensation of the natural evolution of a system is not easily realized exactly, it can be achieved approximately: for instance, in a chemical system the concentrations of some species can be kept constant by the reservoirs, as it was assumed by most authors for studying non-equilibrium reactive systems [1].

We also suppose that *if the constraints are relaxed*, the natural evolution of the system asymptotically reaches an equilibrium distribution $p^e(\boldsymbol{x},\boldsymbol{a})$. The reaction rates now depend not only on $\boldsymbol{x}$, but also on $\boldsymbol{a}$ and, according to the dynamic definition of equilibrium considered in Section 3.1, they satisfy the detailed balance relation

$$w(\boldsymbol{x}',\boldsymbol{a}'/\boldsymbol{x},\boldsymbol{a})p^e(\boldsymbol{x},\boldsymbol{a}) = w(\boldsymbol{x},\boldsymbol{a}/\boldsymbol{x}',\boldsymbol{a}')p^e(\boldsymbol{x}',\boldsymbol{a}') . \tag{47}$$

(Here, we consider that variables $\boldsymbol{x}$ and $\boldsymbol{a}$ are time reversal invariant. Eq. (47) would not hold if we would include fluxes among the variables, as is done in extended thermodynamics. In the quasi-stationary approximation we assume that this is not the necessary.)

In Kubo approximation, (47) becomes, with the notation of Section 3.5

$$\begin{aligned}&\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})\exp\left(-V\Phi^e(\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})\right)\\ &\quad=\widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}}+\boldsymbol{h}/V,\widehat{\boldsymbol{a}}+\boldsymbol{k}/V)\exp(-V\Phi^e(\widehat{\boldsymbol{x}}+\boldsymbol{h}/V,\widehat{\boldsymbol{a}}+\boldsymbol{k}/V)) ,\end{aligned} \tag{48}$$

where we expressed $p^e(\boldsymbol{x},\boldsymbol{a})$ in terms of Φ^e, the information potential *of the unconstrained system*

$$p^e(\boldsymbol{x},\boldsymbol{a}) \propto \exp[-V\Phi^e(\boldsymbol{x}/V,\boldsymbol{a}/V)] . \tag{49}$$

If we now submit the system to constraints which maintain the variables $\boldsymbol{a}$ constant, its non-equilibrium information potential Φ^0 can be defined according to the method of Section 3.6.

The following inequality is proved in Appendix B.

Let us call $-q$ the (algebraic) amount of entropy, or equivalently $+q$ the amount of information, which has to be provided to the system per unit time in order to maintain the variables $\boldsymbol{a}$ constant, against their "natural", unconstrained evolution. Then it can be shown that

$$-\frac{\mathrm{d}}{\mathrm{d}t}\Phi^e(\langle\widehat{\boldsymbol{x}}\rangle,\widehat{\boldsymbol{a}})+q \geqslant -\frac{\mathrm{d}}{\mathrm{d}t}\Phi^0(\langle\widehat{\boldsymbol{x}}\rangle) , \tag{50}$$

where $\langle\widehat{\boldsymbol{x}}\rangle(t)$ corresponds to the deterministic evolution of the constrained system.

Moreover, in (50) the equality only holds if at the macroscopic stationary state $\langle\widehat{\boldsymbol{x}}\rangle^0$ we have for all $\boldsymbol{h}$, $\boldsymbol{k}$

$$\widehat{w}(\boldsymbol{h},\boldsymbol{k};\langle\widehat{\boldsymbol{x}}\rangle^0,\widehat{\boldsymbol{a}}) = \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\langle\widehat{\boldsymbol{x}}\rangle^0,\widehat{\boldsymbol{a}}) \tag{51}$$

which is the macroscopic detailed balance relation.

Inequality (50) is remarkable. We already knew that $-\mathrm{d}\Phi^0(\langle\widehat{\boldsymbol{x}}\rangle)/\mathrm{d}t$, which is the rate of information dissipation inside the system, is positive, as well as the left-hand side of (50), which is the total rate of entropy creation due to the natural processes. Inequality (50) asserts that the rate of entropy creation is larger than the rate of information dissipation that can be observed inside the system, except if detailed balance holds at the stationary state: in this case only, both rates are equal. This can be related to the fact that, in general, a non-equilibrium stationary state can only be maintained by the action of appropriate "unnatural" mechanisms, which are not contained in the phenomena observable in the system itself, and contribute to create entropy.

When energy is a relevant macroscopic variable, an interesting, energetic form of inequality (50) can be given. As a matter of fact, if T^R is the temperature of the reservoirs, it is seen by comparing Eqs. (29) and (49) that $T^R \Phi^e(\widehat{\langle \boldsymbol{x} \rangle}) \equiv \Psi(\widehat{\langle \boldsymbol{x} \rangle})$ is the maximum work that can be extracted from the system by unit volume when returning to its equilibrium state if the constraints are relaxed. On the other hand $-T^R q$ is the energetic equivalent of q, i.e., the energy which has to be provided to the system per unit time and unit volume in order to maintain the variables $\boldsymbol{a}$ constant. Thus, $-\mathrm{d}\Psi^e(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t + T^R q$ is the rate of energy dissipation of the system, and (50) gives

$$-\,\mathrm{d}\Psi^e(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t + T^R q \geqslant -\,T^R \mathrm{d}\Phi^0(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t \geqslant 0 \tag{52}$$

which shows that the rate of energy dissipation is always larger than the rate of information dissipation, times T^R, except if the stationary state is an equilibrium state, in which case both rates are equal. Finally, this inequality can be written

$$\mathrm{d}\Psi(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t \leqslant T^R q + T^R \mathrm{d}\Phi^0(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t\,. \tag{53}$$

The second law of thermodynamics asserts that $\mathrm{d}\Psi(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t \leqslant T^R q$. Inequality (53) is stronger and implies that the maximum work $\mathrm{d}\Psi(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t$ produced by the system per unit time and unit volume is still smaller, since $\mathrm{d}\Phi^0(\widehat{\langle \boldsymbol{x} \rangle})/\mathrm{d}t \leqslant 0$.

The previous inequalities have been stated and discussed in detail [9,13] for the particular example of reaction–diffusion systems. Inequality (50) expresses that entropy production is smaller in the constrained system than in the complete system including the environment which imposes the constraints. In other cases (see Section 3.4 and Appendix B.2) we can conclude similarly that the entropy production of a system is smaller in a reduced description than in a more detailed one. Although this conclusion is not general and cannot be asserted without adequate hypotheses, it gives a reasonable interpretation to inequality (50)

4. Conclusion

We wanted to define the information potential and to study its properties in a general way. On this purpose, we had to clarify the role and the physical meaning of relative information, which plays a fundamental role in the asymptotic study of a stochastic system, in particular when it tends to a non-equilibrium stationary state. We have shown that relative information can be identified with the total entropy production during the process, which we called statistical extropy, in similarity with the definition of extropy used in irreversible thermodynamics.

In order to describe a system tending to a non-equilibrium stationary state due to external constraints, we have introduced a reduced stochastic description, in terms of the thermodynamic random variables. Under certain conditions, a reduced Master Equation can be written, and we have presented a detailed discussion of the corresponding, coarse-grained statistical extropy, which is smaller and decreases less rapidly than the similar microscopic quantities. This seems natural for a simplified description which does not consider all possible sources of disorder. Nevertheless, although it can be shown in a general way that the coarse-grained extropy is smaller than the microscopic extropy [3], this is not generally true for the corresponding entropy productions.

The coarse-grained stochastic description allowed to define the information potential. This new thermodynamic potential is time-decreasing and minimum at the macroscopic non-equilibrium stationary state, whereas the usual thermodynamic generalized free energy only has these properties if the system tends to an equilibrium stationary state. Furthermore, we have proved a general inequality between the rate of information dissipation in the system and the total rate of entropy creation. The same relation takes a more striking form in case energy is defined: the dissipation of energy is smaller than the dissipation of information (times temperature) in an open system maintained far from equilibrium by external constraints. This inequality, already obtained in the case of reaction–diffusion systems, turns out to be much more general. It is another example showing that coarse-graining tends to decrease the value of entropy production. Once more, however, such a conclusion does not hold for an any kind of reduced description, and it should be analyzed more completely. Such a study is in progress.

Acknowledgements

B.G. and M.M. thank L.S. Schulman for profitable discussions. K.M. thanks for the grants OTKA T26660 and T29542. M.M. and J.T. thank for the grant CNRS-HAS 6558.

Appendix A. Interpretation of non-equilibrium relative information

The interpretation of the relative information $(\{p_i\}/\{p_i^0\})$ as the total entropy change of the system and of the reservoir during the evolution to the stationary state, i.e., the statistical extropy $\Pi(\{p_i\}/\{p_i^0\})$, is only clear if $\{p_i^0\}$ is the *equilibrium distribution* $\{p_i^e\}$. In fact, according to Eq. (11)

$$\begin{aligned} S(\{p_i\}/\{p_i^e\}) &= \sum_i p_i \ln p_i/p_i^e \\ &= -\sum_i p_i^e \ln p_i^e + \sum_i p_i \ln p_i - \sum_\alpha \gamma_\alpha^R(\langle X_\alpha^e\rangle - \langle X_\alpha\rangle) \\ &= \Pi(\{p_i\}/\{p_i^e\}) \end{aligned} \tag{A.1}$$

since, if all extensive quantities are conserved in the exchanges with the reservoirs,

$$-\sum_{\alpha} \gamma_\alpha^R(\langle X_\alpha^e \rangle - \langle X_\alpha \rangle) = \sum_{\alpha} \gamma_\alpha^R(\langle X_\alpha^{Re} \rangle - \langle X_\alpha^R \rangle)$$

is the entropy variation of the reservoirs during the equilibration.

We now consider the relative information $(\{p_i\}/\{p_i^0\})$ in the general case, when $\{p_i^0\}$ is any stationary distribution. If the initial distribution is slightly modified, the corresponding change of the relative information is

$$\delta S(\{p_i\}/\{p_i^0\}) = \delta \sum_i p_i \ln p_i/p_i^0 = \sum_i \delta p_i \ln p_i/p_i^0 \,. \tag{A.2}$$

On the other hand, let us assume that the system under study, **S**, interacts with another, large system, which can be one or several reservoirs in a general sense, and will be denoted by **R**. The large system **R** can exert constraints on **S**, or it can itself be submitted to constraints, so that when $t \to \infty$, **S** and **R** asymptotically reach a stationary state, which generally is not an equilibrium.

We shall denote i the microscopic state of **S**, j the microscopic *state* of **R**, and $p_{ij}(t)$ the probability to find **S** in state i and **R** in state j at time t. The global entropy of **S** and **R** is

$$\begin{aligned} S^{\mathbf{SR}} &= -\sum_{ij} p_{ij} \ln p_{ij} = -\sum_i p_i \ln p_i + \sum_i p_i \left(-\sum_j p_{j/i} \ln p_{j/i} \right) \\ &= S^{\mathbf{S}} + \sum_i p_i S^{\mathbf{R}/i} \,, \end{aligned} \tag{A.3}$$

where, according to classical definitions, $p_i = \sum_j p_{ij}$ is the probability of state i and $S^{\mathbf{S}}$ is the entropy of system **S**, whereas $p_{j/i} = p_{ij}/p_i$ is the conditional probability of state j of **R**, and $S^{\mathbf{R}/i} = -\sum_j p_{j/i} \ln p_{j/i}$ is the conditional entropy of **R**, when **S** is in state i.

We now suppose that when **S** is in a given state i, **R** reaches very rapidly its stationary conditional distribution, so that its conditional entropy $S^{\mathbf{R}/i}$ is practically independent of the distribution $\{p_i\}$ of **S**. This assumption is generally justified when the interactions between **S** and **R** are not too strong, and it is necessary for permitting the “thermodynamic” study of **S**: then, from the stochastic point of view, the role of **R** is reduced to determining the stationary distribution $\{p_i^0\}$.

With this hypothesis, it is seen from Eq. (B.3) that when the distribution $\{p_i\}$ is changed by $\{\delta p_i\}$, the total entropy $S^{\mathbf{SR}}$ is changed by

$$\delta S^{\mathbf{SR}} = -\sum_i \delta p_i \ln p_i + \sum_i \delta p_i S^{\mathbf{R}/i} \,. \tag{A.4}$$

On the other hand, when the stationary distribution $\{p_i^0\}$ is realized, any change $\{\delta p_i\}$ compatible with the constraints exerted on the system should leave the total entropy

$S^{\mathbf{SR}}$ unchanged, so that

$$0 = -\sum_i \delta p_i \ln p_i^0 + \sum_i \delta p_i S^{\mathbf{R}/i} \,. \tag{A.5}$$

Using Eq. (A.5), it is seen from (A.4) that when the distribution $\{p_i\}$ is changed by $\{\delta p_i\}$, the entropy $S^{\mathbf{SR}}$ is changed by

$$\delta S^{\mathbf{SR}} = -\sum_i \delta p_i \ln p_i/p_i^0 = -\delta S(\{p_i\}/\{p_i^0\}) \,. \tag{A.6}$$

Thus, the variation of the system relative information is just the opposite of the total entropy variation, and the relative information $S(\{p_i\}/\{p_i^0\})$ is the total entropy created during the evolution of the system S from its initial distribution $\{p_i\}$ to the stationary distribution $\{p_i^0\}$, i.e., it is the microscopic extropy of the system

$$S(\{p_i\}/\{p_i^0\}) = \Pi(\{p_i\}/\{p_i^0\}) \,. \tag{A.7}$$

This conclusion agrees with Eq. (A.1) in the case of an equilibrium stationary state, and it generalizes it. It should be pointed out that this proof does not assume that extensive variables are conserved during the evolution, contrarily to the simple calculation leading to (A.1).

Appendix B. Stochastic description in macroscopic variables

B.1. Quasi-stationary hypothesis and comparison of microscopic and coarse-grained extropies

With the notations of Section 3, let us consider the relative information of the actual microscopic distribution $\{p_i\}$ with respect to the distribution $\{q_i\}$ defined by (33). It may be observed that

$$S(\{p_i\}/\{p(X_i)/\Gamma(X_i)\}) \geqslant 0 \,,$$

$$\frac{\mathrm{d}}{\mathrm{d}t} S(\{p_i\}/\{p(X_i)/\Gamma(X_i)\}) \leqslant 0 \,.$$

In fact, according to the quasi-equilibrium approximation the distribution $\{q_i\} = \{p(X_i)/\Gamma(X_i)\}$ is a solution of the complete Master Equation (1), as well as $\{p_i\}$. Then, according to the general properties of the relative entropy, inequalities (4) hold. Thus $S(\{p_i\}/\{p(X_i)/\Gamma(X_i)\})$ continuously decreases to 0.

Moreover, it can be noticed that

$$S(\{p_i\}/\{p^0(X_i)/\Gamma(X_i)\}) - S(\{p(\boldsymbol{x})\}/\{p^0(\boldsymbol{x})\}) = S(\{p_i\}/\{p(X_i)/\Gamma(X_i)\})$$

which, together with (4), shows that the microscopic extropy is larger and decreases more rapidly than the coarse-grained extropy. However, both extropies are practically equal if the quasi-stationary hypothesis discussed in Section 3.4 is satisfied.

B.2. The information potential decreases with time

The information potential Φ^0, defined by Eq. (44), is a stationary solution of the Hamilton–Jacobi equation (42), and because $e^u - u - 1 \geqslant 0$, we have

$$0=\sum_{\boldsymbol{h}}\widehat{w}(\boldsymbol{h};\widehat{\boldsymbol{x}})\left(\exp\left(\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}\right)-1\right)\geqslant\sum_{\boldsymbol{h}}\widehat{w}(\boldsymbol{h};\widehat{\boldsymbol{x}})\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}$$

and

$$0\geqslant\sum_{\boldsymbol{h},\widehat{\boldsymbol{x}}}\widehat{w}(\boldsymbol{h};\widehat{\boldsymbol{x}})\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}p(\boldsymbol{x},t)\cong\sum_{\boldsymbol{h}}\boldsymbol{h}\widehat{w}(\boldsymbol{h};\langle\widehat{\boldsymbol{x}}\rangle)\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}(\langle\widehat{\boldsymbol{x}}\rangle)$$

the last equality (at order $1/V$) being due to the sharp peak of $p(\boldsymbol{x},t)$ at $\langle\widehat{\boldsymbol{x}}\rangle(t)$.

But we also have

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\widehat{\boldsymbol{x}}\rangle=\sum_{\boldsymbol{h},\widehat{\boldsymbol{x}}}\widehat{w}(\boldsymbol{h};\widehat{\boldsymbol{x}})\boldsymbol{h}p(\boldsymbol{x},t)\cong\sum_{\boldsymbol{h}}\boldsymbol{h}\widehat{w}(\boldsymbol{h};\langle\widehat{\boldsymbol{x}}\rangle)$$

From the last two equations it follows that

$$0\geqslant\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}\cdot\frac{\mathrm{d}}{\mathrm{d}t}\langle\widehat{\boldsymbol{x}}\rangle=\frac{\mathrm{d}}{\mathrm{d}t}\Phi^0(\langle\widehat{\boldsymbol{x}}\rangle)\,.$$

B.3. The main inequality for systems maintained out of equilibrium

We consider a system described by two classes of macroscopic variables $\boldsymbol{x}$ and $\boldsymbol{a}$, according to the notations and hypopthesis of Section 3.7. In the large volume approximation, the detailed balance equation (48) can straightforwardly be written

$$\ln\frac{\widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})}{\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})}=\left(\boldsymbol{h}\cdot\frac{\partial}{\partial\widehat{\boldsymbol{x}}}+\boldsymbol{k}\cdot\frac{\partial}{\partial\widehat{\boldsymbol{a}}}\right)\Phi^e(\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})\,. \tag{B.1}$$

We now suppose that the system is *maintained away from equilibrium* by appropriate devices which *keep* $\boldsymbol{a}$ *constant*, and that its probability distribution tends to a stationary distribution $p^0(\boldsymbol{x})$, corresponding to the information potential $\Phi^0(\widehat{\boldsymbol{x}})$ introduced in Section 3.6. We have from Eq. (42)

$$\begin{aligned}0&=\sum_{\boldsymbol{h},\boldsymbol{k}}\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})\left(\exp\left(\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}\right)-1\right)\\&=\frac{1}{2}\sum_{\boldsymbol{h},\boldsymbol{k}}\left[\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})\left(\exp\left(\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}\right)-1\right)\right.\\&\qquad\left.+\widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})\left(\exp\left(-\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}\right)-1\right)\right]\,.\end{aligned} \tag{B.2}$$

Let us define

$$u=\boldsymbol{h}\cdot\frac{\partial\Phi^0}{\partial\widehat{\boldsymbol{x}}}\qquad v=\boldsymbol{h}\cdot\frac{\partial\Phi^e}{\partial\widehat{\boldsymbol{x}}}+\boldsymbol{k}\cdot\frac{\partial\Phi^e}{\partial\widehat{\boldsymbol{a}}}\,. \tag{B.3}$$

Then (B.2) can be rewritten, thanks to (B.1)

$$0 = \tfrac{1}{2} \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})(e^{u} - e^{v}) + \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})(e^{-u} - e^{-v})] \,. \tag{B.4}$$

Now, using the inequality $e^u - e^v \geqslant (u-v)e^v$ and (B.1) once more, we obtain

$$\begin{aligned} 0 &\geqslant \tfrac{1}{2} \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})e^{v} - \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})e^{-v})](u-v) \\ &= -\tfrac{1}{2} \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}}) - \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})](u-v) \,. \end{aligned} \tag{B.5}$$

If, as usual the distribution $p(\widehat{\boldsymbol{x}},t)$ is sharply peaked around of $\widehat{\boldsymbol{x}}$, we may write

$$\frac{1}{2}\left\langle \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}}) - \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})]\boldsymbol{h} \cdot \frac{\partial \Phi^0}{\partial \widehat{\boldsymbol{x}}} \right\rangle \cong \frac{\mathrm{d}}{\mathrm{d}t}\Phi^0(\langle \widehat{\boldsymbol{x}} \rangle) \,, \tag{B.6.a}$$

$$\frac{1}{2}\left\langle \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}}) - \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})]\boldsymbol{h} \cdot \frac{\partial \Phi^e}{\partial \widehat{\boldsymbol{x}}} \right\rangle \cong \frac{\mathrm{d}}{\mathrm{d}t}\Phi^e(\langle \widehat{\boldsymbol{x}} \rangle, \widehat{\boldsymbol{a}}) \,, \tag{B.6.b}$$

$$\frac{1}{2}\left\langle \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}}) - \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})]\boldsymbol{k} \cdot \frac{\partial \Phi^e}{\partial \widehat{\boldsymbol{a}}} \right\rangle = -q \,. \tag{B.6.c}$$

The first two inequalities are similar to (48). Eq. (B.6.c) just defines the quantity q. Since, by (49), Φ^e is the extropy per unit volume, q represents the amount of entropy that would be produced in the unconstrained system per unit volume and unit time, due to the corresponding variation of the variables $\boldsymbol{a}$. Thus q is the *entropy extraction rate* in the constrained system: it has to be extracted from it by the devices which maintain **a** constant. Equivalently, $-q$ is the amount of entropy, and q is the amount of information which should be provided to the system per unit volume and per unit time. As a consequence, inequality (B.5) can be written

$$-\frac{\mathrm{d}}{\mathrm{d}t}\Phi^e(\langle \widehat{\boldsymbol{x}} \rangle) + q \geqslant -\frac{\mathrm{d}}{\mathrm{d}t}\Phi^0(\langle \widehat{\boldsymbol{x}} \rangle) \,. \tag{B.7}$$

Here, the equality only holds if it holds in Eq. (B.8), and thus, if $u = v$ for all $\widehat{\boldsymbol{x}}$, which, using (B.2), implies that

$$\frac{\mathrm{d}}{\mathrm{d}t}\Phi^0(\langle \widehat{\boldsymbol{x}} \rangle) = \frac{1}{2}\left\langle \sum_{\boldsymbol{h},\boldsymbol{k}} [\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}}) - \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})] \ln \frac{\widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})}{\widehat{w}(\boldsymbol{h},\boldsymbol{k};\widehat{\boldsymbol{x}},\widehat{\boldsymbol{a}})} \right\rangle \leqslant 0 \tag{B.8}$$

since each term in the sum of the right-hand side is negative.

In the stationary macroscopic state $\langle \widehat{\boldsymbol{x}} \rangle^0$, the left-hand side of (B.8) should vanish, so that we have for any $\boldsymbol{h}, \boldsymbol{k}$

$$\widehat{w}(\boldsymbol{h},\boldsymbol{k};\langle \widehat{\boldsymbol{x}} \rangle^0,\widehat{\boldsymbol{a}}) = \widehat{w}(-\boldsymbol{h},-\boldsymbol{k};\langle \widehat{\boldsymbol{x}} \rangle^0,\widehat{\boldsymbol{a}}) \tag{B.9}$$

which is the macroscopic detailed balance.

Inequality (B.7) is just inequality (50), which is commented in Section 3.7.

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