

Creation, Dissipation and Recycling of Resources in Non-Equilibrium Systems

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In this article, we define stochastic dynamics for a system coupled to reservoirs. The rules for forward and backward transitions are related by a generalized detailed balance identity involving the system and its reservoirs. We compare the variation of information and of entropy. We define the Carnot dissipation and prove that it can be expressed in terms of cyclic transformations. Lower bounds for partial dissipations are also studied, as well as the effect of switching off certain reservoirs. We also study the near degeneracy of the stochastic matrix, relate it to phase transitions and we show that the reduced dynamics on the set of phases is a permutation. Finally, we relate these concepts to heat, work and more generally to the dissipation and creation of resources, in general systems.

KEY WORDS: Non-equilibrium; dissipation; stochastic dynamics.

1. INTRODUCTION

In a mechanical, physico-chemical or biological system, things happen only when the system is out of equilibrium. By comparison, in equilibrium, all possible transitions in the system are balanced, so that no net fluxes are produced and as a consequence the system appears to be inert. The only way to reach a stationary non-equilibrium state is for the system to be coupled to reservoirs that impose conditions incompatible with the equilibrium. These assertions, although in a way tautological, are not easy to formulate mathematically so that they include a broad category of systems.

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It seems to us clear that many systems, whether they be physicochemical, biological, ecological, and economic, must satisfy these tautological assertions. There have been many, many attempts to describe particular systems out of equilibrium. Indeed this was one of the original aims of thermodynamics, namely to relate heat and work (see, among many references, refs. 1–8). More general formalisms have also been developed and thermodynamic state functions have been defined valid for relatively general systems (see, e.g., refs. 2, 4, 6, 10), or for more specific systems. Examples include reaction-diffusion systems (see, e.g., refs. 3, 4, 8–10), usually with large volume asymptotics,^(11,12) biochemical systems (see, e.g., refs. 7–9, 14) or small systems like molecular motors (see ref. 7 and references therein for the original models and ref. 14 for a more recent review) as well as examples of entropy production.⁽¹⁵⁾

Our aim is to build a framework valid for general out of equilibrium systems. This framework will be, as a consequence, of a rather abstract nature; for example, it should apply to large systems (like standard non-equilibrium thermodynamical systems) as well as to small systems (like biochemical systems), and thus this framework should not depend on large volume asymptotics, or a many-particle limit or an energy concept. Several years ago, we developed a master equation-based framework, using a stochastic matrix formalism. The theory of dissipation of information in a Markovian discrete system has been introduced in the mathematical theory of communication (see ref. 17, for the initial reference), leading to the concept of relative information (refs. 18 and 19) between two probability distributions on the state space X

$$S(p|q) = \sum_{x \in X} p(x) \log \frac{p(x)}{q(x)}.$$

From this definition, one deduces that, S is non-negative, and S is zero if and only if $p = q$. Moreover, $S(p|q)$ decreases under any Markovian evolution. This idea has been also applied in refs. 20 and 21 to physicochemical systems, where the link with the standard free energy is explicit. In ref. 16 we applied these ideas to generalize the fluctuation-dissipation theorem and the Onsager relations, in both cases *far* from equilibrium, as well as to a path space entropy notion. This has led us to the general definition of first order phase transition for stochastic systems,⁽²²⁾ to notions of hierarchical relaxation⁽²³⁾ and to the definition of coarse graining using distances, constructed on the state space from the left eigenstates and the corresponding relaxation times of the Markovian stochastic dynamics.⁽²⁴⁾ The possibility of using Markovian stochastic dynamics on a discrete state space is a basic hypothesis of most approaches to statistical mechanics and

to thermodynamics. It is a mathematical translation of the physical fact that there is a separation of time scales, so that a coarse grained description of the system can be used. The assumption is that the dynamics inside each "grain" is so fast that each "grain" is in a stationary state. It is also the underlying hypothesis of all macroscopic descriptions of flows, in particular in hydrodynamics.

Our basic assumption is that a Markovian stochastic dynamics on a certain coarse-grained state space is a correct description of the system, due to much faster relaxation times inside a grain, than between different grains.

This hypothesis may be wrong in certain instances. See ref. 25 for a discussion in the context of chemical kinetics of the limit of a Markovian theory of chemical rate constants, ref. 26 for the effect of correlations in generalized thermodynamics and hydrodynamics, ref. 27 for memory effects and long tail laws in molecular hydrodynamics, ref. 28 for memory effects in solids, and many other references.

Thus in our approach, the first central notion, which seems valid for any kind of natural system, is the notion of coarse-graining: it describes the basic relation between the observer and the system, and thus has partly a subjective character, and anyway, it depends on the processes of observation or on the apparatus and the technique available to the observer.

In physics, it leads to the related notions of entropy, reduced description, adiabatic elimination of variables, macrostates, etc. In chemistry, it leads to the notion of chemical species. In economics, it is related to the notion of aggregation and the concept of value. For example, the definition of the chemical species "water" depends on the technique which is available: usually it would refer to a certain molecule and one would coarse grain various rotational or vibrational states. But, with more elaborate technique, one may have to distinguish different species of water according to their internal states.

A second basic notion is the notion of fluxes, loops, cycles in chemistry, biochemistry, ecology as well as economics. Fluxes and cycles are created and maintained by competing external reservoirs. *It is the treatment of reservoirs and external transitions that is central to most of the present article.* Indeed, an external observer of a system will observe a global dynamics, the dynamics of the currents or fluxes of energy, matter, or various quantities between the system and its reservoirs. In equilibrium these currents are zero, and the non-equilibrium stationary state is induced only because certain reservoirs maintain external fluxes. The prototype is the Carnot engine where two reservoirs impose a difference of temperatures and as a consequence, a third reservoir receives work, the total effect of the engine being to channel energy into certain macroscopic degrees of freedom of the work reservoir. Or a plant uses the photon reservoir of the

sun to store energy in special degrees of freedom in the form of potential energy in highly energetic, metastable chemical bonds. The stochastic dynamics will be inferred from the global dynamics of the external currents. This general picture of non-equilibrium systems implies that it is advantageous to take the reservoirs into account explicitly in the stochastic dynamics (except for the limiting case of equilibrium dynamics), because what often matters for the users or observers of a system is the nature of the transitions, of the substances exchanged between the system and its reservoirs, as well as the rates of these exchanges, even if these substances are waste-products. On the other hand, we do not want to completely include the reservoirs in the system under consideration, although we should include how the reservoirs are modified during their interactions with the system whose rates are given by the stochastic matrix elements. Finally, a third notion is the reservoir. Any practitioner of statistical physics knows that it is a highly non-trivial concept, leading to theoretical difficulties. We shall try to make as clear as possible the assumptions that are used in our work.

It is our aim in this article, to introduce a formalism to solve these problems, at least in the context of classical systems (no quantum effects are considered) and of Markovian dynamics (separation of time scales).

Summary of results. In Section 2, we briefly recall the general master equation formalism and various notations. This formalism is made more specific in Section 3 where we explicitly introduce the coarse graining using an *a priori* given entropy function, as well as the transitions between the system and the reservoir. Two basic hypotheses are made, in particular that each transition satisfies detailed balance for the microcanonical ensemble of the system and reservoirs. In Section 4 a general inequality relating the variation of the information potential and the total entropy of the system and reservoirs is derived. In Sections 5 and 6 the Carnot dissipation is introduced, and calculated explicitly using the cycles of transitions in the system. This generalizes the calculation of Hill⁽⁸⁾ to any system. In Section 7, we consider the effect of switching off certain reservoirs and the initial relaxation towards a new stationary state. In Section 8, we generalize the phase transition formalism of ref. 22 to the case where eigenvalues with modulus near 1 are complex. We show that there is again a set of phases, so that the induced coarse grained dynamics between the phases is a permutation, at an intermediate time scale. In Section 9, we introduce the notion of resources and we give a lower bound for the dissipation of a resources. Finally, in Section 10 we develop examples and relate our theory to the theory of reaction-diffusion systems in the large volume limit at a fixed temperature. Moreover, we show explicitly for 3 or 4 state systems that the topology of the possible transitions with the reservoirs is important.

2. STOCHASTIC DYNAMICS IN GENERAL

In this section we introduce mathematical notations to describe the systems that we consider and discuss the physical hypotheses under which this mathematical description is valid. We maintain the discussion as general as possible.

A certain system is described by a state space X which is supposed to be discrete (and usually finite, not necessarily large). A state x is a point in X . Here, the description of the system by states x is already a coarse-grained description obtained from a more fundamental but not necessarily microscopic one. In particular, we can define an entropy function $s(x) \geq 0$, which is the logarithm of the number of fundamental states which become coarse-grained in the description of the reduced state x .

We assume that time is discrete, the unit time step being δt . The dynamics of the system is described by a stochastic matrix R_{xy} : R_{xy} is the probability that the transition $y \rightarrow x$ occurs in one time step, δt . In particular

$$0 \leq R_{xy} \leq 1, \quad \sum_x R_{xy} = 1.$$

A state of the system is a probability distribution $p(x)$ on X , so that

$$\sum_x p(x) = 1.$$

After one time step δt , the state $p(x, t)$ at time t becomes $p(x, t + \delta t)$

$$p(x, t + \delta t) = \sum_y R_{xy} p(y, t) \equiv R p(\cdot, t)(x) \quad (2.1)$$

p will be considered a right vector. If A is an observable of the system, we define its average with respect to the state p as:

$$\langle A \rangle_p = \sum A(x) p(x).$$

After one time step δt , $A(x)$ becomes $A(x, \delta t)$ defined so that, as usual

$$\langle A(\delta t) \rangle_p = \langle A \rangle_{p(\delta t)}$$

or

$$A(x, \delta t) = \sum_y A(y) R_{yx} = (AR)_x. \quad (2.2)$$

and A will be considered a left vector.

It is also useful to introduce the variations δ of quantities in one time step, namely

$$\delta p(x, t) = p(x, t + \delta t) - p(x, t) = \sum_y R_{xy} p(y, t) - \sum_y R_{yx} p(x, t) \quad (2.3)$$

$$\delta A(x, t) = A(x, t + \delta t) - A(x, t) = \sum_y R_{yx} (A(y, t) - A(x, t)). \quad (2.4)$$

The matrix R has the eigenvalue 1 which we assume to be non-degenerate. The right eigenvector of this eigenvalue is the stationary state $p_s(x) \equiv p_0(x)$ satisfying

$$R p_s = p_s.$$

We assume the ergodicity property, namely

$$p_s(x) > 0 \quad \text{for all } x \in X.$$

The left eigenvector for the eigenvalue 1 is

$$A_0(x) = 1 \quad \text{for all } x \in X.$$

The other eigenvalues are λ_k with $|\lambda_k| \leq 1$.

The dynamics given by R is an equilibrium dynamics or a detailed balance dynamics if the detailed balance condition is satisfied, namely:

$$R_{xy} p_s(y) = R_{yx} p_s(x) \quad \text{for all } x, y. \quad (2.5)$$

For any probability distribution $p(x)$, we can define the current as the skew-symmetric matrix

$$J_{xy}^{(p)} = R_{xy} p(y) - R_{yx} p(x). \quad (2.6)$$

The stationary current $J_{xy}^{(s)}$ is obtained for $p = p_s$. It is identically 0 for detailed balance dynamics.

We see that if the state is $p(x, t)$, then

$$\begin{aligned} \delta \langle A \rangle_{p(t)} &= \langle A \rangle_{p(t+\delta t)} - \langle A \rangle_{p(t)} \\ &= \sum_{x, y} A(x) J_{xy}^{(p(t))}. \end{aligned}$$

The entropy of a probability distribution is as usual

$$S(p) = -\sum p(x) \log p(x). \quad (2.7)$$

The relative entropy of two probability distributions p, q is

$$S(p|q) = \sum p(x) \log \frac{p(x)}{q(x)}. \quad (2.8)$$

Then $S(p|q) \geq 0$ and is 0 if and only if $p = q$. Moreover, it can be proved that $S(p|q)$ is non-increasing under any stochastic evolution

$$0 \leq S(Rp|Rq) \leq S(p|q) \quad (\text{see, e.g., ref. 19}) \quad (2.9)$$

For an equilibrium system with inverse temperature β the stationary state can be written

$$\begin{aligned} p_{eq}(x) &= \frac{1}{Z} \exp(-\beta h(x)) \\ &= \exp(-\beta(h(x) - F_{eq})) \end{aligned}$$

where $Z = \exp(-\beta F_{eq})$ defines the equilibrium free energy. In that case

$$S(p|p_{eq}) = \beta(F(p) - F_{eq}),$$

where $F(p)$ is the free energy of the state p , namely

$$F(p) = \langle h \rangle_p - \frac{1}{\beta} S(p).$$

It is also known and easy to see that S decreases by coarse-graining, namely if \tilde{p}, \tilde{q} are coarse-grained probabilities of p and q on a reduced state space \tilde{X} , then

$$0 \leq S(\tilde{p}|\tilde{q}) \leq S(p|q). \quad (2.10)$$

In this equation we assume a collection of disjoint subsets $X_{\tilde{x}}$ of X such that $X = \bigcup_{\tilde{x} \in \tilde{X}} X_{\tilde{x}}$. Then we define

$$\begin{aligned} \tilde{p}(\tilde{x}) &= \sum_{x \in X_{\tilde{x}}} p(x) \\ p(x|\tilde{x}) &= \begin{cases} 0 & \text{if } x \notin X_{\tilde{x}} \\ \frac{p(x)}{\tilde{p}(\tilde{x})} & \text{if } x \in X_{\tilde{x}} \end{cases} \end{aligned}$$

and we easily verify that (see ref. 19)

$$S(p|q) = S(\tilde{p}|\tilde{q}) + \sum_{\tilde{x}} \tilde{p}(\tilde{x}) S(p(\cdot|\tilde{x})|q(\cdot|\tilde{x})).$$

For future use, we note that for any probability distribution p on X , and any stochastic dynamics R , there is a small δt expansion

$$S(p|Rp) = \frac{1}{2} \sum_x p(x) \left(\frac{1}{p(x)} \sum_y J_{xy}^{(p)} \right)^2 + O((\delta t)^3), \quad (2.11)$$

where the first term is $O((\delta t)^2)$. To prove (2.11) note that

$$\begin{aligned} \frac{(Rp)(x)}{p(x)} &= R_{xx} + \sum_{y \neq x} R_{xy} \frac{p(y)}{p(x)} \\ &= 1 + \frac{1}{p(x)} \sum_y J_{xy}^{(p)}. \end{aligned}$$

Then

$$\begin{aligned} S(p|Rp) &= \sum_x p(x) \log \frac{p(x)}{(Rp)(x)} \\ &= -\sum_{x,y} J_{xy}^{(p)} + \frac{1}{2} \sum_x p(x) \left(\frac{1}{p(x)} \sum_y J_{xy}^{(p)} \right)^2 + O((\delta t)^3). \end{aligned}$$

The first term, however, is identically 0 because J is skew-symmetric.

The interpretation of $S(p|Rp)$ is the following: We know that $-\log p(x)$ is the information that one gains from measuring the actual state x , knowing that the probability distribution was p , and that $S(p)$ is the average (or expected) information gained in such a measurement. Then $-\sum p(x) \log(Rp)(x)$ is the average information gained if one measures the actual state after one time step δt of the evolution by the stochastic dynamics R , knowing that the probability distribution is p and $S(p|Rp)$ is the variation in one time step of the average information, knowing that the probability distribution was p .

Remark. The sum in Eq. (2.11) makes sense in the continuum limit of x . In this case $p(x)$ should be replaced by $\hat{p}(x) dx$ and R_{xy} by $dx \hat{r}_{xy}$, where $\hat{p}(x)$ and \hat{r}_{xy} are probability densities.

The description of the dynamics on the space X as a stochastic Markovian dynamics is valid provided that each point, $x \in X$, represents

a set of “microscopic” states such that the “exact” dynamics (of which the stochastic one is a reduction) has fast time scales compared to the time scale for changing the “grain” x . This means that we have a separation of time scales between various degrees of freedom (see also Section 8 of this article, ref. 22 for application to the dynamics of phases and ref. 24 for discussion of the basis of grain selection). The hypothesis of separation of time scales is a matter of contingency. It depends on the system studied and may or may not be a correct assumption. But it is the standard assumption which is at the foundation of standard statistical mechanics and thermodynamics.

3. RESERVOIRS AND THE STOCHASTIC DYNAMICS

We assume that the system X is coupled to various reservoirs indexed by $\ell = 1, \dots, r$. The reservoir ℓ is described by its state space Ω_ℓ with states $\xi_\ell \in \Omega_\ell$. Each state has an entropy $s_\ell(\xi_\ell)$. If the joint state $(x, (\xi_\ell)_{\ell=1, \dots, r})$ of the system and its reservoirs is known, the entropy of the joint state is

$$S(x, (\xi_\ell)) = s(x) + \sum_{\ell=1}^r s_\ell(\xi_\ell). \tag{3.1}$$

During a variation $y \rightarrow x$ of the system X , it may happen that the states of the reservoirs Ω_ℓ also vary. Our notation for the reservoir variation is $\eta_\ell \rightarrow \xi_\ell$.

In particular, a given variation $y \rightarrow x$ of the state of X can be realized by different kinds of mechanisms involving or not involving the reservoirs. More precisely we consider various transitions α as mappings

$$\alpha: (y, (\eta_\ell)) \in X \times \prod_{\ell} \Omega_\ell \rightarrow (x, (\xi_\ell)) \in X \times \prod_{\ell} \Omega_\ell \tag{3.2}$$

(which are not necessarily defined for all states) and we assume the following hypotheses.

Hypothesis 1. In a transition α , as in (3.2), the variations of the states of the reservoirs Ω_ℓ are functions of the states y, x of the system X and of the transition that is considered.

Thus, given y and x , only certain η_ℓ may be allowed, and for each such η_ℓ a particular ξ_ℓ is fixed.

We shall also assume that to any transition, there is an associated inverse transition α^{-1} such that

$$\alpha^{-1}(\alpha(y, (\eta_\ell))) = (y, (\eta_\ell)).$$

We denote by $R_{xy}^{(\alpha)}$ the probability per unit time step δt , that the transition α occurs between states y and x of X . We assume that $R_{xy}^{(\alpha)}$ depends only on y and α , x being known when y and α are known. We also make the following hypothesis.

Hypothesis 2. Each transition α satisfies an independent detailed balance relation, namely if

$$\alpha(y, (\eta_\ell)) = (x, (\xi_\ell))$$

then

$$R_{xy}^{(\alpha)} \exp(S(y, (\eta_\ell))) = R_{yx}^{(\alpha^{-1})} \exp(S(x, (\xi_\ell))). \quad (3.3)$$

If α is not defined between y and x , we define

$$R_{xy}^{(\alpha)} = 0.$$

In this case α^{-1} is also not defined between x and y and we take

$$R_{yx}^{(\alpha^{-1})} = 0.$$

We define the stochastic matrix R_{xy} by

$$R_{xy} = \sum_{\alpha} R_{xy}^{(\alpha)} \quad (3.4)$$

the sum being taken on all transitions α (or inverse transitions) which relate y to x (for $y \neq x$) and as usual

$$R_{xx} = 1 - \sum_{y \neq x} R_{yx}. \quad (3.5)$$

Remark. By this construction, we have further specialized to R such that $R_{xy} \neq 0$ implies $R_{yx} \neq 0$.

Among all possible transitions, we distinguish

– internal transitions α which do not change the states of the reservoirs

$$\alpha(y, (\eta_\ell)) = (x, (\eta_\ell))$$

– external transitions α' which change the states of the reservoirs. An external transition is of type ℓ if it changes only the state of X and the state

of the reservoir ℓ , so $\xi_\ell \neq \eta_\ell$, but not the states of reservoirs $k \neq \ell$, for which $\xi_k = \eta_k$. By a proliferation of reservoirs and α s, one can demand that each α involve changes in at most a single reservoir, but this is not necessary for now.

For an internal transition α , Eq. (3.3) reduces to

$$R_{xy}^{(\alpha)} \exp(s(y)) = R_{yx}^{(\alpha^{-1})} \exp(s(x)) \tag{3.6}$$

and for an external transition α of type ℓ ,

$$R_{xy}^{(\alpha)} \exp(s(y) + s_\ell(\eta_\ell)) = R_{yx}^{(\alpha^{-1})} \exp(s(x) + s_\ell(\xi_\ell)). \tag{3.7}$$

We discuss briefly Hypotheses 1 and 2, which are obviously related.

Hypothesis 1 implies that for a given transition α , the variations of the states of the reservoirs are known in terms of the variation of the state of X . It means that external transitions satisfy conservation laws. As a consequence, one can consider the joint system, system X together with the reservoirs Ω_ℓ , as a closed system denoted $X + (\Omega_\ell)$.

Hypothesis 2 says that in this closed system $X + (\Omega_\ell)$ the quotient of the rates of transitions α and α^{-1} is equal to the quotient of the volumes of the initial state $(y, (\eta_\ell))$ and of the final state $(x, (\xi_\ell))$ (in the closed system), these volumes being equal, by definition, to the exponential of the entropies of the states. This is effectively a statement of detailed balance for the entire ‘‘universe,’’ $X + (\Omega_\ell)$ (more below).

Moreover, this detailed balance relation satisfied by a given transition depends only on that particular transition and is independent of all the other transitions occurring in the system. Each transition acts independently, with rates satisfying a detailed balance relation so that each transition, by itself would tend to bring the system back to equilibrium with the reservoir associated with that transition.

We can rewrite Eq. (3.3) as

$$\frac{R_{xy}^{(\alpha)}}{R_{yx}^{(\alpha^{-1})}} = \exp \left[s(x) - s(y) + \sum_\ell (s_\ell(\xi_\ell) - s_\ell(\eta_\ell)) \right]. \tag{3.8}$$

Equation (3.8) implies that $\sum_\ell (s_\ell(\xi_\ell) - s_\ell(\eta_\ell))$ depends only on x and y and this fact is a consequence of Hypothesis 1.

As a consequence of Eq. (3.3), the closed system $X + (\Omega_\ell)$ has a detailed balance equilibrium probability distribution

$$P(x, (\xi_\ell)) = \exp(S(x, (\xi_\ell))) \quad (\text{up to a normalizing factor}) \tag{3.9}$$

when we consider the transition probabilities $R_{xy}^{(\alpha)}$ as transition probabilities for the closed system $X + (\Omega_\ell)$ which are independent of the states of the reservoirs. Nevertheless, the stationary probability for the system X , is not obtained by a simple summation over the reservoir state (ξ_ℓ): if this were the case, $p_s(x)$ would be proportional to $\exp(s(x))$. The reason is precisely the conservation laws between X and its reservoirs, so that $p_s(x)$ is a constrained sum over the (ξ_ℓ). We next give an example illustrating this point.

Example. Consider a system X whose states are labelled only by their energy content, $e = n\varepsilon$, where ε is a quantum of energy and n is an integer. This system interacts with two thermal reservoirs Ω_j , $j = 1, 2$ whose state space is also characterized by an energy variable only, $e_j = n_j\varepsilon$ (again n_j is an integer) and the temperature of Ω_j is β_j^{-1} . The entropy of Ω_j is

$$s_j(e_j) = \beta_j e_j.$$

The total energy $E_T = e + e_1 + e_2$ is conserved in each transition. The closed system $X + \Omega_1 + \Omega_2$ has the equilibrium distribution, up to a normalizing factor,

$$\begin{aligned} P(e, e_1, e_2) &= \exp(s(e) + \beta_1 e_1 + \beta_2 e_2) \\ &= \exp(s(e) + (\beta_1 - \beta_2) e_1 - \beta_2 e + \beta_2 E_T). \end{aligned}$$

If $\beta_1 = \beta_2$, this is also the canonical probability distribution $\exp(-\beta(e - \frac{1}{\beta}s(e)))$ with the standard free energy $f(e) = e - \frac{1}{\beta}s(e)$ for the system X . For $\beta_1 \neq \beta_2$, a stationary probability distribution is obtained by summing $P(e, e_1, e_2)$ for $0 \leq n_1 \leq N_T - n$, with $N_T = E_T/\varepsilon$, $n = e/\varepsilon$, but it does not satisfy the master equation as is usual in these circumstances. In fact, there are only two kinds of transitions, one for each reservoir

$$R_{n+1, n}^{(1+)} \exp(s(n\varepsilon) + \beta_1 n_1 \varepsilon) = R_{n, n+1}^{(1-)} \exp(s((n+1)\varepsilon) + \beta_1 (n_1 - 1)\varepsilon)$$

corresponding to transitions with reservoir 1

$$(1 \pm): (n, n_1, n_2) \rightarrow (n \pm 1, n_1 \mp 1, n_2)$$

and transitions

$$R_{n+1, n}^{(2+)} \exp(s(n\varepsilon) + \beta_2 n_2 \varepsilon) = R_{n, n+1}^{(2-)} \exp(s((n+1)\varepsilon) + \beta_2 (n_2 - 1)\varepsilon)$$

corresponding to transitions with reservoir 2

$$(2 \pm): (n, n_1, n_2) \rightarrow (n \pm 1, n_1, n_2 \mp 1).$$

4. AN INEQUALITY RELATING THE VARIATIONS OF INFORMATION AND ENTROPY

We define the information potential (see ref. 12) as

$$\Phi(x) = \log p_s(x). \quad (4.1)$$

Thus the entropy of the stationary state is $-\langle \Phi \rangle_{p_s}$. Recall that the variation of an observable $A(x)$ (for the system X) in one time step is

$$\delta A(x) = \sum_y R_{yx}(A(y) - A(x)). \quad (4.2)$$

This applies in particular to Φ . But Eq. (4.2) cannot be applied to the variation of $S(x, (\xi_\ell))$ in one time step, because this variation depends not only on the variation $x \rightarrow y$ of the state of X , but also on the nature α of the transition. Nevertheless, we can define for a given x :

$$\delta S(x, (\xi_\ell)) = \sum_\alpha R_{yx}^{(\alpha)}(S(y, (\eta_\ell)) - S(x, (\xi_\ell))) \quad (4.3)$$

where in the summation in Eq. (4.3)

$$(y, (\eta_\ell)) = \alpha(x, (\xi_\ell)).$$

We want to prove the following inequality, valid for a given (x, ξ_ℓ) :

$$\delta \Phi(x) \leq \delta S(x, (\xi_\ell)) \quad (4.4)$$

Inequality (4.4) means that the variation of the information in the stationary state is always less than the variation of the total entropy.

We prove the inequality (4.4). The master equation for $p_s(x)$ can be written

$$\sum_{\alpha, y} R_{xy}^{(\alpha)} p_s(y) - \sum_{\alpha, y} R_{yx}^{(\alpha^{-1})} p_s(x) = 0 \quad (4.5)$$

for all $x \in X$. Using Eq. (3.3), we have

$$R_{xy}^{(\alpha)} = R_{yx}^{(\alpha^{-1})} \exp(S(x, (\xi_\ell)) - S(y, (\eta_\ell))).$$

After reindexing the summation in Eq. (4.5), this equation can be rewritten as

$$\sum_\alpha R_{yx}^{(\alpha^{-1})} [\exp(\Phi(y) - \Phi(x) + S(x, (\xi_\ell)) - S(y, (\eta_\ell))) - 1] = 0$$

Using the fact that $e^a - 1 \geq a$ with equality if and only if $a = 0$, we deduce

$$\sum_{\alpha, y} R_{yx}^{(\alpha^{-1})} [\Phi(y) - \Phi(x) + S(x, (\xi_\ell)) - S(y, (\eta_\ell))] \leq 0 \quad (4.6)$$

which after rearrangements and using Eqs. (4.2) and (4.3) gives the inequality (4.4).

We have equality for all x in (4.4), if and only if for all y , and all transitions $\alpha: (y, (\eta_\ell)) \rightarrow (x, (\xi_\ell))$

$$\Phi(x) - \Phi(y) = S(x, (\xi_\ell)) - S(y, (\eta_\ell))$$

which implies that the system is in detailed balance, because then Eq. (3.3) implies that for all y and all α

$$R_{xy}^{(\alpha)} \exp(\Phi(y)) = R_{yx}^{(\alpha^{-1})} \exp(\Phi(x)).$$

Remark. It is in general not true that $\delta\Phi(x) \geq 0$ for a given $x \in X$. In particular, if one takes a point x_0 where $\Phi(x_0)$ is maximum, it is clear that in general $\delta\Phi(x_0)$ will be negative. On the other hand, in the large volume limit, it has been proved in ref. 12, that Φ increases along the deterministic flow associated with the master equation or the Fokker–Planck equation. Moreover in this case, at a point where Φ is maximum, the vector field of the deterministic flow also has a zero. On the other hand, under the discrete stochastic dynamics of the Master equation, it can happen that Φ decreases. The main problem, in the large volume limit, is that the deterministic flow is not a correct approximation to the stochastic dynamics for very long times. (of the order of the exponential of the volume) (see, e.g., ref. 12). The question of large volume limits will be examined in another publication.

5. DISSIPATION IN THE STATIONARY STATE

(a) For any transition α , we can write Eq. (3.3) as

$$R_{xy}^{(\alpha)} = K_{xy}^{(\alpha)} \exp \frac{1}{2} (S(x, (\xi_\ell)) - S(y, (\eta_\ell))) \quad (5.1)$$

where $K_{xy}^{(\alpha)}$ is symmetric, namely

$$K_{xy}^{(\alpha)} = K_{yx}^{(\alpha^{-1})} \quad \text{and} \quad \alpha(y, (\eta_\ell)) = (x, (\xi_\ell)). \quad (5.2)$$

(b) Let us now define the Carnot dissipation in the stationary state $p_s(x)$ as

$$\mathcal{D} = \frac{1}{2} \sum_{x, y, \alpha} [S(x, (\xi_\ell)) - S(y, (\eta_\ell))] J_{xy}^{(\alpha)} \tag{5.3}$$

where $J_{xy}^{(\alpha)}$ is the current of the transition α

$$J_{xy}^{(\alpha)} = R_{xy}^{(\alpha)} p_s(y) - R_{yx}^{(\alpha^{-1})} p_s(x) \tag{5.4}$$

so that

$$J_{yx}^{(\alpha^{-1})} = -J_{xy}^{(\alpha)}. \tag{5.5}$$

Now

$$\sum_{x, y, \alpha} K_{xy}^{(\alpha)} J_{xy}^{(\alpha)} = 0.$$

Indeed, in the sum in the previous equation, for each couple (α, y) of the sum, we can find also the couple (α^{-1}, x) in the sum and because of Eqs. (5.2)–(5.5)

$$K_{xy}^{(\alpha)} J_{xy}^{(\alpha)} + K_{yx}^{(\alpha^{-1})} J_{yx}^{(\alpha^{-1})} = 0.$$

So \mathcal{D} becomes, using Eq. (5.1),

$$\begin{aligned} \mathcal{D} &= \sum_{x, y, \alpha} (\log R_{xy}^{(\alpha)}) J_{xy}^{(\alpha)} \\ &= \frac{1}{2} \sum_{x, y, \alpha} (\log R_{xy}^{(\alpha)} - \log R_{yx}^{(\alpha^{-1})}) J_{xy}^{(\alpha)} \end{aligned} \tag{5.6}$$

which can be rewritten as

$$\mathcal{D} = \frac{1}{2} \sum_{x, y, \alpha} J_{xy}^{(\alpha)} \log \left(\frac{R_{xy}^{(\alpha)} p_s(y)}{R_{yx}^{(\alpha^{-1})} p_s(x)} \right) \tag{5.7}$$

Eq. (5.7) follows because for any fixed y , for the stationary state, one has

$$\sum_{x, \alpha} J_{xy}^{(\alpha)} = 0.$$

This implies, because of Eq. (5.5), that

$$\mathcal{D} \geq 0 \tag{5.8}$$

and $\mathcal{D} = 0$ if and only if $J_{xy}^{(\alpha)} = 0$ for all α and all y (namely detailed balance).

Remark. In ref. 20, a different notion of dissipation was introduced, namely

$$\frac{1}{2} \sum_{x,y} J_{xy} \log \left(\frac{R_{xy} p_s(y)}{R_{yx} p_s(x)} \right).$$

This quantity is not \mathcal{D} (the Carnot dissipation). In general for a given variation $y \rightarrow x$ of the state of X , the variation of the entropy of the reservoir depends on the actual nature of the transition (labelled by α in Eqs. (5.3)–(5.7)).

We see also that the dissipation \mathcal{D} is equal to the dissipation of the reservoirs, because

$$\sum_{y,\alpha} (s(x) - s(y)) J_{xy}^{(\alpha)} = 0$$

so that Eq. (5.4) is reduced to

$$\mathcal{D} = \frac{1}{2} \sum_{x,y,\alpha} \left(\sum_{\ell} (s_{\ell}(\xi_{\ell}) - s_{\ell}(\eta_{\ell})) \right) J_{xy}^{(\alpha)}. \quad (5.9)$$

(c) We now discuss the dissipation of information in the system X . If one starts from the state y , the dissipation of information is $-\sum R_{xy} \log R_{xy}$. If y is distributed according to the stationary probability distribution, the average dissipation of information in one time step δt , for the system X is

$$D = -\sum_{x,y} R_{xy} p_s(y) \log R_{xy} > 0. \quad (5.10)$$

It is easy to see that

$$\begin{aligned} D &= -\sum_x \sum_y p_s(y) R_{xy} \log R_{xy} \\ &\leq -\sum_x \left(\sum_y R_{xy} p_s(y) \right) \log \left(\sum_y R_{xy} p_s(y) \right) \equiv S(p_s) \end{aligned}$$

because p_s is the stationary state of X . This can be rewritten as

$$0 < D \leq S(p_s). \quad (5.11)$$

Notice that one can define another dissipation of information. For the system together with its reservoirs, let this be

$$D_T \equiv - \sum_{x, y, \alpha} R_{xy}^{(\alpha)} p_s(y) \log R_{xy}^{(\alpha)}.$$

6. CALCULATION OF DISSIPATION USING CYCLES

In this section, we calculate the Carnot dissipation using cycles in the state space X . First recall the construction of the stationary state.

We can consider X to be a graph whose vertices are the points $x \in X$ and the edges are the pairs (x, y) , provided $R_{xy} \neq 0$ (so that $R_{yx} \neq 0$ by our hypothesis). Fix $x_0 \in X$. A spanning tree of root x_0 is an acyclic subgraph of the set X , containing all the points of X , and which is oriented in such a way that all the edges (x, y) are pointing towards x_0 . We call $\mathcal{C}(x_0)$ the set of spanning trees of root x_0 . If $T \in \mathcal{C}(x_0)$, we define the quantity

$$R(T) = \prod_{[x, y] \in T} R_{xy} \tag{6.1}$$

where $[x, y]$ is an oriented edge of T , the orientation being from y to x .

We recall the following well-known result, which has been discovered or rediscovered many times (see, e.g., refs. 8, 9, 16, and 29). The stationary state $p_s(x)$ is

$$p_s(x) = \frac{1}{Z} \sum_{T \in \mathcal{C}(x)} R(T) \tag{6.2}$$

where Z is the normalization factor; obviously

$$Z = \sum_{x \in X} \sum_{T \in \mathcal{C}(x)} R(T). \tag{6.3}$$

This is the analogue of the partition function in a non-equilibrium situation.

We consider now a transition $\alpha \in A$ where A is the set of all possible transitions and we want to calculate the current of that transition (in the state p_s)

$$J_{xy}^{(\alpha)} = R_{xy}^{(\alpha)} p_s(y) - R_{yx}^{(\alpha^{-1})} p_s(x). \tag{6.4}$$

We calculate the term $R_{xy}^{(\alpha)} p_s(y)$, using Eq. (6.2). Begin with a spanning tree of root y , $T \in \mathcal{C}(y)$, and look at $R_{xy}^{(\alpha)} R(T)$. There are two cases

(i) T contains the oriented edge $[y, x]$ and thus $R(T)$ contains R_{yx} . In this case, if we reverse the orientation of $[y, x]$ in T (and only of this edge), we obtain a tree $T' \in \mathcal{C}(x)$ and $R(T')$ is identical to $R(T)$ except that R_{yx} in $R(T)$ has been replaced by R_{xy} . Moreover the correspondence between the trees $T \in \mathcal{C}(y)$ with $[y, x] \in T$ and the trees $T' \in \mathcal{C}(x)$ with $[x, y] \in T'$ is one-to-one. Now

$$R_{xy}^{(\alpha)} R_{yx} - R_{yx}^{(\alpha^{-1})} R_{xy} = R_{xy}^{(\alpha)} \sum_{\alpha' \neq \alpha^{-1}} R_{yx}^{(\alpha')} - R_{yx}^{(\alpha^{-1})} \sum_{\alpha' \neq \alpha} R_{xy}^{(\alpha')}.$$

So this type of tree $T \in \mathcal{C}(y)$ (resp. $T' \in \mathcal{C}(x)$) containing $[y, x]$ (resp. $[x, y]$) generates a contribution to $J_{xy}^{(\alpha)}$ which is

$$\frac{1}{Z} \left(R_{xy}^{(\alpha)} \sum_{\alpha' \neq \alpha^{-1}} R_{yx}^{(\alpha')} - R_{yx}^{(\alpha^{-1})} \sum_{\alpha' \neq \alpha} R_{xy}^{(\alpha')} \right) \left(\sum_{T \in \mathcal{C}(y)} \frac{R(T)}{R_{yx}} \right). \quad (6.5)$$

(ii) $T \in \mathcal{C}(y)$ does not contain the oriented edge $[y, x]$. Because T is a spanning tree, there is a unique sequence of oriented edges going from x to y in T $[y, x_n], [x_n, x_{n-1}], \dots, [x_1, x]$ (with $n \geq 1$) and this generates a corresponding product in $R(T)$, namely

$$R_{yx_n} R_{x_n x_{n-1}} \cdots R_{x_1 x}.$$

Now in the product $R_{xy}^{(\alpha)} p_s(y)$, this tree $T \in \mathcal{C}(y)$ generates the contribution

$$R_{xy}^{(\alpha)} R_{yx_n} R_{x_n x_{n-1}} \cdots R_{x_1 x}$$

corresponding to the oriented cycle

$$[x, y], [y, x_n], [x_n, x_{n-1}], \dots, [x_1, x]$$

where all the points are different. We say that the cycle is *simple*. Moreover, if we reverse the orientation of this cycle we obtain

$$[y, x], [x, x_1], [x_1, x_2], \dots, [x_{n-1}, x_n], [x_n, y]$$

and the oriented path $[x, x_1], \dots, [x_n, y]$ induces from T a tree $T' \in \mathcal{C}(x)$ which is identical to T except that the path leading from x to y in T has been reversed to a path leading from y to x in T' .

Moreover, if we delete from T the edges $[y, x_n], [x_n, x_{n-1}], \dots, [x_1, x]$, we obtain a union of disjoint trees spanning the rest of the graph, with possible roots at $y, x_n, x_{n-1}, \dots, x_1, x$; this is a *forest of trees* F with roots on

the cycle y, x_n, \dots, x_1, x , spanning the graph X deprived of this cycle. This forest F is exactly the same as the one for T' and we call

$$R(F) = \prod_{[y', x'] \in F} R_{y'x'} \tag{6.6}$$

the contribution of this forest.

So, we see that the trees $T \in \mathcal{C}(y)$ (and the related trees $T' \in \mathcal{C}(x)$) which both do not contain $[y, x]$ (resp. $[x, y]$) as an edge, give a contribution to $J_{xy}^{(\alpha)}$ which is

$$\frac{1}{Z} \sum_{c \in C(x, y)} (P_{xy}^{(\alpha)}(c) - P_{yx}^{(\alpha^{-1})}(\bar{c})) \sum_{F \in \mathcal{F}(c)} R(F) \tag{6.7}$$

with the following notations:

(1) $C(x, y)$ is the set of oriented simple cycles containing the oriented edge $[x, y]$ (and containing at least three vertices).

(2) If $c \in C(x, y)$ is a cycle, $c = ([x, y], [y, x_n], [x_n, x_{n-1}], \dots, [x_1, x])$

$$P_{xy}^{(\alpha)}(c) = R_{xy}^{(\alpha)} R_{yx_n} R_{x_n x_{n-1}} \cdots R_{x_1 x} \tag{6.8}$$

(3) \bar{c} is the reverse cycle and $P_{yx}^{(\alpha)}(\bar{c})$ is the corresponding contribution

$$P_{yx}^{(\alpha)}(\bar{c}) = R_{yx}^{(\alpha^{-1})} R_{x_n y} R_{x_{n-1} x_n} \cdots R_{xx_1} \tag{6.9}$$

(4) If c is a cycle, $\mathcal{F}(c)$ is the set of all forests with roots on the cycle c , which span the whole graph X , deprived of the edges of the cycle, and $R(F)$ is given as in Eq. (6.6).

As a consequence $J_{xy}^{(\alpha)}$ is the sum of the contributions given by (6.5) and (6.7). We can obviously write this sum of two kinds of terms as a sum of type (6.7), provided we allow in $C(x, y)$ degenerate cycles $[x, y], [y, x]$ with a contribution

$$P_{xy}^{(\alpha)}([x, y], [y, x]) = R_{xy}^{(\alpha)} R_{yx}$$

$$P_{yx}^{(\alpha^{-1})}([y, x], [x, y]) = R_{yx}^{(\alpha^{-1})} R_{xy}$$

because in Eq. (6.5) $\frac{R(T)}{R_{yx}}$ (for $[y, x] \in T$) is a contribution of the type $R(F)$ for the forest F obtained by deleting $[y, x]$ from X . With this convention,

$$J_{xy}^{(\alpha)} = \frac{1}{Z} \sum_{c \in C(x, y)} (P_{xy}^{(\alpha)}(c) - P_{yx}^{(\alpha^{-1})}(\bar{c})) \sum_{F \in \mathcal{F}(c)} R(F) \tag{6.10}$$

We introduce an abbreviated notation for the variation of S during a transition α , starting from state $y \in X$

$$\begin{aligned} d^{(\alpha)}S(y) &= S(x, (\xi_\ell)) - S(y, (\eta_\ell)) \\ \alpha(y, (\eta_\ell)) &= (x, (\xi_\ell)). \end{aligned} \quad (6.11)$$

We take now a cycle

$$C = ([x, y], [y, x_n], \dots, [x_1, x])$$

and use the fact that

$$R_{x_{i+1}x_i} = \sum_{\alpha_i} R_{x_{i+1}x_i}^{(\alpha_i)} \quad (\text{Eq. (3.4)})$$

$$R_{x_{i+1}x_i}^{(\alpha_i)} = K_{x_{i+1}x_i}^{(\alpha_i)} \exp\left(\frac{1}{2}d^{(\alpha_i)}S(x_i)\right) \quad (\text{Eq. (5.1)})$$

so that

$$\begin{aligned} P_{xy}^{(\alpha)}(c) &= \sum_{\alpha_0, \dots, \alpha_n} K_{xy}^{(\alpha)} K_{yx_n}^{(\alpha_n)} \dots K_{x_1x}^{(\alpha_0)} \\ &\quad \times \exp\left[\frac{1}{2}(d^{(\alpha)}S(y) + d^{(\alpha_n)}S(x_n) + \dots + d^{(\alpha_0)}S(x))\right]. \end{aligned}$$

But by Eq. (5.2), we have

$$\begin{aligned} K_{xy}^{(\alpha)} &= K_{yx}^{(\alpha^{-1})} \\ d^{(\alpha^{-1})}S(x) &= -d^{(\alpha)}S(y) \end{aligned}$$

so that we obtain

$$\begin{aligned} &\frac{1}{2}(P_{xy}^{(\alpha)}(c) - P_{yx}^{(\alpha^{-1})}(\bar{c})) \\ &= \sum_{\alpha_1 \dots \alpha_{n+1}} K_{yx_n}^{(\alpha_{n+1})} \dots K_{x_1x}^{(\alpha_1)} K_{xy}^{(\alpha)} \\ &\quad \times \sinh\left[\frac{1}{2}(d^{(\alpha_{n+1})}S(x_n) + \dots + d^{(\alpha_1)}S(x_1) + d^{(\alpha)}S(y))\right]. \end{aligned} \quad (6.12)$$

We define now a cycle of transitions γ

$$\gamma = (\alpha_{n+1}, \alpha_n, \dots, \alpha_1, \alpha; y) \quad (6.13)$$

to be read from right to left, such that y is a point in X , indeed the initial point, and α, α_1, \dots are transitions so that

$$(\alpha_{n+1} \circ \alpha_n \circ \dots \circ \alpha_1 \circ \alpha)(y) = y.$$

A cycle as in (6.13) gives a cycle $c(\gamma)$ in X

$$c(\gamma) = ([x, y], [y, x_n], \dots, [x_1, x]) \tag{6.14}$$

but it is clear that in general the cycle γ contains more information than $c(\gamma)$, because γ specifies the nature of the transitions.

We shall denote by $\Gamma^{(\alpha)}(y)$ the set of cycles γ (initial point y and first transition α) as in Eq. (6.13) such that $c(\gamma)$ is a simple cycle (two points of $c(\gamma)$ are distinct).

We denote by $d_\gamma S$ the total variation of S over γ

$$d_\gamma S = d^{(\alpha_{n+1})}S(x_n) + \dots + d^{(\alpha_1)}S(x_1) + d^{(\alpha)}S(x). \tag{6.15}$$

Using this notation and Eq. (6.12), we see that Eq. (6.10) can be rewritten as

$$J_{xy}^{(\alpha)} = \frac{2}{Z} \sum_{\gamma \in \Gamma^{(\alpha)}(y)} (K_{yx_n}^{(\alpha_{n+1})} \dots K_{x_1x}^{(\alpha_1)} K_{xy}^{(\alpha)} \sinh(\frac{1}{2}d_\gamma S)) \sum_{F \in \mathcal{F}(c(\gamma))} R(F) \tag{6.16}$$

where in the sum,

$$\gamma = (\alpha_{n+1}, \dots, \alpha_1, \alpha; y).$$

We also allow $n = 0$, in which case $\gamma = (\alpha^{-1}, \alpha; y)$. We can now calculate the Carnot dissipation given by Eq. (5.3). Using the notation of Eq. (6.11), we have

$$\mathcal{D} = \frac{1}{2} \sum_{y, \alpha, x} d^{(\alpha)}S(y) J_{xy}^{(\alpha)}.$$

But using Eq. (6.16), we see immediately by rearranging the sums

$$\mathcal{D} = \frac{1}{Z} \sum_{\gamma} K_{yx_n}^{(\alpha_{n+1})} \dots K_{x_1x}^{(\alpha_1)} K_{xy}^{(\alpha)} (d_\gamma S) \sinh(\frac{1}{2}d_\gamma S) \sum_{F \in \mathcal{F}(c(\gamma))} R(F) \tag{6.17}$$

where now the sum is over all possible cycles

$$\gamma = (\alpha_{n+1}, \alpha_n, \dots, \alpha_1, \alpha; y). \tag{6.18}$$

But $x \sinh x$ is non-negative and equals zero only at $x = 0$, so that $\mathcal{D} \geq 0$ and is zero if and only if for each cycle γ , either $d_\gamma S = 0$ or the cycle has no weight, i.e., the product along the cycle of the matrix elements

$$R_{yx_n}^{(\alpha_{n+1})} \dots R_{xy}^{(\alpha)} = 0.$$

The expression (6.17) for \mathcal{D} can be rewritten as

$$\mathcal{D} = \sum_{\gamma} (d_{\gamma} S) I_{\gamma} \quad (6.19)$$

where I_{γ} is a net current along the cycle γ namely

$$I_{\gamma} = \frac{1}{Z} K_{yx_n}^{(\alpha_{n+1})} \dots K_{x_1 x}^{(\alpha_1)} K_{xy}^{(\alpha)} \sinh\left(\frac{1}{2} d_{\gamma} S\right) \sum_{F \in \mathcal{F}(c(\gamma))} R(F). \quad (6.20)$$

If we split the sinh function, we see that

$$I_{\gamma} = I_{\gamma}^{+} - I_{\gamma}^{-}.$$

Then

$$\frac{I_{\gamma}^{+}}{I_{\gamma}^{-}} = \exp(d_{\gamma} S).$$

We can interpret I_{γ} as the number of times a cycle γ is performed in a unit time step δt (see also, e.g., ref. 8 for a less general formalism, at a fixed temperature).

Near equilibrium, the $d^{(\alpha)} S$ are small and one can expand the sinh function to first order. One obtains as usual a quadratic expansion for \mathcal{D} (as in ref. 8)

$$\mathcal{D} \sim \frac{1}{2} \sum_{\gamma} k_{\gamma} (d_{\gamma} S)^2 \quad (6.21)$$

where

$$k_{\gamma} = \frac{1}{Z} K_{yx_n}^{(\alpha_{n+1})} \dots K_{xy}^{(\alpha)} \sum_{F \in \mathcal{F}(c(\gamma))} R(F).$$

We can interpret Eq. (6.20) as a diagonalization procedure for the quadratic form \mathcal{D} in terms of the $d_{\gamma} S$. We notice that each cycle γ contributes a positive term in the Carnot dissipation.

7. SWITCHING OFF RESERVOIRS

(a) We consider a stochastic dynamics as in Section 3, defined by the $R^{(\alpha)}$. Suppose that we suddenly switch off certain external transitions α .

Namely, we assume that one can express the set of external transitions as $A_{\text{ext}} = A'_{\text{ext}} \cup A''_{\text{ext}}$, and we define a new dynamics \tilde{R} by the formulas:

$$\begin{aligned} \tilde{R}^{(\alpha)} &= R^{(\alpha)} & \text{for } \alpha \in A'_{\text{ext}} \cup A^{\text{int}} \\ \tilde{R}^{(\alpha)} &= 0 & \text{for } \alpha \in A''_{\text{ext}}. \end{aligned} \tag{7.1}$$

We assume that if $\alpha \in A'_{\text{ext}}$ (resp. A''_{ext}), then also the inverse transition $\alpha^{-1} \in A'_{\text{ext}}$ (resp. A''_{ext}). The diagonal elements R_{xx} of R are modified accordingly (so as to restore $\sum_y R_{xy} = 1$).

We can define the relative entropy $S(p_s | \tilde{R}p_s)$ exactly as in Eq. (2.11) with the current

$$\tilde{J}_{xy}^{(p_s)} = \tilde{R}_{xy} p_s(y) - \tilde{R}_{yx} p_s(x).$$

where p_s is the stationary state of R . But we know that in the dynamics R , for the stationary state one has

$$\sum_y J_{xy}^{(p_s)} = 0$$

and

$$\tilde{R}_{xy} = \sum_{\substack{\alpha \in A'_{\text{ext}} \\ \alpha \text{ internal}}} R_{xy}^{(\alpha)} = R_{xy} - \sum_{\alpha \in A''_{\text{ext}}} R_{xy}^{(\alpha)}$$

so that

$$\begin{aligned} -\tilde{J}_{xy}^{(p_s)} &= \sum_{\alpha \in A''_{\text{ext}}} R_{xy}^{(\alpha)} p_s(y) - \sum_{\alpha \in A''_{\text{ext}}} R_{yx}^{(\alpha)} p_s(x) \\ &= \sum_{\alpha \in A''_{\text{ext}}} (R_{xy}^{(\alpha)} p_s(y) - R_{yx}^{(\alpha^{-1})} p_s(x)). \end{aligned}$$

Then from Eq. (2.11), we obtain

$$S(p_s | \tilde{R}p_s) = \frac{1}{2} \sum_x p_s(x) \left(\frac{1}{p_s(x)} \sum_y \sum_{\alpha \in A''_{\text{ext}}} J_{xy}^{(\alpha)(p_s)} \right)^2 + O(\delta t^3). \tag{7.2}$$

Here $\sum_{\alpha \in A''_{\text{ext}}} J_{xy}^{(\alpha)(p_s)}$ is the sum of currents of the dynamics R , due to the external transitions that have been switched off.

(b) Let us again split the set A_{ext} of external transition α , as $A_{\text{ext}} = A'_{\text{ext}} \cup A''_{\text{ext}}$ and define the quantity

$$\mathcal{D}_{A'} = \frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} J_{xy}^{(\alpha)} \log \left(\frac{R_{xy}^{(\alpha)} p_s(y)}{R_{yx}^{(\alpha^{-1})} p_s(x)} \right). \quad (7.3)$$

Here, as before, the splitting $A = A' \cup A''$ is such that if $\alpha \in A'$, then $\alpha^{-1} \in A'$ also. Clearly

$$\mathcal{D}_{A'} \geq 0. \quad (7.4)$$

As a consequence, we can expand the quantity $\mathcal{D}_{A'}$ as we did in Section 5, to obtain

$$\frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} d^{(\alpha)} S(y) J_{xy}^{(\alpha)} = \mathcal{D}_{A'} + \frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} (\Phi(x) - \Phi(y)) J_{xy}^{(\alpha)} \quad (7.5)$$

using the definition (6.11) of $d^{(\alpha)}$. But

$$d^{(\alpha)} S(y) = s(x) - s(y) + d^{(\alpha)} \left(\sum_{\ell} s_{\ell} \right) (y) \quad (7.6)$$

(we recall that by our assumption $d^{(\alpha)}(\sum_{\ell} s_{\ell})(y)$ depends only on y and α).

Thus we can rewrite (7.5) using the inequality (7.4) as

$$\begin{aligned} \frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} d^{(\alpha)} \left(\sum_{\ell} s_{\ell} \right) (y) J_{xy}^{(\alpha)} &= \mathcal{D}_{A'} + \frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} (\Phi(x) - s(x) - (\Phi(y) - s(y))) J_{xy}^{(\alpha)} \\ &\geq \frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} (\Phi(x) - s(x) - (\Phi(y) - s(y))) J_{xy}^{(\alpha)}. \end{aligned} \quad (7.7)$$

One can interpret the inequality (7.7) in two ways.

(1) In general, the variation of the entropies of the reservoirs associated with a subset A' of the external transitions is not a positive quantity. Only the total variation of the entropies of all reservoirs for all transitions is positive. Nevertheless, this variation of the entropies of the reservoirs associated with a subset A' of external transitions is bounded from below by the corresponding variation of the state function $\Phi - s$, where Φ is the information potential $\log p_s$ and s is the entropy state function of the system.

(2) A second interpretation is the following. Write $A_{\text{ext}} = A' \cup A''$ and, as in Eq. (7.1), define a new dynamics \tilde{R} obtained by switching off the transitions $\alpha \in A''$. The stationary state p_s of the initial dynamics R is no longer the stationary state of the new dynamics \tilde{R} , so that in the first time step δt , p_s starts to evolve. Then the quantity

$$\frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} (d^{(\alpha)}S)(y) J_{xy}^{(\alpha)} \tag{7.8}$$

is the variation in the first time step δt after the transitions $\alpha \in A''$ have been switched off, of the total entropy (system and its reservoirs), averaged over the stationary state (from which we were starting initially and which is beginning to be displaced by the new dynamics). This quantity (7.8) has no reason to be positive (heat, for example, will flow in or out). Nevertheless, it is always larger than the corresponding variation of the information potential

$$\frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} (d^{(\alpha)}S)(y) J_{xy}^{(\alpha)} \geq \frac{1}{2} \sum_{\substack{x, y \in X \\ \alpha \in A'}} (\Phi(x) - \Phi(y)) J_{xy}^{(\alpha)}. \tag{7.9}$$

8. NEAR DEGENERACY AND PHASE TRANSITIONS

In ref. 22, we developed a general theory of first order phase transitions for any stochastic dynamics. Our main result was the following: Let us assume that the stochastic matrix R has $r - 1$ real eigenvalues different from 1, but very close to 1, and that all the other eigenvalues are far from 1. Then the system X has r different phases which are long lived. Namely, one can find r disjoint subsets K_1, \dots, K_r of X and r probability distributions $p_1 \cdots p_r$ such that

- (i) the p_j are approximate eigenstates of R^s of eigenvalue 1 for s not too large.
- (ii) p_j is almost supported by K_j in the sense that the probability of $\complement K_j$ (the complementary set of K_j) for p_j is very small.
- (iii) the union of all $K_j, \cup_{j=1}^r K_j$, exhausts X , up to a set of very small probability for the stationary state p_s of X .

In this section we extend this result to the case when R has complex eigenvalues with modulus close to 1.

Let us assume that R has

- (i) $2m$ complex conjugate eigenvalues $\alpha_1, \alpha_1^*, \dots, \alpha_m, \alpha_m^*$, with complex eigenstates $u_1 + iv_1, \dots, u_m + iv_m$
- (ii) ℓ real eigenvalues $\beta_1, \dots, \beta_\ell$ (different from 1) with real eigenstates w_1, \dots, w_ℓ , and that the null space of these eigenvalues is exhausted by these eigenvectors (i.e., no Jordan form is needed for α or β).

We also assume that there exists an intermediate time scale t (t is an integer here) such that for all $1 \leq j \leq m$, all $1 \leq k \leq \ell$

- (i) $1 - |\alpha_j|^t$ and $1 - |\beta_k|^t$ are small of order ε
- (ii) $|\lambda'|^t \leq \varepsilon$ for all eigenvalues λ' different from the α_j 's and β_k 's.

Thus, the modulus of the eigenvalues of $R^t, \alpha_j^t, \alpha_j^{*t}, \beta_k^t$ are very close to 1, while the modulus of the other eigenvalues of R^t are far away from 1.

We assume also that there exist integers p_j and q_j such that

$$\alpha_j = |\alpha_j| \exp\left(\frac{2i\pi p_j}{q_j}\right) \quad (8.1)$$

and that $Q = \prod_{j=1}^p q_j \leq 0(t)$. Using the results of ref. 22, we see that the matrix R^Q has eigenvalues 1, $|\alpha_j|^Q, \beta_k^Q$ very close to 1, and the other eigenvalues λ^Q are far from 1, so that R^Q has a phase transition (in the sense of ref. 22), with $r = 2m + \ell + 1$ phases (each $|\alpha_j|^Q$ is doubly degenerate). We call p_1, \dots, p_r the states associated with these phases for R^Q . The construction of ref. 22 shows that the phases p_1, \dots, p_r are, up to a small vector (of the order of $|\lambda|^t$ for the eigenvalues λ of R different from the α_j and β_j), linear combinations of the stationary state p_s and the eigenstates u_j, v_j and w_k of the $|\alpha_j|^Q$ and β_k^Q .

Call V the vector space generated by p_1, \dots, p_r . Up to small error, R maps V into itself because V is essentially generated by p_s, u_j, v_j, w_k .

Moreover the eigenvalues of $R|_V$ are 1, α_j, α_j^* and β_k and thus $(R|_V)^Q$ has eigenvalues 1, $|\alpha_j|^Q, |\beta_j|^Q$ which are 1 up to ε . That is,

$$(R|_V)^Q \simeq \text{Id}_V + O(\varepsilon) \quad (\varepsilon \text{ definition Eq. (8.1)}). \quad (8.2)$$

Now consider the set $\Phi = \{p_1, \dots, p_r\}$ of the r phases of R^Q . We want to prove that $R|_V$ induces a stochastic matrix C on the set Φ , modulo ε . We know that for all $1 \leq k \leq r$

$$Rp_k \equiv (R|_V) p_k = \sum_{j=1}^r c_{jk} p_j + O(\varepsilon) \quad (8.3)$$

We must prove that up to $O(\varepsilon)$:

- (i) $0 \leq c_{jk} \leq 1$
- (ii) $\sum_{j=1}^r c_{jk} = 1$

(i) The probability distributions p_j are supported by disjoint subsets S_j , $j = 1, \dots, r$ of X , up to error ε . So if we take the value of Eq. (8.3) at x and sum over $x \in S_{j_0}$, we obtain

$$\sum_{x \in S_{j_0}} (Rp_k)(x) = \sum_{j=1}^r c_{jk} \sum_{x \in S_{j_0}} p_j(x) \pmod{\varepsilon}$$

The first member of this equation is a real number between 0 and 1, because p_k is a probability distribution and R is stochastic, and the second member is $c_{j_0k} \pmod{\varepsilon}$, so that

$$0 \leq c_{j_0k} \leq 1 \pmod{\varepsilon}$$

(ii) Now let us take the value of Eq. (8.3) at x and sum over all $x \in X$. We obtain

$$1 = \sum_{x \in X} (Rp_k)(x) = \sum_{j=1}^r c_{jk} \sum_{x \in X} p_j(x) = \sum_{j=1}^r c_{jk} + O(\varepsilon)$$

so that we have proved that (c_{jk}) is stochastic matrix (indexed by the set Φ of the phases), at least, up to terms $O(\varepsilon)$. The stationary probability distribution p_s is in V so that one can find real numbers, π_1, \dots, π_r with

$$p_s(x) = \sum_{j=1}^r \pi_j p_j(x) + O(\varepsilon).$$

By summing over $x \in X$, we have

$$\sum_{j=1}^r \pi_j = 1 + O(\varepsilon)$$

and by summing over $x \in S_j$, we have $\sum_{x \in S_j} p_s(x) = \pi_j + O(\varepsilon)$ ($\text{supp } p_j \subset S_j$) so that $0 \leq \pi_j \leq 1$ up to $O(\varepsilon)$ terms.

Moreover the vector $\pi = (\pi_j)_{j=1 \dots r}$ is the right eigenvector of eigenvalue 1 of the matrix $C = (c_{jk})$ and is a probability distribution. Indeed π_j is the stationary probability of phase number j :

$$\pi_j = \sum_{x \in S_j} p_s(x) + O(\varepsilon). \tag{8.4}$$

Let $q = (q_j)_{j=1, \dots, r}$ be any probability distribution on the set Φ of the r phases and let us calculate $S(q|\pi)$. The fundamental property of S (Eq. (2.9)) implies that in the evolution C on the set of phases

$$S(q|\pi) \geq S(Cq|\pi) \geq \dots \geq S(C^{\mathcal{Q}}q|\pi) \simeq S(q|\pi).$$

This follows because $C^{\mathcal{Q}} \simeq \text{Id}_V + O(\varepsilon)$, due to Eq. (8.2), and the fact that C is $R|_V$ in the basis of the p_j , using Eq. (8.3). This means that for any probability distribution q on the set of phases Φ

$$S(q|\pi) \simeq S(Cq|\pi) + O(\varepsilon). \quad (8.5)$$

From these results, we shall conclude that R induces on the set of phases Φ , up to error ε , a stochastic matrix which is a permutation of the phases.

To prove this, we need the following lemma.

Lemma. let X be a finite set, M a stochastic matrix on X such that for any probability distribution q on X

$$S(q|q_s) = S(Mq|q_s) \quad (8.6)$$

where q_s is the stationary state of M . Then M is a permutation matrix (assuming $q_s(x) \neq 0$ for all $x \in X$).

Proof of the Lemma. Take for $q(x) = \delta_{x,y}$ for a given $y \in X$, so that equality (8.6) means

$$-\log q_s(y) = \sum_x M_{xy} \log \frac{M_{xy}}{q_s(x)}.$$

Using the fact that $\sum M_{xy} = 1$, because M is stochastic, one obtains

$$\sum_x M_{xy} \log M_{xy} = \sum_x M_{xy} \log \frac{q_s(x)}{q_s(y)}. \quad (8.7)$$

Now take for y a point x_0 in X with

$$q_s(x_0) = \min_{x \in X} q_s(x).$$

So the second member of Eq. (8.7) is obviously ≥ 0 while the first member is obviously ≤ 0 ; therefore they are both 0, which means that each term (≥ 0) of the second member of Eq. (8.7) is 0, and each term (≤ 0) of the first member of Eq. (8.7) is 0. This implies that for all $x \in X$, $M_{xx_0} = 0$ or 1,

so that there is only a single x_1 with $M_{x_1x_0} = 1$ and for $x \neq x_1$, $M_{xx_0} = 0$. Moreover $q_s(x_1) = q_s(x_0)$.

If $x_1 = x_0$, $\{x_0\}$ is a trivial cycle by itself and we can remove x_0 from X and use a recursion argument.

If $x_1 \neq x_0$, we apply Eq. (8.7) to $y = x_1$ and by the same argument as before (also using the fact that $q_s(x_1) = q_s(x_0)$, so that $\log[q_s(x_0)/q_s(x_1)] = 0$), we deduce that there is a (unique) x_2 with

$$M_{x_2x_1} = 1, \quad M_{xx_1} = 0, \quad x \neq x_2$$

$$q_s(x_2) = q_s(x_1) = q_s(x_0).$$

Now $x_2 \neq x_1$, because if $x_2 = x_1$ we would have

$$q_s(x_1) \geq M_{x_1x_2}q_s(x_2) + M_{x_1x_0}q_s(x_0) = 2q_s(x_0),$$

which is impossible.

If $x_2 = x_0$, then $\{x_1, x_0\}$ is a cycle and we can remove $\{x_1, x_0\}$ from X and use recursion.

If $x_2 \neq x_0$, we apply Eq. (8.7) to $y = x_2$ and use $\log[q_s(x_0)/q_s(x_2)] = \log[q_s(x_1)/q_s(x_2)] = 0$. Then there is a unique x_3 with

$$M_{x_3x_2} = 1, \quad M_{xx_2} = 0, \quad x \neq x_3$$

$$q_s(x_3) = q_s(x_2) = q_s(x_1) = q_s(x_0).$$

etc...

Finally, we see that for any y , there exists a unique x with

$$M_{xy} = 1, \quad M_{zy} = 0 \quad (z \neq x)$$

So M is a permutation matrix.

9. CREATION AND DISSIPATION OF RESOURCES

In this section, we make more specific assumptions about the system and its reservoirs and interpret various quantities.

Assume that there exists a set \mathcal{A} of state functions $f_\lambda(x)$ defined on the state space X of the system, for $\lambda \in \mathcal{A}$. These functions are “resources,” for example energy in a physical system or water in an ecological system. Assume also that any reservoir Ω_ℓ , $1 \leq \ell \leq r$, is associated with a function $f_{\lambda(\ell)}$ for a certain λ (ℓ), so that $\lambda(\bullet)$ is a mapping

$$\lambda(\bullet): \{1, \dots, r\} \rightarrow \mathcal{A}.$$

Hypothesis 3. We assume that for any $1 \leq \ell \leq r$, $f_{\lambda(\ell)}$ is also a state function on the space Ω_ℓ of the reservoir ℓ and that the value of $f_{\lambda(\ell)}$ characterizes the state ξ_ℓ of Ω_ℓ . In particular, the entropy $s_\ell(\xi_\ell)$ of Ω_ℓ , is a function $s_\ell(f_{\lambda(\ell)})$.

Hypothesis 4. We assume that each external transition $\alpha \in A_{\text{ext}}$ is associated with a specific reservoir $\Omega_{\ell(\alpha)}$; in other words, it is a transition of type $\ell(\alpha)$ so that during the transition α , the state y of the system X and the state $\eta_{\ell(\alpha)}$ of the reservoir $\Omega_{\ell(\alpha)}$ vary, and the other reservoirs do not vary. Thus

$$\alpha: (y, (\eta_\ell)) \rightarrow (x, (\xi_\ell)) \quad (9.1)$$

with $\xi_\ell = \eta_\ell$ for $\ell \neq \ell(\alpha)$. Moreover, we assume that during the transition, α , defined as in (9.1), $f_{\lambda(\ell(\alpha))}$ is a conserved quantity, so that

$$f_{\lambda(\ell(\alpha))}(x) - f_{\lambda(\ell(\alpha))}(y) = f_{\lambda(\ell(\alpha))}(\eta_{\ell(\alpha)}) - f_{\lambda(\ell(\alpha))}(\xi_{\ell(\alpha)}) \quad (9.2)$$

where $(y, (\eta_\ell)) = (x, (\xi_\ell))$.

We comment briefly these two hypotheses. The whole system + reservoirs has certain resources which are measured by state functions f_λ ($\lambda \in A$). Each reservoir Ω_ℓ is the reservoir of a specific resource $\lambda(\ell)$ and the amount of that resource in the reservoir Ω_ℓ characterizes the state ξ_ℓ of the reservoir. In particular, the entropy s_ℓ of Ω_ℓ is a function of the amount of associated resource in the reservoir Ω_ℓ . We also assume that each external transition $\alpha \in A_{\text{ext}}$ couples the system to a single reservoir $\Omega_{\ell(\alpha)}$ and the corresponding resource $f_{\lambda(\ell(\alpha))}$ is conserved during the transition α . This means that external transitions are processes of exchange or transport of the corresponding resource between the system X and the reservoir $\Omega_{\ell(\alpha)}$ to which X is coupled during the transition α . We introduce an abbreviated notation:

$$\lambda(\alpha) \equiv (\lambda(\ell(\alpha))) \quad \text{for } \alpha \in A_{\text{ext}}. \quad (9.3)$$

We do not assume, at first, that there are conserved quantities. In particular, during the internal transition $\alpha \in A_{\text{int}}$, the state functions f_λ may, in general, vary.

Remark. These two hypotheses may not be valid. An external transition could couple the system to several reservoirs simultaneously, and the conserved quantities, during that transition, could themselves be functions of the various f_λ of the reservoirs.

The inequality $\mathcal{D} \geq 0$ for the Carnot dissipation can be rewritten by summing over the resources f_λ . We obtain

$$\sum_\lambda \sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} s_{\ell(\alpha)}(f_\lambda)(\eta_{\ell(\alpha)}) \geq 0 \tag{9.4}$$

with

$$d^{(\alpha)} s_\ell(f_\lambda)(\eta_\ell) = s_\ell(f_\lambda(\xi_\ell)) - s_\ell(f_\lambda(\eta_\ell)) \tag{9.5}$$

where $\alpha(y, (\eta_\ell)) = (x, (\xi_\ell))$ is the transition. Moreover, we also obtain a lower bound, as a particular case of inequality (7.7), by fixing a certain $\lambda \in \mathcal{A}$ and summing over all external transitions $\alpha \in A_{\text{ext}}^{(\lambda)}$ such that $\lambda(\alpha) = \lambda$.

$$\sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} s_{\ell(\alpha)}(f_\lambda)(\eta_\ell) \geq \sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} (\Phi - s)(y). \tag{9.6}$$

On the other hand, $f_\lambda(x)$ is a state function on X and it varies only during external transitions $\alpha \in A_{\text{ext}}^{(\lambda)}$ with $\lambda(\alpha) = \lambda$ and possibly during internal transitions $\alpha \in A_{\text{int}}$. So

$$\sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} f_\ell(y) + \sum_{\substack{\alpha \in A_{\text{int}} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} f_\lambda(y) = 0. \tag{9.7}$$

The second sum in Eq. (9.7) is the internal production of the resource f_λ inside the system X during internal transitions, while the first sum in Eq. (9.7) is the net variation of the resource f_λ due to the coupling to the reservoirs associated with the resource f_λ .

During the transition $\alpha: (y, (\eta_\ell)) \rightarrow (x, (\xi_\ell))$ one has

$$d^{(\alpha)} f_\lambda(y) = -d^{(\alpha)} f_\lambda(\eta_\ell) \tag{9.8}$$

so that

$$\sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x, y}} J_{xy}^{(\alpha)} d^{(\alpha)} f_\lambda(\eta_\ell) = \sum_{\substack{\alpha \in A_{\text{int}} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} f_\lambda(y). \tag{9.9}$$

Equations (9.6)–(9.9) are generalized forms of Carnot efficiency inequalities for the resource f_λ .

Finally Eq. (9.6) can be rewritten as

$$\sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} \Phi \leq \sum_{\substack{\{\alpha: \lambda(\alpha)=\lambda\} \\ x, y \in X}} J_{xy}^{(\alpha)} d^{(\alpha)} S(y, (\eta_\ell)). \tag{9.10}$$

This says that the variation of the information potential during certain external transitions is less than the variation of total entropy during the same transitions.

10. EXAMPLES AND APPLICATIONS; HEAT AND WORK

Example 1. Detailed balance systems.

In detailed balance systems, at equilibrium, all transitions have a zero current by definition. The dissipation, or partial dissipations are all 0. Nothing happens at equilibrium.

Example 2. Reaction diffusion systems at a fixed temperature.

These systems have been considered in refs. 10 and 12. The state space of the system is characterized by the number of particles of various chemical species, possibly in different cells. The reservoirs are reservoirs of certain species at a given temperature β^{-1} and given chemical potentials, and there is also a reservoir of energy at temperature β^{-1} . So, there are chemical species $i = 1, \dots, s$ and chemical species $\ell = 1, \dots, r$ whose number of particles are denoted by x_i and a_ℓ respectively. An element of the state space is $((x_i)_{i=1, \dots, s}, (a_\ell)_{\ell=1, \dots, r})$. For any ℓ , there is a single reservoir Ω_ℓ with state ξ_ℓ which is the number of particles of species ℓ in the reservoir Ω_ℓ . The entropy of Ω_ℓ is

$$s_\ell(\xi_\ell) = \beta m_\ell \xi_\ell \quad (10.1)$$

where β^{-1} is the temperature, m_ℓ is the chemical potential of species ℓ in the reservoir Ω_ℓ . The resource corresponding to Ω_ℓ is $f_\ell(x, a) = a_\ell$.

There is also an energy reservoir Ω_0 . Its state ξ_0 is an energy content and its entropy is

$$s_0(\xi_0) = \beta \xi_0 \quad (10.2)$$

The corresponding resource $f_0(x, a)$ is a state function corresponding to the internal energy. The free energy is

$$F(x, a) = f_0(x, a) - \beta^{-1} s(x, a) \quad (10.3)$$

where $s(x, a)$ is the entropy of the system. There are two kinds of transitions:

(i) transitions α_ℓ^\pm of exchange of a particle of species ℓ between the system and the reservoir Ω_ℓ .

$$\alpha_\ell^{\pm 1}((y, b), (\eta_\ell)_{\ell \geq 0}) \rightarrow ((x, a), (\xi_\ell)_{\ell \geq 0}) \quad (10.4)$$

with

$$\begin{aligned} x_i &= y_i \\ a_k &= b_k \quad (k \neq \ell) \quad a_\ell = b_\ell \pm 1 \\ \xi_k &= \eta_k \quad (k \neq \ell) \quad \xi_\ell = \eta_\ell \mp 1. \end{aligned}$$

During the transition α_ℓ the variation of the total entropy is

$$s(x, a) - s(y, b) - \beta m_\ell$$

and we have

$$\frac{R_{(x, a), (y, b)}^{(\alpha_\ell)}}{R_{(y, b), (x, a)}^{(\alpha_\ell^{-1})}} = \exp(s(x, a) - s(y, b) - \beta m_\ell) \quad (10.5)$$

(ii) There are also chemical reactions inside the system which change the number of particles x_i and a_ℓ . These reactions induce a variation of the energy content of the system which is then exchanged with the energy reservoir. There is no exchange of particles with the reservoir. For a chemical reaction:

$$\alpha: ((y, b), (\eta_\ell)_{\ell \geq 0}) \rightarrow ((x, a), (\xi_\ell)_{\ell \geq 0}) \quad (10.6)$$

we see that the differences $x_i - y_i$, $a_\ell - b_\ell$ are given by the stoichiometric numbers of the reaction. We have also $\xi_\ell = \eta_\ell$ for $\ell \geq 1$, but $\xi_0 - \eta_0 =$ energy released by the reaction $= f_0(y, b) - f_0(x, a)$. The total entropy of $((y, b), (\eta_\ell)_{\ell \geq 0})$ is

$$s(y, b) + \beta \eta_0 + \beta \sum_{\ell \geq 1} m_\ell \eta_\ell$$

and the variation of the total entropy in the process α is

$$s(x, a) - s(y, b) + \beta(f_0(y, b) - f_0(x, a)) = \beta(F(y, b) - F(x, a)).$$

Thus

$$\frac{R_{(x, a), (y, b)}^{(\alpha)}}{R_{(y, b), (x, a)}^{(\alpha^{-1})}} = \exp(\beta(F(y, b) - F(x, a))). \quad (10.7)$$

In the absence of reservoirs Ω_ℓ of species $\ell \geq 1$, but in presence of the reservoirs of energy Ω_0 , the only processes are the chemical processes related by Eq. (10.7). So the system reaches the thermal equilibrium distribution $\exp(-\beta F(x, a))$ and is in detailed balance. The role of the reservoirs $(\Omega_\ell)_{\ell > 1}$ of species ℓ , is to maintain the chemical potential m_ℓ of species ℓ constant in the stationary state of the system. If the imposed value m_ℓ is not the chemical potential $\frac{\partial F}{\partial a_\ell}$ at the minimum of the free energy F , the system will reach a stationary state which is not an equilibrium state.

It is easy, for such species ℓ , to rewrite inequality (9.6). There is only one exchange process with the reservoirs, which changes species ℓ , which is α_ℓ . During α_ℓ , s_ℓ varies by $-\beta m_\ell$. The inequality (9.6) can therefore be rewritten as

$$-\beta m_\ell \sum_{\substack{(y, b) \in X \\ (x, a) \in X}} J_{(x, a), (y, b)}^{(\alpha_\ell)} \geq \sum_{\substack{(y, b) \in X \\ (x, a) \in X}} J_{(x, a), (y, b)}^{(\alpha_\ell)} \delta^{(\alpha_\ell)}(\Phi - s)(y, b). \quad (10.8)$$

For the energy reservoir we obtain:

$$\beta \sum_{\substack{\alpha \text{ chemical} \\ (y, b) \in X \\ (x, a) \in X}} J_{(x, a), (y, b)}^{(\alpha)} (f_0(y, b) - f_0(x, a)) \geq \sum_{\substack{\alpha \text{ chemical} \\ (y, b) \in X \\ (x, a) \in X}} J_{(x, a), (y, b)}^{(\alpha)} \delta^{(\alpha)}(\Phi - s)(y - s) \quad (10.9)$$

where, in these two inequalities we define as usual

$$(\delta^{(\alpha)}g)(y, b) = g(x, a) - g(y, b).$$

The total dissipation \mathcal{D} in the stationary state is the sum of the first members of inequalities (10.8) and (10.9). Because the sum of the second members is zero, due to the fact that $\Phi - s$ is a state function, we see that $\mathcal{D} \geq 0$, as we already know. Moreover, we can also rewrite inequality (10.9) as

$$\sum_{\substack{\alpha \text{ chemical} \\ (y, b) \in X \\ (x, a) \in X}} J_{(x, a), (y, b)}^{(\alpha)} (\delta^{(\alpha)}\Phi)(y, b) \leq -\beta \sum_{\substack{\alpha \text{ chemical} \\ (y, b) \in X \\ (x, a) \in X}} J_{(x, a), (y, b)}^{(\alpha)} (\delta^{(\alpha)}F)(y, b). \quad (10.10)$$

The variation of the information potential during chemical processes is less than the variation of the free energy.

Remark. The situation of homogeneous reaction-diffusion system at a fixed temperature was discussed at length in refs. 10 and 12 but with the following differences.

(1) time was a continuous rather than a discrete variable.

(2) we discussed the situation of large volume asymptotics so that the numbers of particles are replaced by concentrations (taking continuous values). In this context, we obtained more specific properties for the information potential which are not in general valid for a discrete system (see also Section 1 above for motivation). We could also study the relaxation to the stationary (non-equilibrium state) and derive a general inequality relating the rate of dissipation and the rate of variation of the information potential.

Inhomogeneous reaction-diffusion systems (with several temperatures and fixed chemical potentials) will be discussed elsewhere.

Example 3. The Carnot engine.

In the Carnot engine, the system X is coupled to three energy reservoirs $\Omega_1, \Omega_2, \Omega_\infty$. The only resource $f_0(x)$ is an energy variable, which can be exchanged with the reservoirs. The variables of the reservoirs are ξ_1, ξ_2, ξ_∞ with the entropies:

$$s_1(\xi_1) = \beta_1 \xi_1 \quad s_2(\xi_2) = \beta_2 \xi_2 \quad s_\infty(\xi_\infty) = 0.$$

The system has both internal transitions (which conserve the energy $f_0(x)$) and external transitions with the reservoirs. Recalling that the dissipation in the stationary state \mathcal{D} is non-negative, we obtain

$$\sum_{\substack{y \in X \\ x \in X}} J_{xy}^{(\alpha_1)} \delta^{(\alpha_1)} s_1 + \sum_{\substack{y \in X \\ x \in X}} J_{xy}^{(\alpha_2)} \delta^{(\alpha_2)} s_2 \geq 0. \tag{10.11}$$

where α_1, α_2 are the transitions coupling X to the reservoirs Ω_1, Ω_2 . Moreover because f_0 does not vary during the internal transitions, in the stationary state we have

$$0 = \sum_{\substack{y \in X \\ x \in X}} J_{xy}^{(\alpha_1)} \delta^{(\alpha_1)} f_0(y) + \sum_{\substack{y \in X \\ x \in X}} J_{xy}^{(\alpha_2)} \delta^{(\alpha_2)} f_0(y) + \sum_{\substack{y \in X \\ x \in X}} J_{xy}^{(\alpha_\infty)} \delta^{\alpha_\infty} f_0(y). \tag{10.12}$$

With obvious notation, this can be rewritten as

$$0 = \delta_1 Q_1 + \delta_2 Q_2 + \delta_\infty W \tag{10.13}$$

where $\delta_1 Q_1$ (resp. $\delta_2 Q_2$, resp. $\delta_\infty W$) is the energy gained by X in the transition coupling X to Ω_1 (resp. to Ω_2 , resp. to Ω_∞) and inequality (10.11) is thus

$$-\beta_1 \delta_1 Q_1 - \beta_2 \delta_2 Q_2 = \mathcal{D} \geq 0. \quad (10.14)$$

Assume $\beta_1 < \beta_2$. By eliminating $\delta_2 Q_2$ between (10.13) and (10.14) we obtain the Carnot inequality

$$-\delta_\infty W = \left(\frac{\beta_2 - \beta_1}{\beta_2} \right) \delta_1 Q_1 - \frac{\mathcal{D}}{\beta_2} \leq \frac{\beta_2 - \beta_1}{\beta_2} \delta_1 Q_1 \quad (10.15)$$

($-\delta_\infty W$ is the work that can be extracted from the engine and $\delta_1 Q_1$ is the heat coming from the hot reservoir).

In fact, from inequality (9.6), we obtain

$$-\beta_1 \delta_1 Q_1 - \beta_2 \delta_2 Q_2 \geq (\delta_1 + \delta_2)(\Phi - s) \quad (10.16)$$

where $(\delta_1 + \delta_2)(\Phi - s)$ is the variation of $\Phi - s$ during the external transitions coupling X to the energy reservoirs Ω_1, Ω_2 . From this we deduce

$$-\delta_\infty W \leq \frac{1}{\beta_2} (\delta_1 + \delta_2)(s - \Phi) + \frac{\beta_2 - \beta_1}{\beta_2} \delta_1 Q_1. \quad (10.17)$$

In case $(\delta_1 + \delta_2)(s - \Phi) \leq 0$, this would provide a worse bound than the usual Carnot estimate

$$-\delta_\infty W \leq \frac{\beta_2 - \beta_1}{\beta_2} \delta_1 Q_1.$$

It can happen that $\delta_\infty W \geq 0$, so that the system X receives work from the reservoir Ω_∞ . In this case, the Carnot engine is a refrigerator. But in any case, the dissipation \mathcal{D} is positive.

Example 4. Three-state systems.

(a) Generalities. We consider here the simplest systems which can present non-trivial currents, namely three-state systems. Although they are simple, there are surprises. The states of the system X are labelled $\{1, 2, 3\}$. The stochastic matrix is R_{xy} and the stationary state is

$$\begin{aligned}
 p_s(1) &= \frac{1}{Z} (R_{12}R_{23} + R_{13}R_{32} + R_{12}R_{13}) \\
 p_s(2) &= \frac{1}{Z} (R_{21}R_{13} + R_{23}R_{31} + R_{21}R_{23}) \\
 p_s(3) &= \frac{1}{Z} (R_{31}R_{12} + R_{32}R_{21} + R_{31}R_{32})
 \end{aligned} \tag{10.18}$$

here Z is the normalization factor. The current of the total transition $i \rightleftharpoons j$ is J_{12}

$$\begin{aligned}
 J_{12} &= (R_{12}p_s(2) - R_{21}p_s(1)) \\
 J_{12} &= \frac{1}{Z} (R_{12}R_{23}R_{31} - R_{13}R_{32}R_{21}) \quad \text{and} \\
 J_{12} &= J_{23} = J_{31} \quad (\text{by conservation of currents}).
 \end{aligned}$$

We shall denote:

$s(x)$ the entropy of the state x

$e(x)$ the energy of the state x (it will be the only resource of the system and its reservoirs).

$\Omega_a, \Omega_b, \Omega_\infty$ the energy reservoirs at temperature $\beta_a^{-1}, \beta_b^{-1}$ and the work reservoir respectively. Ω_a has entropy $\beta_a e_a$, Ω_b has entropy $\beta_b e_b$ (e_a and e_b are the energies of Ω_a and Ω_b), and Ω_∞ has entropy 0.

In all situations, the transitions will be external transitions with one of the reservoirs and they conserve energy.

(b) 1st situation: a single cycle.

We assume that $1 \rightleftharpoons 2$ is at temperature β_a^{-1} , $2 \rightleftharpoons 3$ is at temperature β_b^{-1} , $3 \rightleftharpoons 1$ is the work transition, so that we can define

$$\begin{aligned}
 R_{21} &= a \exp\left(\frac{1}{2}(s_{21} - \beta_a e_{21})\right) \\
 R_{12} &= a \exp\left(\frac{1}{2}(s_{12} - \beta_a e_{12})\right) \\
 R_{32} &= b \exp\left(\frac{1}{2}(s_{32} - \beta_b e_{32})\right) \\
 R_{23} &= b \exp\left(\frac{1}{2}(s_{23} - \beta_b e_{23})\right) \\
 R_{31} &= c \exp\left(\frac{1}{2}s_{31}\right) \\
 R_{13} &= c \exp\left(\frac{1}{2}s_{13}\right)
 \end{aligned}$$

Here $s_{xy} = s(x) - s(y)$, $e_{xy} = e(x) - e(y)$. The current is

$$J_{21} = \frac{2abc}{Z} \sinh \left[\frac{1}{2} (\beta_b e_{23} + \beta_a e_{12}) \right] = J_{32} = J_{13}. \quad (10.19)$$

In the transition $1 \rightarrow 2$, the variation of the entropy of the reservoir Ω_a is $\beta_a e_{12}$ and in the transition $2 \rightarrow 3$, the variation of the entropy of Ω_b is $\beta_b e_{23}$. The total Carnot dissipation is thus:

$$\mathcal{D} = \frac{2abc}{Z} (\beta_b e_{23} + \beta_a e_{12}) \sinh \left(\frac{1}{2} (\beta_b e_{23} + \beta_a e_{12}) \right) \quad (10.20)$$

which is obviously positive.

Assume that $\beta_a < \beta_b$ (Ω_a is the hot reservoir)

$$\delta_a Q_a = e_{21} J_{21}$$

$$\delta_\infty W = e_{13} J_{13} = e_{13} J_{21}.$$

Let us assume that $e(2) > e(1)$, so $e_{21} > 0$. Then $J_{21} > 0$ if $\beta_b e_{23} + \beta_a e_{12} > 0$, and $\delta_\infty W < 0$ if $e(1) < e(3)$. The Carnot efficiency is

$$\eta \equiv \frac{|\delta_\infty W|}{\delta_a Q_a} = \frac{e_{31}}{e_{21}}. \quad (10.21)$$

Because $(\beta_b - \beta_a) e_{21} + \beta_b e_{13} > 0$, we see that

$$\eta < \frac{\beta_b - \beta_a}{\beta_b}.$$

We could also have $e_{21} > 0$ but $J_{21} < 0$, in which case the work is > 0 and $\delta_a Q_a < 0$, so that the three state system functions as a refrigerator.

(c) 2nd situation: three cycles.

Let us assume that $\beta_a < \beta_b$ and the transitions $1 \rightleftharpoons 2$, $2 \rightleftharpoons 3$ are external transitions with the reservoir Ω_a , so

$$\begin{cases} R_{xy}^{(a)} = a \exp\left(\frac{1}{2}(s_{xy} - \beta_a e_{xy})\right) \\ (x, y) = (1, 2), (2, 1), (2, 3), (3, 1) \end{cases} \quad (10.22)$$

On the other hand the transitions $1 \rightleftharpoons 3$ are of two types: a transition with the reservoir Ω_b

$$R_{xy}^{(b)} = b \exp\left(\frac{1}{2}(s_{xy} - \beta_b e_{xy})\right) \quad (10.23)$$

$$(x, y) = (1, 3), (3, 1)$$

or transition with the reservoir Ω_∞ (work transition)

$$R_{xy}^{(W)} = c \exp\left(\frac{1}{2}s_{xy}\right) \quad (x, y) = (1, 3), (3, 1) \quad (10.24)$$

so that

$$R_{xy} = R_{xy}^{(b)} + R_{xy}^{(W)} \quad (x, y) = (1, 3), (3, 1).$$

In this case, there are three cycles. After calculation we obtain

$$J_{12} = J_{23} = \frac{1}{Z} (R_{23}R_{31}R_{12} - R_{32}R_{21}R_{13}) \quad (10.25)$$

$$J_{12} = J_{23} = \frac{2}{Z} \left[a^2 b \sinh\left(\frac{1}{2}(\beta_b - \beta_a) e_{13}\right) + a^2 c \sinh\left(\frac{1}{2}\beta_a e_{31}\right) \right]$$

One can also obtain the current of the transition $1 \rightleftharpoons 3$ with the reservoir at temperature β_b^{-1}

$$J_{13}^{(b)} = R_{13}^{(b)} p_s(3) - R_{31}^{(b)} p_s(1)$$

$$= \frac{1}{Z} [(R_{13}^{(b)} R_{31}^{(W)} - R_{31}^{(b)} R_{13}^{(W)})(R_{32} + R_{12}) + R_{13}^{(b)} R_{32} R_{21} - R_{31}^{(b)} R_{12} R_{23}]$$

or after calculation

$$J_{13}^{(b)} = \frac{2}{Z} \left[abc \sinh\left(\frac{\beta_b e_{31}}{2}\right) \left(\exp\left(\frac{1}{2}s_{32} - \frac{\beta_a}{2} e_{32}\right) + \exp\left(\frac{1}{2}s_{12} - \frac{\beta_a}{2} e_{12}\right) \right) + a^2 b \sinh\left(\frac{\beta_b - \beta_a}{2} e_{31}\right) \right]. \quad (10.26)$$

The variation of entropy of the reservoir Ω_a is

$$-(J_{21}\beta_a e_{21} + J_{23}\beta_a e_{23}) = J_{23}\beta_a e_{31}.$$

The variation of entropy of the reservoir Ω_b is

$$-J_{13}^{(b)} \beta_b e_{13}.$$

The total Carnot dissipation is thus

$$\mathcal{D} = e_{31}(\beta_a J_{23} + \beta_b J_{13}^{(b)}).$$

Using Eqs. (10.25) and (10.26), we obtain

$$\begin{aligned} \mathcal{D} = \frac{2}{Z} \left[abc \beta_b e_{31} \sinh \left(\frac{\beta_b e_{31}}{2} \right) \left(\exp \left(\frac{1}{2} s_{32} - \frac{\beta_a}{2} e_{32} \right) + \exp \left(\frac{1}{2} s_{12} - \frac{\beta_a}{2} e_{12} \right) \right) \right. \\ \left. + a^2 c \beta_a e_{31} \sinh \left(\frac{\beta_a e_{31}}{2} \right) + a^2 b (\beta_b - \beta_a) e_{31} \sinh \left(\frac{1}{2} (\beta_b - \beta_a) e_{31} \right) \right]. \end{aligned} \quad (10.27)$$

\mathcal{D} is indeed positive; in fact each term of Eq. (10.27) is positive. Each term corresponds to one of the three cycles.

The current $J_{13}^{(W)} = R_{13}^{(W)} p_s(3) - R_{31}^{(W)} p_s(1)$ of the work transition is obtained using the conservation law for currents in the stationary state (at state 3).

$$J_{13}^{(W)} = -(J_{23} + J_{13}^{(b)}).$$

We obtain from Eqs. (10.25) and (10.26)

$$\begin{aligned} J_{13}^{(W)} = -\frac{2}{Z} \left[(abc) \sinh \left(\frac{\beta_b e_{31}}{2} \right) \left(\exp \left(\frac{1}{2} s_{32} - \frac{\beta_a}{2} e_{32} \right) \right. \right. \\ \left. \left. + \exp \left(\frac{1}{2} s_{12} - \frac{\beta_a}{2} e_{12} \right) \right) + a^2 c \sinh \left(\frac{1}{2} \beta_a e_{31} \right) \right]. \end{aligned} \quad (10.28)$$

The work exchanged between the system and Ω_∞ , is

$$\delta_\infty W = e_{13} J_{13}^{(W)}$$

so that $\delta_\infty W > 0$. This means that the system is always extracting work from the reservoir Ω_∞ .

We also see that if $\beta_b > \beta_a$ (Ω_∞ is the hot reservoir), the heat exchanged with Ω_b is

$$\delta_b Q_b = e_{13} J_{13}^{(b)} < 0 \quad (\text{see Eq. (10.26)})$$

while the heat exchanged with Ω_a is

$$\delta_a Q_a = e_{13} J_{23} < 0 \quad (\text{see Eq. (10.25)})$$

and the system pumps work and transforms it into heat in both reservoirs (if $\beta_b > \beta_a$). On the other hand if $\beta_b < \beta_a$, $\delta_\infty W > 0$ (the system pumps work) but it may work as a refrigerator.

(d) 3rd situation.

In this situation, transitions $1 \rightleftharpoons 2$ are at temperature β_a , transitions $2 \rightleftharpoons 3$ are at temperature β_b and transitions $1 \rightleftharpoons 3$ are either at temperature β_b or are transitions of work

$$R_{xy}^{(a)} = a \exp\left(\frac{1}{2}(s_{xy} - \beta_a e_{xy})\right) \quad (x, y) = (1, 2), (2, 1)$$

$$R_{xy}^{(b)} = b \exp\left(\frac{1}{2}(s_{xy} - \beta_b e_{xy})\right) \quad (x, y) = (2, 3), (3, 2), (1, 3), (3, 1)$$

$$R_{xy}^{(W)} = c \exp\left(\frac{1}{2}s_{xy}\right) \quad (x, y) = (1, 3), (3, 1)$$

and

$$R_{xy} = R_{xy}^{(b)} + R_{xy}^{(W)} \quad (x, y) = (1, 3), (3, 1).$$

Again $J_{12} = J_{23} = \frac{1}{Z} (R_{23} R_{31} R_{12} - R_{32} R_{21} R_{13})$

$$J_{23} = \frac{2}{Z} \left[ab^2 \sinh\left(\frac{1}{2}(\beta_b - \beta_a) e_{12}\right) + abc \sinh\left(\frac{1}{2}\beta_a e_{21} + \beta_b e_{32}\right) \right]$$

and

$$J_{13}^{(b)} = \frac{2}{Z} \left[bc \sinh\left(\frac{\beta_b e_{31}}{2}\right) \left(b \exp\left(\frac{1}{2}s_{32} - \frac{\beta_b}{2} e_{32}\right) + a \exp\left(\frac{1}{2}s_{12} - \frac{\beta_a}{2} e_{12}\right) \right) \right. \\ \left. + ab^2 \sinh\left(\left(\frac{\beta_b - \beta_a}{2}\right) e_{21}\right) \right]$$

$$J_{13}^{(W)} = -(J_{13}^{(b)} + J_{23})$$

$$= \frac{2}{Z} \left[abc \sinh\left(\frac{1}{2}\beta_a e_{12} + \frac{1}{2}\beta_b e_{23}\right) \right. \\ \left. + bc \sinh\left(\frac{\beta_b e_{13}}{2}\right) \left(b \exp\left(\frac{1}{2}s_{32} - \frac{\beta_b}{2} e_{32}\right) + a \exp\left(\frac{1}{2}s_{12} - \frac{\beta_a}{2} e_{12}\right) \right) \right].$$

Here

$$\begin{aligned} \delta_\infty W &= e_{13} J_{13}^{(W)} \\ &= \frac{2}{Z} \left[abce_{13} \sinh \left(\frac{\beta_a e_{13}}{2} + \frac{\beta_b - \beta_a}{2} e_{23} \right) \right. \\ &\quad \left. + bce_{13} \sinh \left(\frac{\beta_b e_{13}}{2} \right) \left(b \exp \frac{1}{2} \left(s_{32} - \frac{\beta_b}{2} e_{32} \right) + a \exp \frac{1}{2} \left(s_{12} - \frac{\beta_a}{2} e_{12} \right) \right) \right]. \end{aligned}$$

If we want $\delta_\infty W < 0$, so that the system is an engine, we need the first term of this expression to be negative so that certainly $(\beta_b - \beta_a) e_{23} < 0$.

The conclusion of the analysis of the three state system is that depending on the topology of the transitions in connection with the distribution of temperatures among these transitions, the system can act as a motor, a refrigerator or can transform work into heat.

Example 5. Two spins at different temperatures.

This system is a four-state system. The system is formed of two spins σ_1, σ_2 each spin $\sigma_i = \{-1, +1\}$ with Hamiltonian

$$\begin{aligned} H(\sigma_1, \sigma_2) &= H_1(\sigma_1) + H_2(\sigma_2) + H_{12}(\sigma_1, \sigma_2) \\ H_i(\sigma_i) &= E \left(\frac{1 + \sigma_i}{2} \right) \quad (E > 0) \\ H_{12}(\sigma_1, \sigma_2) &= -\frac{J\sigma_1\sigma_2}{2} \quad (J > 0). \end{aligned}$$

The entropy $s(\sigma_1, \sigma_2) = 0$. Each spin σ_i is coupled to a thermal reservoir Ω_i at temperature β_i^{-1} . Moreover σ_1 is coupled to a work reservoir. The entropy of the reservoir Ω_i is $s_i(e_i) = \beta_i e_i$ where e_i is the energy of Ω_i and the entropy of the work reservoir is 0. We have transitions with the reservoirs:

$$\begin{aligned} R_{(-\sigma_1, \sigma_2)(\sigma_1, \sigma_2)}^{(1)} &= a_1 \exp \left[-\frac{\beta_1}{2} (H(-\sigma_1, \sigma_2) - H(\sigma_1, \sigma_2)) \right] \\ R_{(\sigma_1, -\sigma_2)(\sigma_1, \sigma_2)}^{(2)} &= a_2 \exp \left[-\frac{\beta_2}{2} (H(\sigma_1, -\sigma_2) - H(\sigma_1, \sigma_2)) \right] \\ R_{(-\sigma_1, \sigma_2)(\sigma_1, \sigma_2)}^{(W)} &= b. \end{aligned}$$

Moreover we have an external transition where the two spins exchange their values, which keeps constant the energy content

$$R_{(\sigma_2, \sigma_1)(\sigma_1, \sigma_2)} = c \quad \text{for } \sigma_1 \neq \sigma_2.$$

Here

$$H(-\sigma_1, \sigma_2) - H(\sigma_1, \sigma_2) = -E\sigma_1 + J\sigma_1\sigma_2$$

$$H(\sigma_1, -\sigma_2) - H(\sigma_1, \sigma_2) = -E\sigma_{12} + J\sigma_1\sigma_2.$$

We can consider now the total amount of work per unit time step. The transitions which produce work are $(-+) \rightleftharpoons (++)$, $(--) \rightleftharpoons (+-)$, and during the transition $(-+) \rightarrow (++)$ the energy of the system varies by $E - J$ and during the transition $(--) \rightarrow (+-)$ it varies by $E + J$. The amount of work is

$$\delta_\infty W = (E - J) J_{(++) , (-+)}^{(W)} + (E + J) J_{(+ -) , (--)}^{(W)}.$$

It is proved in Appendix A, that $\delta_\infty W < 0$ so that in any circumstance, the system provides work to the reservoir of work Ω_∞ .

Remark. This behavior is to be contrasted with the behavior of the three-state system studied in Example 4, 2nd situation.

Example 6. External transitions involving several reservoirs.

In Section 9, we considered the case where each external transition has a given type ℓ , namely each external transition couples the system with only one reservoir. This hypothesis is realistic (and indeed realized) in most physico-chemical or biochemical systems, because various reactions occur independently. On the other hand, economical or ecological systems will not, in general obey such a rule. For example, an economic transaction between a system and its environment, involves an exchange of goods *and* money which may go to two different “reservoirs,” and the two parts of the transactions cannot be dissociated. If they are dissociated for example when one pays in advance, the system must have memory—which indeed it has. But then, the stochastic matrix formalism does not express memory effects.

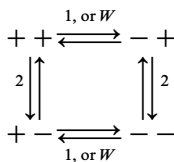
11. CONCLUSION

In this article, we have specialized the general master equation formulation of the dynamics of a system in order to be able to treat reservoirs

explicitly. As observed from the outside, a system which is in a non-equilibrium stationary state exchanges resources with certain reservoirs which may have zero entropy and the overall dynamics can be reduced, again from an external point of view, to the currents of various resources in or out the system. We have defined and calculated various dissipations of these resources and given lower bounds for these dissipations in term of state functions. Moreover, a number of simple examples show that the topology of the transitions with the reservoirs may be important in order to extract usable resources, like work.

APPENDIX A. CALCULATIONS FOR THE TWO-SPIN SYSTEM

The four states and their transitions are arranged as



For $++$, the spanning trees of root $++$ are



For $-+$, the spanning trees of root $-+$ are



$$\begin{aligned}
 p_s(+, +) = & (R_{(++), (-+)}^{(1)} + R_{(++), (-+)}^{(W)}) R_{(++), (+-)}^{(2)} (R_{(+-, (--))}^{(1)} + R_{(+-, (--))}^{(W)}) \\
 & + R_{(++), (+-)}^{(2)} (R_{(++), (-+)}^{(1)} + R_{(++), (-+)}^{(W)}) (R_{(-+, (--))}^{(2)}) \\
 & + R_{(++), (+-)}^{(2)} (R_{(+-, (--))}^{(1)} + R_{(+-, (--))}^{(W)}) R_{(-+, (-+)}^{(2)} \\
 & + (R_{(++), (-+)}^{(1)} + R_{(++), (-+)}^{(W)}) R_{(-+, (--))}^{(2)} (R_{(--), (+-)}^{(1)} + R_{(--), (+-)}^{(W)}).
 \end{aligned}$$

We need

$$\begin{aligned}
 H(++)-H(-+) &= E-J \\
 H(++)-H(+-) &= E-J \\
 H(+-)-H(--)= &E+J \\
 H(-+)-H(--)= &E+J
 \end{aligned}$$

$$\begin{aligned}
p_s(++) &= \left(a_1 \exp \left(-\frac{\beta_1}{2} (E-J) \right) + b \right) \\
&\quad \times a_2 \exp \left(-\frac{\beta_2}{2} (E-J) \right) \left(a_1 \exp \left(-\frac{\beta_1}{2} (E+J) \right) + b \right) \\
&\quad + a_2 \exp \left(-\frac{\beta_2}{2} (E-J) \right) \left(a_1 \exp \left(-\frac{\beta_1}{2} (E-J) \right) + b \right) \\
&\quad \times a_2 \exp \left(-\frac{\beta_2}{2} (E+J) \right) \\
&\quad + a_2 \exp \left(-\frac{\beta_2}{2} (E-J) \right) \left(a_1 \exp \left(-\frac{\beta_1}{2} (E+J) \right) + b \right) \\
&\quad \times a_2 \exp \left(+\frac{\beta_2}{2} (E+J) \right) \\
&\quad + \left(a_1 \exp \left(-\frac{\beta_1}{2} (E-J) \right) + b \right) \\
&\quad \times a_2 \exp \left(-\frac{\beta_2}{2} (E+J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E+J) \right) + b \right) \\
p_s(-+) &= \left(a_1 \exp \left(+\frac{\beta_1}{2} (E-J) \right) + b \right) \\
&\quad \times a_2 \exp \left(-\frac{\beta_2}{2} (E-J) \right) \left(a_1 \exp \left(-\frac{\beta_1}{2} (E+J) \right) + b \right) \\
&\quad + a_2 \exp \left(-\frac{\beta_2}{2} (E+J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E+J) \right) + b \right) \\
&\quad \times a_2 \exp \left(\frac{\beta_2}{2} (E-J) \right) \\
&\quad + a_2 \exp \left(-\frac{\beta_2}{2} (E+J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E-J) \right) + b \right) \\
&\quad \times a_2 \exp \left(-\frac{\beta_2}{2} (E-J) \right) \\
&\quad + a_2 \exp \left(-\frac{\beta_2}{2} (E+J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E+J) \right) + b \right) \\
&\quad \times \left(a_1 \exp \left(+\frac{\beta_1}{2} (E-J) \right) + b \right).
\end{aligned}$$

For $+-$, the spanning trees are



$$\begin{aligned}
 p_s(+-) &= a_2 \exp\left(\frac{\beta_2}{2}(E-J)\right) \left(a_1 \exp\left(-\frac{\beta_1}{2}(E-J)\right) + b \right) \\
 &\quad \times \left(a_2 \exp\left(-\frac{\beta_2}{2}(E+J)\right) \right) \\
 &\quad + \left(a_1 \exp\left(-\frac{\beta_1}{2}(E+J)\right) + b \right) a_2 \exp\left(\frac{\beta_2}{2}(E+J)\right) \\
 &\quad \times \left(a_1 \exp\left(\frac{\beta_1}{2}(E-J)\right) + b \right) \\
 &\quad + \left(a_1 \exp\left(-\frac{\beta_1}{2}(E+J)\right) + b \right) a_2 \exp\left(\frac{\beta_2}{2}(E-J)\right) \\
 &\quad \times \left(a_1 \exp\left(-\frac{\beta_1}{2}(E-J)\right) + b \right) \\
 &\quad + a_2 \exp\left(\frac{\beta_2}{2}(E-J)\right) \left(a_1 \exp\left(-\frac{\beta_1}{2}(E+J)\right) + b \right) \\
 &\quad \times a_2 \exp\left(\frac{\beta_2}{2}(E+J)\right).
 \end{aligned}$$

For $--$, the spanning trees are



and finally

$$\begin{aligned}
 p_s(--) &= a_2 \exp\left(\frac{\beta_2}{2}(E+J)\right) \left(a_1 \exp\left(+\frac{\beta_1}{2}(E-J)\right) + b \right) \\
 &\quad \times a_2 \exp\left(-\frac{\beta_2}{2}(E-J)\right) \\
 &\quad + \left(a_1 \exp\left(\frac{\beta_1}{2}(E+J)\right) + b \right) a_2 \exp\left(\frac{\beta_2}{2}(E-J)\right) \\
 &\quad \times \left(a_1 \exp\left(-\frac{\beta_1}{2}(E-J)\right) + b \right)
 \end{aligned}$$

$$\begin{aligned}
 & + \left(a_1 \exp \left(\frac{\beta_1}{2} (E + J) \right) + b \right) a_2 \exp \left(\frac{\beta_2}{2} (E + J) \right) \\
 & \times \left(a_1 \exp \left(\frac{\beta_1}{2} (E - J) \right) + b \right) \\
 & + a_2 \exp \left(\frac{\beta_2}{2} (E + J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E + J) \right) + b \right) \\
 & \times a_2 \exp \left(\frac{\beta_2}{2} (E - J) \right).
 \end{aligned}$$

We have not written the normalization factor $\frac{1}{Z}$. The total current along the full cycle is

$$\begin{aligned}
 J_{(++) , (+-)}^{(2)} &= \frac{1}{Z} [R_{(++) , (+-)}^{(2)} (R_{(+-) , (--)}^{(1)} + R_{(+-) , (--)}^{(W)}) \\
 & \quad \times (R_{(--), (-+)}^{(2)})(R_{(-+) , (++)}^{(1)} + R_{(-+) , (++)}^{(W)})\text{-reverse}] \\
 J_{(++) , (+-)}^{(2)} &= \frac{1}{Z} \left[a_2 \exp \left(-\frac{\beta_2}{2} (E - J) \right) \left(a_1 \exp \left(-\frac{\beta_1}{2} (E + J) \right) + b \right) \right. \\
 & \quad \times a_2 \exp \left(\frac{\beta_2}{2} (E + J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E - J) \right) + b \right) \\
 & \quad - a_2 \exp \left(\frac{\beta_2}{2} (E - J) \right) \left(a_1 \exp \left(\frac{\beta_1}{2} (E + J) \right) + b \right) \\
 & \quad \left. \times a_2 \exp \left(-\frac{\beta_2}{2} (E + J) \right) \left(a_1 \exp \left(-\frac{\beta_1}{2} (E - J) \right) + b \right) \right].
 \end{aligned}$$

After regrouping, we obtain

$$\begin{aligned}
 J_{(++) , (+-)}^{(2)} &= \frac{2a_2^2}{Z} \left[a_1^2 \sinh(\beta_2 - \beta_1) J + a_1 b \left(\sinh \left(\beta_2 J - \frac{\beta_1}{2} (E + J) \right) \right. \right. \\
 & \quad \left. \left. + \left(\sinh \left(\beta_2 J + \frac{\beta_1}{2} (E - J) \right) \right) + b^2 \sinh \beta_2 J \right].
 \end{aligned}$$

Then we get for the work transitions

$$\begin{aligned}
 J_{(++) , (-+)}^{(W)} &= -\frac{2b}{Z} \left[a_1^2 \sinh \frac{\beta_1 (E - J)}{2} \left(a_2^2 e^{-\beta_2 E} + 2a_1 a_2 e^{-\frac{\beta_2 E}{2}} \operatorname{ch} \left(\frac{\beta_1 (E + J) - \beta_2 J}{2} \right) \right) \right. \\
 & \quad \left. + 2a_2 b e^{-\frac{\beta_2 E}{2}} \operatorname{ch} \frac{\beta_2 J}{2} \right) + a_2^2 b \sinh \beta_2 J + a_2^2 a_1 \sinh \left(\frac{\beta_1 (E + J)}{2} - \beta_2 J \right) \right].
 \end{aligned}$$

and the variation of energy is $H(++)-H(-+)=E-J$. In the same way

$$\begin{aligned} J_{(+ -), (- -)}^{(W)} = & -\frac{2b}{Z} \left[a_1 \sinh \frac{\beta_1}{2} (E+J) \left(a_2^2 e^{\beta_2 E} + 2a_2 b e^{\frac{\beta_2 E}{2}} \operatorname{ch} \frac{\beta_2 J}{2} \right. \right. \\ & \left. \left. + 2a_1 a_2 e^{\frac{\beta_2 E}{2}} \operatorname{ch} \left(\frac{\beta_2 J}{2} + \frac{\beta_1}{2} (E-J) \right) \right) \right. \\ & \left. \left. + a_2^2 b \sinh(\beta_2 J) + a_2^2 a_1 \sinh \left(\beta_2 J + \frac{\beta_1}{2} (E-J) \right) \right] \right] \end{aligned}$$

and the variation of energy is $H(+ -)-H(--)=E+J$. The variation of the work is then:

$$\delta_\infty W = (E-J) J_{(++), (-+)}^{(W)} + (E+J) J_{(+ -), (--)}^{(W)}$$

or expanding

$$\begin{aligned} \delta_\infty W = & -\frac{2b}{Z} \left[a_1 (E-J) \sinh \frac{\beta_1 (E-J)}{2} \left(a_2^2 e^{-\beta_2 E} \right. \right. \\ & \left. \left. + 2a_1 a_2 e^{-\frac{\beta_2 E}{2}} \operatorname{ch} \left(\frac{\beta_1 (E+J) - \beta_2 J}{2} \right) + 2a_2 b e^{-\frac{\beta_2 E}{2}} \operatorname{ch} \left(\frac{\beta_2 J}{2} \right) \right) \right. \\ & \left. \left. + a_1 (E+J) \sinh \frac{\beta_1 (E+J)}{2} \left(a_2^2 e^{\beta_2 E} + 2a_1 a_2 e^{\frac{\beta_2 E}{2}} \operatorname{ch} \left(\frac{\beta_1 (E-J) + \beta_2 J}{2} \right) \right) \right. \right. \\ & \left. \left. + 2a_2 b e^{\frac{\beta_2 E}{2}} \operatorname{ch} \left(\frac{\beta_2 J}{2} \right) \right) + 2a_2^2 b E \sinh(\beta_2 J) \right. \\ & \left. \left. + a_2^2 a_1 \left((E-J) \sinh \left(\frac{\beta_1 (E+J)}{2} - \beta_2 J \right) \right. \right. \right. \\ & \left. \left. \left. + (E+J) \sinh \left(\frac{\beta_1 (E-J)}{2} + \beta_2 J \right) \right) \right) \right]. \quad (\text{A1}) \end{aligned}$$

We shall show that the square bracket in this last expression (A.1) is positive. Here E, J, a_1, a_2, b are positive. The only possibly negative terms are the last terms in $a_2^2 a_1$ which become after reduction

$$2a_2^2 a_1 \left[E \sinh \frac{\beta_1 E}{2} \operatorname{ch} \left(\frac{\beta_1 J}{2} - \beta_2 J \right) - J \sinh \left(\frac{\beta_1 J}{2} - \beta_2 J \right) \operatorname{ch} \frac{\beta_1 E}{2} \right]. \quad (\text{A2})$$

The only possibility for the terms (A.2) to be negative is that $\beta_1/2 > \beta_2$ and moreover that $J > E$ because if (A.2) is negative, we must have

$$J \operatorname{th} \left(\frac{\beta_1 J}{2} - \beta_2 J \right) > E \operatorname{th} \left(\frac{\beta_1 E}{2} \right).$$

Now let us collect together in the bracket of (A.1) the various terms in $a_2^2 a_1$. We see that

$$(J-E) \sinh \left(\beta_1 \frac{(J-E)}{2} \right) e^{-\beta_2 E} + (E+J) \sinh \left(\beta_1 \left(\frac{(E+J)}{2} \right) \right) e^{\beta_2 E}$$

is of the type $ue^{-\beta_2 E} + ve^{\beta_2 E}$ with $0 < u < v$ and is always larger than $u+v$ for $E > 0$. So the sum of the terms in the bracket of (A.1) which contain $a_2^2 a_1$ is larger than

$$\begin{aligned} & (J-E) \sinh \left(\beta_1 \left(\frac{(J-E)}{2} \right) \right) + (J+E) \sinh \left(\beta_1 \left(\frac{(E+J)}{2} \right) \right) \\ & + 2E \sinh \left(\frac{\beta_1 E}{2} \right) \operatorname{ch} \left(\frac{\beta_1 J}{2} - \beta_2 J \right) - 2J \sinh \left(\frac{\beta_1 J}{2} - \beta_2 J \right) \operatorname{ch} \left(\frac{\beta_1 E}{2} \right) \end{aligned}$$

and obviously this is

$$\begin{aligned} & \geq 2J \sinh \frac{\beta_1 J}{2} \operatorname{ch} \left(\frac{\beta_1 E}{2} \right) - 2J \sinh \left(\frac{\beta_1 J}{2} - \beta_2 J \right) \operatorname{ch} \left(\frac{\beta_1 E}{2} \right) \\ & > 0. \end{aligned}$$

As a consequence $\delta_\infty W < 0$, and thus, this system always produces work on the reservoir Ω_∞ .

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