Variational nonequilibrium thermodynamics of reaction-diffusion systems. III. Progress variables and dissipation of energy and information

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We continue, in this article, to develop the formalism of nonequilibrium thermodynamics in variational form. We prove that in the framework of progress variables, the Hamilton–Jacobi equation has always a simple solution, and we prove that this solution becomes a state function if and only if there is a thermodynamic equilibrium for the system. We study an inequality between the dissipation of energy and of information, and we discuss the notion of relative entropy. Finally we also study in detail the case of a system with one chemical species, where all the previous quantities can be calculated explicitly. © *2001 American Institute of Physics.*
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I. INTRODUCTION

In two previous publications[1] (referred to below as Parts I and II), we have introduced a new formalism for nonequilibrium thermodynamics of reaction-diffusion systems at a fixed temperature (see Refs. 2 and 3 for general references as well as different approaches to these questions and Ref. 4 for applications of this formalism). The dynamics of such systems can be described by a Master Equation (Ref. 2) because the rate constants of all processes, chemical or diffusive are well defined, the temperature being kept fixed. The stationary probability distribution on the state space is the stationary solution of this Master equation $P_s(x)$ (x is the label of the state of the system) and, following Kubo *et al.*,[5,6] it can be approximated in the large volume approximation as

$$P_S(x) \simeq U_0(x)\exp(-V\Phi(x)),$$

where U_0 is a prefactor, V is the volume of the system, and Φ is the information potential.[1,4]

This approximation is valid at least away from criticality. In an equilibrium situation, the information potential would be $F(x)/k_BT$, where F is the free energy per unit volume. In general, Φ satisfies a Hamilton–Jacobi equation of a nonstandard form and its properties have been studied in Part I. We have applied these results to the study and approximation of rate constants, first passage times and eigenvalue of the Master equation in Part II. A more general formalism for non equilibrium statistical mechanics was introduced in Refs. 7–9, for any stochastic dynamics, and was used to prove a fluctuation dissipation theorem and derive generalized Onsager relations as well as a general approach to first order phase transitions in nonequilibrium situations.[9]

In this work, we study the information potential in term of the progress variables (see Ref. 3) and we derive a Hamilton–Jacobi equation in term of these variables, although this does not lead to a state function in general (see Sec. II). In Sec. III, we also state and derive an inequality relating the dissipation of energy to the dissipation of information which is valid for any reaction-diffusion system at fixed temperature. This inequality was also derived in a slightly less general context in Ref. 10. In Sec. IV, we study the relative entropy. In Sec. V, we examine the action of external reservoirs maintaining a nonequilibrium situation in the system. We show that the natural condition is that the reservoirs maintain constant certain chemical potentials of certain species rather than the corresponding concentrations. We prove that the information potential in progress variables induces a state function in the space of concentration variables (which is then the information potential in these variables), if and only if the reservoirs maintain external conditions compatible with the existence of a thermodynamic equilibrium. We show also that the information potential in progress variables is the work performed by the reservoirs to maintain the non equilibrium situation in the system. In Sec. VI, we examine the case of a chemical system with only one chemical species varying freely. A conclusion summarizes our results and certain detailed proofs are given in the appendices.

II. DYNAMICS OF PROGRESS VARIABLES

A. Fundamental processes and progress variables

We consider a vessel of fixed volume V, containing two kinds of chemical species:

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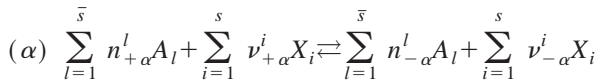[b)]Electronic mail: moreau@lptl.jussieu.fr
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(i) Chemical species denoted X_i, $i=1,...,s$, which are varying freely according to natural chemical reactions in V. We denote n_i the number of particles X_i and $x_i = n_i/V$ their concentration;

(ii) Chemical species denoted A_l, $l=1,...,\bar{s}$, which are completely under the control of external reservoirs. This means that at any time t, the concentrations $a_l(t)$, $l=1,...,\bar{s}$ are imposed by the external reservoirs.

The state of the system is given by the set of numbers $\{x_i\} i=1,...,s$ which specify the concentrations of the freely varying species. The concentrations $\{a_l(t)\}$, $l=1,...,\bar{s}$ may be functions of the state variables x_i. The simplest situation is the case where the reservoirs maintain each a_l at a fixed concentration independent of t. We allow such a general variation $a_l(t)$ in Sec. II–IV and we shall discuss in more detail the action of the reservoirs in Sec. V.

The species are reacting and diffusing according to p fundamental processes, which are all reversible, of the type

$$(\alpha) \quad \sum_{l=1}^{\bar{s}} n^l_{+\alpha} A_l + \sum_{i=1}^{s} \nu^i_{+\alpha} X_i \rightleftarrows \sum_{l=1}^{\bar{s}} n^l_{-\alpha} A_l + \sum_{i=1}^{s} \nu^i_{-\alpha} X_i$$

and $\alpha = 1,...,p$ labels the processes. By convention, the forward process is from left to right and the backward process is from right to left.

We denote by $r_\alpha(t)$ the number of forward processes minus the number of backwards processes of type α, up to time t. In particular,

$$n_i(t) = n_i(0) + \sum_\alpha \tau^i_\alpha r_\alpha(t), \tag{2.1}$$

where τ^i_α is the difference between the stoichiometric numbers $\nu^i_{\pm\alpha}$,

$$\tau^i_\alpha = \nu^i_{-\alpha} - \nu^i_{+\alpha}.$$

We denote by u_α the algebraic number of processes α per unit volume

$$u_\alpha = \frac{r_\alpha}{V} \tag{2.2}$$

and call these numbers the progress variables, according to the usual denomination.

Finally, we define by $\Omega^\pm_\alpha$ the probability per unit time that a forward or backward process of type α occurs in V. Because of Eq. (2.1), written in rescaled variables, namely,

$$x_i(t) = x_i(0) + \sum_\alpha \tau^i_\alpha u_\alpha(t), \tag{2.3}$$

the $\Omega^\pm_\alpha$ can be considered as functions of the u_β, the $x_i(0)$ and the a_l.

B. Dynamics of progress variables

We call $Q(r,t)$ the probability that at time t, r_α processes of type α have occurred, $\alpha = 1,...,p$. We denote by $\delta_{\alpha\beta}$ the Kronecker symbol. Then Q satisfies the following Master equation (see Part I and Ref. 2 for general references):

$$\frac{\partial Q(r,t)}{\partial t} = \sum_\beta \left[\Omega^+_\beta(\{r_\alpha - \delta_{\alpha\beta}\}) Q(\{r_\alpha - \delta_{\alpha\beta}\},t) \right]$$

$$+ \Omega^-_\beta(\{r_\alpha + \delta_{\alpha\beta}\}) Q(\{r_\alpha + \delta_{\alpha\beta}\},t)$$

$$- (\Omega^+_\beta(r) + (\Omega^-_\beta(r))) Q(r,t)]. \tag{2.4}$$

We use now the rescaled progress variables $u_\alpha = r_\alpha/V$ as in the definition of Eq. (2.2), to define the rescaled probability density $q(u,t)$ and rates $\omega^\pm_\alpha$ by

$$Q(r,t) = \frac{1}{V^p} q(u,t),$$

$$\Omega^\pm_\alpha(r) = V\omega^\pm_\alpha(u),$$

and Eq. (2.4), can be rewritten,

$$\frac{1}{V}\frac{\partial q(u,t)}{\partial t} = \sum_\beta \left[\omega^+_\beta\left(\left\{u_\alpha - \frac{\delta_{\alpha\beta}}{V}\right\}\right) q\left(\left\{u_\alpha - \frac{\delta_{\alpha\beta}}{V}\right\},t\right) \right.$$

$$+ \omega^-_\beta\left(\left\{u_\alpha + \frac{\delta_{\alpha\beta}}{V}\right\}\right) q\left(\left\{u_\alpha + \frac{\delta_{\alpha\beta}}{V}\right\},t\right)$$

$$\left. - (\omega^+_\beta(u) + \omega^-_\beta(u) q(u,t)) \right]. \tag{2.5}$$

For large V, we obtain an approximate Fokker–Planck equation in the usual way from Eq. (2.5),

$$\frac{\partial q(u,t)}{\partial t} = -\sum_\beta \frac{\partial}{\partial u_\beta}((\omega^+_\beta - \omega^-_\beta)q)$$

$$+ \frac{1}{2V}\sum_\beta \frac{\partial^2}{\partial u^2_\beta}((\omega^+_\beta + \omega^-_\beta)q). \tag{2.6}$$

However, it has been shown that this equation does not give the correct results for stationary state and the large time dynamics of the full Master equation (see Ref. 11 and Part I).

C. Approximation dynamics for large V

For large V, following Kubo[5] and other authors[6] (see also Part I for a systematic use), one can try a formal asymptotic expansion for $q(u,t)$ (which is reminiscent of the WKB-expansion in quantum mechanics),

$$q(u,t) = \exp(-V\psi)\left[U_0 + \frac{1}{V}U_1 + \cdots \right]. \tag{2.7}$$

The variations of the prefactor U_0 are usually negligible compared to the variations of the dominant exponential $\exp(-V\Phi)$. However, the prefactor becomes preponderant near criticality, when the argument of the exponential vanishes. On the other hand, the method of Kubo would make no sense if U_0 was singular. For all these reasons, a further study of the prefactor is necessary for a sound mathematical foundation of the present formalism. This study, which is somewhat intricate and needs abstract topological arguments, will be presented elsewhere.[15]

The expansion (2.7) can be used either in the Fokker–Planck equation Eq. (2.6), or directly in the Master equation

(2.5). In both cases, it is easily shown (as in Part I) that the function ψ satisfies a Hamilton–Jacobi equation in progress variables,

$$H'\left(u, \frac{\partial \psi}{\partial u}\right) = 0, \tag{2.8}$$

where H' is either the Fokker–Planck Hamiltonian H'_{FP} or the Master Hamiltonian H'_M,

$$H'_{FP}(u, \pi) = \sum_{\beta} \left[(\omega_\beta^+ - \omega_\beta^-) \pi_\beta + \tfrac{1}{2}(\omega_\beta^+ + \omega_\beta^-) \pi_\beta^2 \right], \tag{2.9}$$

$$H'_M(u, \pi) = \sum_{\beta} \left[\omega_\beta^+ (\exp(\pi_\beta) - 1) \right.$$
$$\left. + \omega_\beta^- (\exp(-\pi_\beta) - 1) \right], \tag{2.10}$$

where π_β is the conjugate momentum of u_β. As in Part I, we have

$$H'_M(u, \pi) = H'_{FP}(u, \pi) + 0(|\pi|^3). \tag{2.11}$$

We notice here that all the results proved in Part I for the Hamilton–Jacobi equation associated with the Master equation are valid for the Hamilton–Jacobi equation in progress variables.

D. Relation with the usual master equation

The usual Master equation (see Part I) is an equation for functions of the state variables (here the x_i). Although the formal derivation of the usual Master equation and of its approximations (Fokker–Planck and Hamilton–Jacobi) are the same as in Sec. II C, their physical meaning is completely different, because the u_α are not state variables. They are related to the state variables by Eq. (2.3). If one knows the u_α, *one can deduce the variation of the state variables $x_i(t) - x_i(0)$ but in general not conversely.* In part I, we have been using the x_i variables and we introduced the rate per unit volume $w_r(x)$ of a transition, $\{x_i\} \rightarrow \{x_i + (r_i/V)\}$. It is clear that

$$w_r(x) = \sum_{\alpha: \tau_\alpha^i = r_i} \omega_\alpha^+(x) + \sum_{\alpha: \tau_\alpha^i = r_i} \omega_\alpha^-(x). \tag{2.12}$$

The usual Kramers–Moyal expansion of the Master equation (see Refs. 2, 4, 11, and Part I) yields the usual Fokker–Planck equation in concentration variables,

$$\frac{\partial p}{\partial t} = -\sum_i \frac{\partial}{\partial x_i}(A_i p) + \frac{1}{2V} \sum_{i,j} \frac{\partial^2}{\partial x_i \partial x_j}(D_{ij} p),$$

with the following expressions for A_i and D_{ij}:

$$A_i = \sum_r r_i w_r = \sum_\alpha \tau_\alpha^i(\omega_\alpha^+ - \omega_\alpha^-), \tag{2.13}$$

$$D_{ij} = \sum_r r_i r_j w_r = \sum_\alpha \tau_\alpha^i \tau_\alpha^j(\omega_\alpha^+ + \omega_a^-). \tag{2.14}$$

Finally, Eq. (2.3) shows that the evolution remains, for all time, in the subspace $E(x(0))$ of the state space of the $\{x_i\}$, given by parametric equations,

$$E(x(0)) = \left\{ x = \{x_i\} \mid x_i = x_i(0) + \sum_\alpha \tau_\alpha^i u_\alpha \right\}.$$

It is clear that this subspace is the same as the subspace introduced in Part I, Sec. II, because the set of the $2p$ vectors $\pm\{\tau_\alpha^i\}$, $\alpha = 1,...,p$ is exactly the set of the vectors $\{r_i\}$, and each subspace $E(x(0))$ carries a stationary probability distribution. *We shall assume henceforth that we reduce the situation to a given subspace $E(x(0))$, so that the dynamics is irreducible and has a unique stationary state in this subspace.*

Notice that when we do this, we can use d variables $x_1,...,x_d$, where d is the dimension of $E(x(0))$, to parametrize $E(x(0))$. The other variables $x_{d+1},...,x_s$ are still present (so that the chemical processes α are the same) but they are certain linear functions of the $x_1,...,x_d$.

In Part I, we have introduced the Hamiltonian $H_M(x, \zeta)$ of the Master equation,

$$H_M(x, \xi) = \sum_r w_r(x)(e^{r \cdot \zeta} - 1),$$

where ζ_i is the conjugate variable of x_i and

$$r \cdot \xi = \sum_i r_i \xi_i.$$

Let us define now

$$\pi_\alpha = \sum_i \tau_\alpha^i \xi_i,$$
$$x_i = x_i(0) + \sum_\alpha \tau_\alpha^i u_\alpha \tag{2.15}$$

then using Eq. (2.12), the master Hamiltonian H'_M in (u, π) variables reduces to the master Hamiltonian H_M in (x, ξ) variables,

$$H'_M(u, \pi) = H_M(x, \xi). \tag{2.16}$$

In particular, if $\Phi(x)$ is a solution of the Hamilton–Jacobi equation,

$$H_M\left(x, \frac{\partial \Phi}{\partial x}\right) = 0, \tag{2.17}$$

then the function,

$$\psi(u) = \Phi\left(\left\{ x_i(0) + \sum_\alpha \tau_\alpha^i u_\alpha \right\}\right)$$

induces a solution of the Hamilton–Jacobi equation in the progress variable form,

$$H'_M\left(u, \frac{\partial \psi}{\partial u}\right) = 0 \tag{2.18}$$

because

$$\frac{\partial \psi}{\partial u_\alpha} = \sum_i \tau_\alpha^i \frac{\partial \Phi}{\partial x_i}.$$

But conversely, a solution $\psi(u)$ of the Hamilton–Jacobi Eq. (2.18) does not necessarily produce a function in the state variables x and *a fortiori* does not define a solution of Eq. (2.17).

E. Free energy and rate constants in the unconstrained system

We consider now the vessel V, in which the p processes take place, but we switch off the exchanges of molecules A_l, $l=1,...,\bar{s}$ with the reservoirs (but still maintaining the temperature T constant), so that *the concentrations x_i and a_l vary freely* according to the natural chemical processes $\alpha = 1,...,p$ in the vessel. The state will then reach a thermal equilibrium. At thermal equilibrium, the probability distribution on the state space, which consists now of the freely varying concentrations x_i and a_l, is for large V,

$$p_{eq}(\{x_i\},\{a_l\}) \sim U_0 \exp\left(-\frac{VF(x,a)}{k_BT}\right), \qquad (2.19)$$

where F is the free energy (of the state (x,a)) per unit volume, T is the temperature, and U_0 is a prefactor. At equilibrium, all processes α satisfy the condition of detailed balance, which can be written asymptotically, for large V, as

$$\omega_\alpha^+(x,a)\exp\left(-\frac{V}{k_BT}F(x,a)\right)$$

$$= \omega_\alpha^-(x,a)\exp\left(-\frac{V}{k_BT}F\left(\left\{x_i+\frac{\tau_\alpha^i}{V}\right\},\left\{a_l+\frac{t_\alpha^l}{V}\right\}\right)\right),$$

where $t_\alpha^l = n_{-\alpha}^l - n_{+\alpha}^l$, from which we deduce

$$k_BT\log\frac{\omega_\alpha^-}{\omega_\alpha^+} = \sum_i \frac{\partial F}{\partial x_i}\tau_\alpha^i + \sum_l \frac{\partial F}{\partial a_l}t_\alpha^l \quad \text{for all } \alpha. \qquad (2.20)$$

For perfect gases or solutions, one assumes usually that the $\omega_\alpha^\pm$ are given by

$$\omega_\alpha^\pm = k_\alpha^\pm\left(\prod_i x_i^{\nu_{\pm\alpha}^i}\right)\left(\prod_l a_l^{n_{\pm\alpha}^l}\right), \qquad (2.21)$$

where $k_\alpha^\pm$ are temperature dependent constants. It is immediate to check that the usual partial equilibrium form[10]

$$F(x,a) = \sum_i F_i(x_i) + \sum_l F_l(a_l) \qquad (2.22)$$

(where F_i is the free energy of the ideal gas law at temperature T and concentrations x_i) satisfies Eq. (2.20). In fact, the chemical potentials are

$$\mu_i = \frac{\partial F}{\partial x_i} = \frac{dF_i}{dx_i} = k_BT\log x_i + f_i(T) \qquad (2.23)$$

and Eq. (2.20) reduces to the equation

$$k_BT\log\frac{k_\alpha^-}{k_\alpha^+} = \sum_i \tau_\alpha^i f_i(T) + \sum_l t_\alpha^l f_l(T). \qquad (2.24)$$

Here each $f_i(T)$ is calculated using the partition functions of the internal degrees of freedom of the species X_i and Eq. (2.24) is the usual expression for the equilibrium constant

$K_{\alpha,eq}$ of the process α in term of the partition function of the internal degrees of freedom of the species appearing in the process α.

In many circumstances, like for imperfect gases or solutions, electrolytes, etc..., one needs a more general formulation of the free energy $F(x,a)$, not necessarily of the form of Eq. (2.22). This is why we shall work with the most general free energy $F(x,a)$.

From Eq. (2.20), it is easy to see that for all α,

$$\omega_\alpha^+\left[\exp\left(\frac{1}{k_BT}\frac{\partial F}{\partial u_\alpha}\right)-1\right] + \omega_\alpha^-\left[\exp\left(-\frac{1}{k_BT}\frac{\partial F}{\partial u_\alpha}\right)-1\right]=0, \qquad (2.25)$$

where

$$\frac{\partial F}{\partial u_\alpha} = \sum_i \frac{\partial F}{\partial x_i}\tau_\alpha^i + \sum_l \frac{\partial F}{\partial u_l}t_\alpha^l \qquad (2.26)$$

so that F satisfies the Hamilton–Jacobi equation (2.8),

$$H_M'\left(u,\frac{1}{k_BT}\frac{\partial F}{\partial u}\right)=0$$

with H_M' given by Eq. (2.10), where, in $\omega_\beta^\pm$, one uses the variables

$$x_i = x_i(0) + \sum_\alpha \tau_\alpha^i u_\alpha,$$

$$a_l = a_l(0) + \sum_\alpha t_\alpha^l u_\alpha.$$

III. DISSIPATION OF ENERGY AND OF INFORMATION

A. Dissipation of information

From now on, we shall assume again that, on a given subspace $E(x(0))$, the state of the vessel reaches a stationary state $p(x) \sim U_0\exp(-V\Phi)$ with the concentrations a_l being entirely controlled by the reservoirs and having fixed variations $a_l(t)$.

If we consider a state $x=\{x_i\}$, it evolves macroscopically according to the deterministic equations,

$$\frac{dx_i}{dt} = A_i(x) = \sum_\alpha \tau_\alpha^i(\omega_\alpha^+ - \omega_\alpha^-).$$

The value of the state function Φ evolves as

$$\frac{d\Phi}{dt} = \sum_i \frac{\partial\Phi}{\partial x_i}\frac{dx_i}{dt} = \sum_{i,\alpha} (\omega_\alpha^+ - \omega_\alpha^-)\frac{\partial\Phi}{\partial u_\alpha}. \qquad (3.1)$$

We know from Sec. II E, that $H_M'(u,(\partial\Phi/\partial u))=0$. But $e^x - 1 \geq x$, so that

$$0 = \sum_\alpha \left[\omega_\alpha^+\left(\exp\left(\frac{\partial\Phi}{\partial u_\alpha}\right)-1\right) + \omega_\alpha^-\left(\exp\left(-\frac{\partial\Phi}{\partial u_\alpha}\right)-1\right)\right]$$

$$\geq \sum_\alpha (\omega_\alpha^+ - \omega_\alpha^-)\frac{\partial\Phi}{\partial u_\alpha}.$$

As a consequence, we obtain the inequality

$$\frac{\partial\Phi}{dt} \leq 0. \qquad (3.2)$$

Moreover, the equality is attained if and only if for each α, $\omega_\alpha^+(\partial\Phi/\partial u_\alpha)=\omega_\alpha^-(\partial\Phi/\partial u_\alpha)=0$. In particular, if the deterministic state reaches a stationary point $x_i^{(0)}$, for which $A_i(x^{(0)})=0$, then $d\Phi/dt=0$, and $\partial\Phi/\partial u_\alpha=0$ or $\omega_\alpha^+=\omega_\alpha^-=0$.

The quantity $d\Phi/dt$ computed along a deterministic trajectory is always negative. It can be interpreted as a dissipation of information per unit time.

In fact, $V\Phi(x)$ can be considered as the average information which is obtained when the system is observed in the state x rather than being stochastically distributed with the stationary probability distribution $p_s(x)\sim\exp(-V\Phi(x))$, which is the sate of lowest information, when the system is coupled to the various reservoirs of heat and of chemical species A_l. We have

$$V\Phi(x)\simeq\sum_y \delta(y-x)\log\frac{\delta(y-x)}{p_s(y)}\equiv-\log p_s(x),\quad (3.3)$$

where $\delta(y-x)$ is the Dirac distribution at x. The sum of Eq. (3.3) is really on the space of discrete states $x=[n_i/V]$, so that $\delta(y-x)$ is in fact a Kronecker symbol. Along a deterministic path, Φ decreases with time while the state x tends to a deterministic stationary state which is a local minimum of Φ.

More generally, we can define the relative information (see Refs. 7–9, 14) of a probability distributions $p(x,t)$ as

$$I(p|p_s)=\sum_y p(y,t)\log\frac{p(y,t)}{p_s(y)}\quad (3.4)$$

for any stochastic system evolving according to a Markov process with stationary state p_s.

This quantity $I(p|p_s)$ is the average information gained if one knows that the system is in the state $p(y,t)$ at time t, rather than in the state of lowest information $p_s(y)$ (given the reservoirs or, the stochastic mechanisms). $I(p|p_s)$ is the opposite of the relative entropy $S(p|p_0)$ used by various authors (see Refs. 7–9 and 14).

B. Dissipation of energy

We consider now the variation of the free energy along the deterministic trajectory, namely,

$$\frac{dF}{dt}=\sum_i \frac{\partial F}{\partial x_i}\frac{dx_i}{dt}+\sum_l \frac{\partial F}{\partial a_l}\frac{da_l}{dt}$$

which we write as

$$\frac{dF}{dt}=\sum_i \frac{\partial F}{\partial x_i}\frac{dx_i}{dt}+\sum_l \frac{\partial F}{\partial a_l}\left[\frac{da_l}{dt}\right]_c$$

$$-\sum_l \frac{\partial F}{\partial a_l}\left(\left[\frac{da_l}{dt}\right]_c-\frac{da_l}{dt}\right),\quad (3.5)$$

where $[da_l/dt]_c$ is the variation of the a_l due to the various chemical processes α in the vessel V, so that

$$\left[\frac{da_l}{dt}\right]_c=\sum_\alpha (\omega_\alpha^+-\omega_\alpha^-)t_\alpha^l\quad (3.6)$$

and $[da_l/dt]_c-(da_l/dt)$ is the actual variation of the concentration a_l in the reservoir.

In Eq. (3.5) the first two terms are, using Eq. (2.26),

$$\sum_\alpha (\omega_\alpha^+-\omega_\alpha^-)\left(\sum_i t_\alpha^i\frac{\partial F}{\partial x_i}+\sum_l t_\alpha^l\frac{\partial F}{\partial a_l}\right)$$

$$=\sum_\alpha (\omega_\alpha^+-\omega_\alpha^-)\frac{\partial F}{\partial u_\alpha}.\quad (3.7)$$

Now Eq. (2.25) says that for each α,

$$0=\omega_\alpha^+\left[\exp\left(\frac{1}{k_BT}\frac{\partial F}{\partial u_\alpha}-1\right)\right]+\omega_\alpha^-\left[\exp\left(-\frac{1}{k_BT}\frac{\partial F}{\partial u_\alpha}\right)-1\right]$$

$$\geq(\omega_\alpha^+-\omega_\alpha^-)\frac{1}{k_BT}\frac{\partial F}{\partial u_\alpha},$$

so that we deduce

$$\sum_i \frac{\partial F}{\partial x_i}\frac{dx_i}{dt}+\sum_l \frac{\partial F}{\partial a_l}\left[\frac{da_l}{dt}\right]_c=\sum_\alpha (\omega_\alpha^+-\omega_\alpha^-)\frac{\partial F}{\partial u_\alpha}\leq 0.\quad (3.8)$$

On the other hand, the quantity in Eq. (3.5),

$$w\equiv-\sum_l \frac{\partial F}{\partial a_l}\left(\left[\frac{da_l}{dt}\right]_c-\frac{da_l}{dt}\right)=-\sum_l m_l\left(\left[\frac{da_l}{dt}\right]_c-\frac{da_l}{dt}\right)\quad (3.9)$$

is the work given to the system by the reservoirs to impose the evolution $a_l(t)$ for each concentration a_l in the vessel V, where we have denoted by m_l the chemical potential with respect to the species A_l,

$$m_l=\frac{\partial F}{\partial a_l}.$$

Then, from Eqs. (3.5) to (3.9),

$$\frac{dF}{dt}-w\leq 0\quad (3.10)$$

and the quantity $dF/dt-w$ is the dissipation of energy in the system, per unit time.

C. Inequality between the dissipation of information and of energy

It is proven in Appendix A that the dissipation of information and the dissipation of energy satisfy the fundamental inequality,

$$\frac{1}{k_BT}\left(\frac{dF}{dt}-w\right)\leq\frac{d\Phi}{dt}\leq 0,\quad (3.11)$$

so that, in absolute value the dissipation of information is always less than the dissipation of energy. Moreover, there is equality if and only if we have an equilibrium situation.

This inequality has been derived in Ref. 10 in a slightly more restrictive situation. It is completely general (for reaction diffusion systems at a fixed temperature). This is different from the usual inequalities for the rate of production of entropy given by various authors (see Refs. 2 and 12). The main reason is that for non equilibrium situations, it is not easy to relate directly entropy production and energy dissi-

pation. In fact, here $d\Phi/dt$ is not an absolute production of entropy (as in Refs. 2 and 12) but a production of relative entropy as discussed at the end of Sec. III A, and below.

IV. INFORMATION POTENTIAL IN THE CONSTRAINED SYSTEM

In this section, we shall assume that the free energy of the whole vessel V is a given function $F(x,a)$ of the various concentrations, the temperature T being fixed. We recall Eq. (2.20),

$$k_B T \log \frac{\omega_\alpha^-}{\omega_\alpha^+} = \sum_i \frac{\partial F}{\partial x_i} \tau_\alpha^i + \sum_l \frac{\partial F}{\partial a_l} t_\alpha^l. \qquad (4.1)$$

The reservoirs maintain a fixed evolution $a_l(t)$ for each concentration of the species A_l. We call the chemical potentials,

$$\mu_i = \frac{\partial F}{\partial x_i}, \quad m_l = \frac{\partial F}{\partial a_l}. \qquad (4.2)$$

We would like to define a solution of the Hamilton Jacobi equation $H_M'(u,(\partial\Psi/\partial u))=0$ in the progress variables.

A. The action of the reservoirs

We shall assume that the reservoirs of the $\{A_l\}$ act in such a way as to maintain constant the chemical potentials m_l with respect to a_l for all $l=1,...,\bar{s}$, at a value $m_l = m_l^{(0)}$.

For example, when the so-called partial equilibrium situation holds, namely,

$$F(x,a) = F_1(x) + F_2(a), \qquad (4.3)$$

then the $m_l = (\partial F_2/\partial a_l)(a)$ depend only on a and our hypothesis means that the reservoirs maintain the concentrations a_l fixed, which is the standard assumptions for reaction-diffusion systems. In general, however, we shall show below that the constancy of the chemical potentiels m_l is a more natural condition. In this case, we assume that, each time a process α occurs in the vessel V, the reservoirs provide to the vessel a quantity σ_α^l of the species l, in such a way that, for all $l=1,...,\bar{s}$ and all α one has

$$\sum_i \frac{\partial m_l}{\partial x_i} \tau_\alpha^i + \sum_k \frac{\partial m_l}{\partial a_k}(t_\alpha^k + \sigma_\alpha^k) = 0. \qquad (4.4)$$

Equations (4.4) for $l=1,...,\bar{s}$ are the mathematical expressions of the hypothesis of the constancy of the chemical potentials m_l. It should be pointed out that Eq. (4.4) expresses the fact all the $m_l(x,a)$ are maintained constant by the action of reservoirs. In fact, the $m_l(x,a)$ are stochastic variables; the increment of m_l in time Δt is

$$\Delta m_l = \sum_\alpha \left(\sum_i \frac{\partial m_l}{\partial x_i} \tau_\alpha^i + \sum_k \frac{\partial m_l}{\partial a_k}(t_\alpha^k + \sigma_\alpha^k) \right) \Delta u_\alpha,$$

Δu_α being the increment in time Δt of the progress variable u_α of reaction α. But, for given x,a, the Δu_α are independent random variables. Thus, $\Delta m_l=0$ with probability 1, if and only if the coefficients of all the Δu_α are 0, namely, if Eq. (4.4) holds for all α, and determines the quantities σ_α^k.

Remark: If it is assumed as usual that the concentrations a_l, considered as stochastic variables, are maintained constant by the reservoirs, this implies the relation

$$t_\alpha^k + \sigma_\alpha^k = 0 \quad \text{for all} \quad \alpha \quad \text{and} \quad k, \qquad (4.4')$$

which will replace Eq. (4.4) under this assumption. Conditions (4.4) and (4.4′) are equivalent when Eq. (4.3) holds. This is the case in many situations (see Appendix B). However, it seems more natural to assume that the reservoirs maintain the chemical potentials constant for each spaces A_l since the equilibrium conditions between the system and the reservoirs (with respect to the species A_l) are expressed by the equality of these chemical potentials in the system and in the reservoirs.

It could be argued that Eqs. (4.4) or (4.4′) express very strong controls on each species A_l, which are difficult to implement in actual systems. Nevertheless, the hypotheses of the constancy of species A_l are usually assumed in works about the Master equation in chemical contexts. Furthermore, we show in Appendix B, that such hypotheses are justified provided the A_l are local concentrations of the corresponding species, near the interface between the system and the reservoirs.

B. Solution of the Hamilton–Jacobi equation in progress variables

In the function $\log(\omega_\alpha^-/\omega_\alpha^+)$ defined in Eqs. (4.1), we shall replace x_i and a_l by the values

$$x_i = x_i(0) + \sum_\alpha \tau_\alpha^i u_\alpha,$$

$$a_l = a_l(0) + \sum_\alpha (t_\alpha^l + \sigma_\alpha^l) u_\alpha. \qquad (4.5)$$

These expressions give the actual values of the x_i and the a_l, knowing their initial values, after u_α processes of type α, $\alpha=1,...,p$ have occurred. In particular, by definition, the state $\{x_i\}$ of the system remains on the subspace $E(x(0))$ as defined in Sec. II D. When all the x_i and a_l are replaced by their expressions of Eqs. (4.5), the $\log(\omega_\alpha^-/\omega_\alpha^+)$ are functions of the progress variables $\{u_\alpha\}$, depending parametrically of the initial concentration $\{x_i(0)\}$ and $\{a_l(0)\}$. We prove in Appendix C, that

$$\frac{\partial}{\partial u_\beta} \left(\log \frac{\omega_\alpha^-}{\omega_\alpha^+} \right) = \frac{\partial}{\partial u_\alpha} \left(\log \frac{\omega_\beta^-}{\omega_\beta^+} \right). \qquad (4.6)$$

As a consequence, *we can define a function $\Psi(u|x(0),a(0))$ of the u, depending parametrically on the initial values $x(0),a(0)$ of the concentrations such that*

$$\frac{\partial\psi}{\partial u_\beta} = \log \frac{\omega_\beta^-}{\omega_\beta^+}, \qquad (4.7)$$

and Ψ is unique up to an additive constant.

Clearly, Ψ will satisfy for any β,

$$\omega_\beta^+ \left[\exp\left(\frac{\partial\psi}{\partial u_\beta} \right) - 1 \right] + \omega_\beta^- \left[\exp\left(-\frac{\partial\psi}{\partial u_\beta} \right) - 1 \right] = 0, \qquad (4.8)$$

and *a fortiori*, it satisfies the Hamilton–Jacobi equation in progress variables,

$$H'_M\left(u, \frac{\partial \psi}{\partial u}\right) = 0. \tag{4.9}$$

We shall show now that the new solutions satisfying Eq. (4.7) corresponds to a very special path in term of the progress variables, namely the "antideterministic path." We recall here that the usual kinetic deterministic path corresponds to the trivial solution $\Phi = 0$ of the Hamilton–Jacobi equation,

$$H_M(x, \nabla \Phi) = 0.$$

C. The antideterministic path in progress variables

As we have said at the end of Sec. III C, all the results proved in Part I, for $H_M(x, \partial \Phi / \partial x) = 0$ are still valid for the H'_M Eq. (4.9). In particular, we can define the antideterministic path in Sec. V of Part I, by the formula

$$\frac{du_\alpha}{dt} = \frac{\partial H'_M}{\partial \pi_\alpha} = \omega_\alpha^+ e^{\pi_\alpha} - \omega_\alpha^- e^{-\pi_\alpha},$$

$$\pi_\alpha = \frac{\partial \psi}{\partial u_\alpha} = \log \frac{\omega_\alpha^-}{\omega_\alpha^+},$$

so that the antideterministic path satisfies

$$\frac{du_\alpha}{dt} = \omega_\alpha^- - \omega_\alpha^+. \tag{4.10}$$

Thus, the antideterministic path in progress variables is the deterministic path run backwards in time.

D. Comparison of Ψ with the free energy

We have constructed, for given $x(0)$ and $a(0)$, the function $\Psi(u|x(0), a(0))$ of the progress variables using Eq. (4.7). We can now compute the difference

$$W(u|x(0), a) \equiv F(x, a) - k_B T \psi(u|x(0), a), \tag{4.11}$$

where x, a are replaced by their expressions of Eqs. (4.5) in term of the initial values $x(0), a(0)$, and of the progress variables u. It is easy to see from Eqs. (4.11), (4.7), and (4.1) that

$$\frac{\partial W(u|x(0), a)}{\partial u_\beta} = \sum_l \frac{\partial F}{\partial a_l} \sigma_\beta^l = \sum_l m_l^{(0)} \sigma_\beta^l,$$

$m_l^{(0)}$ being the fixed value of the chemical potential m_l.

The deterministic evolution of W is then

$$\frac{dW(u|x(0), a)}{dt} = \sum_{l, \beta} m_l^{(0)} \sigma_\beta^l (\omega_\beta^+ - \omega_\alpha^-)$$

because $du_\beta / dt = \omega_\beta^+ - \omega_\beta^-$. So comparing to Eq. (3.9) we see that

$$\frac{dW(u|x(0), a)}{dt} = w \tag{4.12}$$

is the work done by the reservoirs per unit time, during the evolution of the vessel and the reservoirs. Comparing now Eqs. (4.11) and (4.12), we see that

$$\frac{dF}{dt} - w = k_B T \frac{d}{dt} \psi(u|x(0), a(0)) \leq 0 \tag{4.13}$$

so *that* $k_B T(d/dt)\psi(u|x(0), a(0))$ *is the dissipation of energy per unit time.*

E. The function ψ in the space of concentrations

We have constructed a function $\psi(u|x(0), a(0))$ on the space of progress variables using Eq. (4.7), which is uniquely defined up to an additive constant. We would like to know if ψ corresponds to a state function $\bar{\psi}(x, a)$, using the substitution defined by the progress variables of Eqs. (4.5),

$$x_i = x_i(0) + \sum_\alpha \tau_\alpha^i u_\alpha,$$

$$a_l = a_l(0) + \sum_\alpha (t_\alpha^l + \sigma_\alpha^l) u_\alpha. \tag{4.14}$$

We shall prove the following facts in Appendix C:

(*i*) *Let us assume that there exists a thermodynamic equilibrium state* $(\bar{x}, \bar{a})$, *so that*

$$\omega_\beta^-(\bar{x}, \bar{a}) = \omega_\beta^+(\bar{x}, \bar{a}) \quad \text{for all} \quad \beta,$$

$$m_l(\bar{x}, \bar{a}) = m_l^{(0)} \quad \text{for all} \quad l. \tag{4.15}$$

Then there exists a function $\bar{\psi}(x, a|\bar{x}, \bar{a})$ *such that*

$$\bar{\psi}\left(x_i(0) + \sum \tau_\alpha^i u_\alpha, a_l(0) + \sum (t_\alpha^l + \sigma_\alpha^l)u_\alpha|\bar{x}, \bar{a}\right)$$

$$= \psi(u|x(0), a(0)). \tag{4.16}$$

Moreover, we have

$$\bar{\psi}(x, a|\bar{x}, \bar{a}) = \frac{1}{k_B T}\left(F(x, a) - \sum_i \mu_i(\bar{x}, \bar{a})x_i - \sum_l m_\alpha^l a_l\right) + C \tag{4.17}$$

for a certain constant C which depends of $x(0), a(0), \bar{x}, \bar{a}$.

(*ii*) *If one chooses another solution* $(\bar{x}', \bar{a}')$ *of Eqs. (4.15), then the function* $\bar{\psi}(x, a|\bar{x}, \bar{a}) - \bar{\psi}(x, a|\bar{x}', \bar{a}')$ *is constant during the evolution given by the progress variables* [see Eq. (4.17)].

(*iii*) *The function* $\bar{\psi}(x, a|\bar{x}, \bar{a})$ *satisfies the Hamilton–Jacobi equation associated with the Master equation,*

$$\sum_r w_r(x, a)\left[\exp\left(\sum_i r_i \frac{\partial \bar{\psi}}{\partial x_i}\right) - 1\right] = 0 \tag{4.18}$$

provided that in this equation, (x, a) *are replaced by their expressions (4.5) in term of the progress variables.*

Thus, the function ψ of the progress variables u corresponds to a state function $\bar{\psi}$ if the conditions imposed by the constraints allow the existence of a detailed balance equilibrium.

F. The case of a partial equilibrium free energy

We assume now that Eq. (4.3) holds

$$F(x,a) = F_1(x) + F_2(a). \tag{4.19}$$

In Sec. IV A, we have seen that, in this case, the evolution maintaining the chemical potential m_l of the species A_l is constant, such that,

$$\sigma_\alpha^l = -t_\alpha^l$$

as in Eq. (4.4′), i.e., the reservoirs cancel exactly the action of the chemical processes. In this situation, the concentration a_l of the chemical species A_l can be considered as fixed parameters. The function $\bar{\psi}(x|\bar{x},a)$ satisfies more precise properties than those of Sec. IV E. In fact, it can be asserted, under these conditions, that

(i′) *There exists a function $\bar{\psi}(x|\bar{x},a)$ such that*

$$\bar{\psi}\left(x_i(0) + \sum \tau_\beta^i u_\beta \middle| \bar{x},a \right) = \psi(u|x(0),a) \tag{4.20}$$

if and only if there exists a state $\{\bar{x}_i\}$ such that $\{\bar{x},a\}$ is a thermodynamic equilibrium state, i.e., all processes are in equilibrium at $\{\bar{x},a\}$,

$$\omega_\beta^+(\bar{x},a) = \omega_\beta^-(\bar{x},a) \quad \text{for all} \quad \beta \tag{4.21}$$

and we have

$$\bar{\psi}(\bar{x}|x,a) = \frac{1}{k_B T}\left(F(x,a) - \sum \frac{\partial F_1}{\partial x_i}(\bar{x},a) x_i \right) + C, \tag{4.22}$$

where C is a constant.

(ii′) *If $\bar{x}'$ is another solution of Eq. (4.21) (for given a), $\bar{\psi}(x|\bar{x},a) - \bar{\psi}(x|\bar{x}',a)$ restricted to the subspace $E(x(0))$ is a constant.*

(iii′) *As a function of $x, \bar{\psi}(x|\bar{x},a)$ satisfies the Hamilton Jacobi equation of the Master equation,*

$$\sum_r w_r(x)\left[\exp\left(\sum_i r_i \frac{\partial \bar{\psi}}{\partial x_i} \right) - 1 \right] = 0$$

and the restriction of $\bar{\psi}(x|\bar{x},a)$ to $E(x(0))$ satisfies the Hamilton Jacobi equation of the Master equation on the invariant subspace $E(x(0))$.

(iv′) *If there exists an isolated attracting point of the vector field $A_i(x,a)$ on $E(x(0))$, then $\bar{\psi}(x|\bar{x},a)$ on $E(x(0))$ is the unique regular solution of the Hamilton–Jacobi equation of the Master equation on the subspace $E(x(0))$. This means that $\bar{\psi}(x|\bar{x},a)$ on $E(x(0))$ is the information potential Φ itself.*

The proof of these statements is given in Appendix C. We have seen above, that the function $\psi(u|x(0),0)$ is the restriction to the subspace $E(x(0))$ (parametrized by the progress variables u_β) of a function $\bar{\psi}(x|\bar{x},a)$ if and only of one can find a state $\bar{x}$ such that $(\bar{x},a)$ is the thermal equilibrium state. But, *a priori*, the state $\bar{x}$ does not necessarily belong to the same subspace $E(x(0))$. Finally, the following fact can be easily derived.

(v) *The choice of $\bar{x}$ will depend in general on $s-d$ free parameters (where s is the number of the species X_i and d is*

the dimension of the space $E(x(0))$). It is then always possible to choose $\bar{x}$ in the subspace $E(x(0))$ for any given $x(0)$.

These general statements can be confirmed by explicit calculations in the case where there is only one chemical spaces varying freely in the volume V. In this situation, everything can be calculated explicitly, in particular the non-equilibrium information potential (see Part I).

V. CONCLUSION

In this article, which concludes the first two parts of our general study of nonequilibrium reaction-diffusion systems, we have mainly considered the situation of systems which are maintained out of equilibrium by external constraints. Because of this nonequilibrium situation, the standard thermodynamics potentials are not fully appropriate to study the approach to the stationary nonequilibrium state.

We have defined an information potential in progress variables and we have shown that it can be defined very easily in term of its first order partial derivatives. It is not in general a state function, but it gives exactly the work provided by the reservoirs to maintain the system in a nonequilibrium situation. Moreover we have shown that the information potential in progress variables is a state function if the reservoirs maintain conditions such that the system reaches a thermal equilibrium. In this case, it is identical to the information potential in the concentration variables. We have also discussed in detail the action of the reservoirs and we have shown that a natural condition is that the reservoirs maintain constant certain chemical potentials rather than the concentrations. Finally, we have shown that the dissipation of energy is always larger or equal to the dissipation of information (in absolute value), the equality holding only at equilibrium. Our results are restricted to reaction-diffusion systems at a fixed temperature. Further publications will propose an extension to variable temperature systems as well as a more detailed study of the actions of the reservoirs in stochastic dynamics contexts.[13–15]

APPENDIX A: PROOF OF THE INEQUALITY (3.11)

We have from Eqs. (3.5), (3.9), and (3.8), the equality,

$$\frac{dF}{dt} - w = \sum_i \frac{\partial F}{\partial x_i}\frac{dx_i}{dt} + \sum_l \frac{\partial F}{\partial a_l}\left[\frac{da_l}{dt}\right]_C$$

$$= \sum_\alpha (\omega_\alpha^+ - \omega_\alpha^-)\frac{\partial F}{\partial u_\alpha}, \tag{A1}$$

$$\frac{d\Phi}{dt} = \sum_\alpha (\omega_\alpha^+ - \omega_\alpha^-)\frac{\partial \Phi}{\partial u_\alpha},$$

$$\pi_\alpha = \frac{\partial \Phi}{\partial u_\alpha}, \quad p_\alpha = \frac{1}{k_B T}\frac{\partial F}{\partial u_\alpha}, \tag{A2}$$

so that π_α satisfies the Hamilton–Jacobi equation,

$$\sum_\alpha [\omega_\alpha^+(e^{\pi_\alpha} - 1) + \omega_\alpha^-(e^{-\pi_\alpha} - 1)] = 0 \tag{A3}$$

and p_α satisfies the detailed balance condition,

$$\omega_\alpha^+(e^{p_\alpha}-1)+\omega_\alpha^-(e^{-p_\alpha}-1)=0 \quad \text{for all } \alpha. \tag{A4}$$

From Eqs. (A3) to (A4), by subtraction we obtain

$$\sum_\alpha \left(\omega_\alpha^+(e^{\pi_\alpha}-e^{p_\alpha})+\omega_\alpha^-(e^{-\pi_\alpha}-e^{-p_\alpha})\right)=0. \tag{A5}$$

But $e^y-e^x\geq e^x(y-x)$ with equality only if $y=x$ so that from Eq. (A5),

$$\sum_\alpha \left(\omega_\alpha^+ e^{p_\alpha}(\pi_\alpha-p_\alpha)+\omega_\alpha^- e^{-p_\alpha}(-\pi_\alpha+p_\alpha)\right)\leq 0.$$

By Eq. (A4), $p_\alpha=\log(\omega_\alpha^-/\omega_\alpha^+)$, so that

$$-\sum (\omega_\alpha^+-\omega_\alpha^-)(\pi_\alpha-p_\alpha)\leq 0 \tag{A6}$$

which, by Eqs. (A1), (A2) implies inequality (3.11).

In Eq. (A6), we have equality if and only if $\pi_\alpha=p_\alpha$ for all α, or

$$\Phi = \frac{F}{k_B T} + \text{cst},$$

which means that we are at equilibrium.

APPENDIX B: PROOF OF EQ. (4.6)

We have to prove that for all α, β,

$$\frac{\partial}{\partial u_\alpha}\left(\log\frac{\omega_\beta^-}{\omega_\beta^+}\right) - \frac{\partial}{\partial u_\beta}\left(\log\frac{\omega_\beta^-}{\omega_\beta^+}\right)=0$$

or

$$\frac{\partial}{\partial u_\alpha}\left(\sum_i \mu_i\tau_\beta^i+\sum_l m_l t_\beta^l\right) - \frac{\partial}{\partial u_\beta}\left(\sum_i \mu_i\tau_\alpha^i+\sum_l m_l t_\alpha^l\right)=0. \tag{B1}$$

Now, by definition of our constraints, the m_l stay constant in the evolution of the system, due to the action of reservoir, so we have to verify that

$$\frac{\partial}{\partial u_\alpha}\left(\sum_i \mu_i\tau_\beta^i\right) - \frac{\partial}{\partial u_\beta}\left(\sum_i \mu_i\tau_\alpha^i\right)=0$$

or

$$\sum_j \left[\frac{\partial x_j}{\partial u_\alpha}\frac{\partial}{\partial x_j}\left(\sum_i \mu_i\tau_\beta^i\right) - \frac{\partial x_j}{\partial u_\beta}\frac{\partial}{\partial x_j}\left(\sum_i \mu_i\tau_\alpha^i\right)\right]$$

$$+\sum_k \left[\frac{\partial a_k}{\partial u_\alpha}\frac{\partial}{\partial a_k}\left(\sum_i \mu_i\tau_\beta^i\right)\right.$$

$$\left.-\frac{\partial a_k}{\partial u_\beta}\frac{\partial}{\partial a_k}\left(\sum_i \mu_i\tau_\alpha^i\right)\right]=0. \tag{B2}$$

Here $\partial x_j/\partial u_\alpha=\tau_\alpha^j$, $\partial a_h/\partial u_\alpha=t_\alpha^h+a_\alpha^h$ according to Eq. (4.5). Using $\partial^2 F/\partial x_i\partial x_j=\partial\mu_i/\partial x_j=\partial\mu_j/\partial x_i$, the first summation in Eq. (B2) disappears, so that Eq. (B2) reduces to

$$\sum_{k,i}\left[(t_\alpha^k+\sigma_\alpha^k)\tau_\beta^i-(t_\beta^k+\sigma_\beta^k)\tau_\alpha^i\right]\frac{\partial\mu_i}{\partial a_k}=0. \tag{B3}$$

Now by Eq. (4.4),

$$t_\alpha^k+\sigma_\alpha^k=-\sum_{l,j} M_{kl}^{-1}\frac{\partial m_l}{\partial x_j}\tau_\alpha^j,$$

where $M_{hl}=\partial m_l/\partial a_k$ and M^{-1} is the inverse of the matrix M. Thus, Eq. (B3) reduces to

$$\sum_{k,i,j,l} M_{kl}^{-1}\frac{\partial m_l}{\partial x_j}\frac{\partial\mu_i}{\partial a_k}(\tau_\alpha^j\tau_\beta^i-\tau_\beta^j\tau_\alpha^i)=0. \tag{B4}$$

But

$$\sum_{\Sigma kl} M_{kl}^{-1}\frac{\partial m_l}{\partial x_j}\frac{\partial\mu_i}{\partial a_k}=\sum_{kl} M_{kl}^{-1}\frac{\partial^2 F}{\partial a_l\partial x_j}\frac{\partial^2 F}{\partial a_k\partial x_i}$$

is a symmetric quantity in i,j because M_{kl} is $\partial^2 F/\partial a_k\partial a_l$ and so M^{-1} is symmetric and Eq. (B4) obviously holds.

Remarks

(1) If, instead of Eq. (5.4) expressing that the chemical potentials m_l are constant, we assume that the concentrations a_l are constants, it is easily found that Eq. (B1) is equivalent to

$$\sum_{i,k}(\tau_\alpha^i t_\beta^k-\tau_\beta^i t_\alpha^k)\frac{\partial m_k}{\partial x_i}=0. \tag{B5}$$

Equation (B5) obviously holds if the m_k are functions of the a_l only, in which case the constancy of the chemical potentials m_l is indeed equivalent to the constancy of the concentration a_k. Otherwise, Eq. (B5) implies relations between the x and the a which, in general, are not compatible with the kinetic equations. So, in general, Eq. (4.6) holds only if we assume the constancy of the chemical potential m_l.

(2) It has been observed in Sec. V A, that relations (4.4) or (4.4′) imply a very strong control on the species A_l which could be difficult to realize in practice. Nevertheless, such a control could be effective, at least in the following situation: All species in the system are free (i.e., evolve according the chemical laws). However some of them, say X_l can be directly and rapidly exchanged with the reservoirs by diffusion processes for example at the interfaces with the reservoirs. This can be expressed by pseudochemical reactions,

$$X_l\rightleftarrows A_l,$$
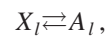
with A_l denoting the same chemical species as X_l, but considered inside the reservoirs. If the rate of exchange from A_l to X_l is assumed to be constant (which it a standard hypothesis), this will correspond to a strictly constant concentration or chemical potential for A_l. On the other hand the chemical potential for A_l is independent of the X, so that we recover the general formalism, just by considering that A_l is also a chemical species of the system.

APPENDIX C: THE FUNCTION ψ AS A STATE FUNCTION

We recall from Eqs. (4.7) and (4.1) that

$$\frac{\partial\psi}{\partial u_\beta}=\log\frac{\omega_\beta^-}{\omega_\beta^+}=\frac{1}{k_B T}\left(\sum_i \mu_i\tau_\beta^i+\sum_l m_l^{(0)}t_\beta^l\right)$$

so its differential is

$$d\psi = \frac{1}{k_B T}\left(\sum_{i,\beta} \mu_i \tau^i_\beta du_\beta + \sum_{l,\beta} m^{(0)}_l t^l_\beta du_\beta \right). \qquad (C1)$$

1. Proof of (i), Sec. IV E

ψ comes from a function $\bar{\psi}$ depending on x, a [using the substitution of Eqs. (4.5)], if and only if $d\psi$ can be rewritten as a linear combination of the dx_i and da_l with the variations given by Eqs. (4.5),

$$dx_i = \sum \tau^i_\beta du_\beta,$$

$$da_l = \sum (t^l_\alpha + \sigma^l_\alpha) du_\alpha, \qquad (C2)$$

with coefficients depending on (x,a) (and no more on u_β). From Eq. (C1) using Eqs. (C2), we have

$$d\psi = \frac{1}{k_B T}\left(\sum_i \mu_i dx_i + \sum_l m^{(0)}_l da_l \right)$$

$$- \frac{1}{k_B T}\sum_{l,\beta} m^{(0)}_l \sigma^l_\beta du_\beta. \qquad (C3)$$

In Eq. (C3) the first term is exactly

$$\frac{1}{k_B T} dF(x,a)$$

because $\mu_i = \partial F / \partial x_i$, $m^{(o)}_l = \partial F / \partial a_l$ maintained constant during the evolution. So we need to prove that the last summation in Eq. (C3) can be rewritten as a linear combination of the dx_i and da_l given by Eq. (C2), namely, to find γ_i, θ_l,

$$\sum_{l,\beta} m^{(0)}_l \sigma^l_\beta du_\beta = \sum_i \gamma_i dx_i + \sum_l \theta_l da_l$$

$$= \sum_{i,\beta} \gamma_i \tau^i_\beta du_\beta + \sum_{l,\beta} \theta_l (t^l_\beta + \sigma^l_\beta) du_\beta.$$

So we must have for all β,

$$\sum_l m^{(0)}_l \sigma^l_\beta = \sum_i \gamma_i \tau^i_\beta + \sum_l \theta_l (t^l_\beta + \sigma^l_\beta). \qquad (C4)$$

Under the hypothesis of (i) of Sec. IV E, there exists a $(\bar{x},\bar{a})$ with

$$\omega^-_\beta(\bar{x},\bar{a}) = \omega^+_\beta(\bar{x},\bar{a}),$$

$$m^{(0)}_l = m_l(\bar{x},\bar{a}).$$

From Eq. (4.1), we have for all β,

$$\sum_l \mu_i(\bar{x},\bar{a}) \tau^i_\beta + \sum_l m^{(0)}_l t^l_\beta = 0, \qquad (C5)$$

and we can solve Eq. (C4) with

$$\theta_l = m^{(0)}_l, \quad \gamma_i = \mu_i(\bar{x},\bar{a}).$$

Then Eq. (C3) becomes

$$d\psi = \frac{1}{k_B T}\left(dF(x,a) - \sum_i \mu_i(\bar{x},\bar{a}) dx_i - \sum_l m^{(0)}_l da_l \right),$$

and we can take

$$\bar{\psi}(x,a|\bar{x},\bar{a}) = \frac{1}{k_B T}\left(F(x,a) - \sum_i \mu_i(\bar{x},\bar{a}) x_i \right.$$

$$\left. - \sum_l m^{(0)}_l a_l \right) + C, \qquad (C6)$$

where C is a constant adjusted so that

$$\bar{\psi}(0|x(0),a(0)) = \bar{\psi}(x(0),a(0)|\bar{x},\bar{a})).$$

This proves the assertion (i) of Sec. IV E.

2. Proof of (ii), Sec. IV E

Let us consider two equilibrium states $(\bar{x},\bar{a})$ and $(\bar{x}',\bar{a}')$. From Eq. (C6), one has

$$\bar{\psi}(x,a|\bar{x},\bar{a}) - \bar{\psi}(x,a|\bar{x}',\bar{a}')$$

$$= -\frac{1}{k_B T}\left(\sum_i (\mu_i(\bar{x},\bar{a}) - \mu_i(\bar{x}',\bar{a}')) x_i \right) + \text{cst}.$$

We replace x_i by its value of Eq. (4.5),

$$x_i = x_i(0) + \sum \tau^i_\beta u_\beta,$$

and use Eq. (C5), to deduce that for all β,

$$\sum_i \mu_i(\bar{x},\bar{a}) \tau^i_\beta - \sum \mu_i(\bar{x}',\bar{a}') \tau^i_\beta = 0,$$

so when we replace x and a by their expression in term of the progress variables, given by Eq. (4.5), we see that

$$\bar{\psi}(x,a|\bar{x},\bar{a}) - \bar{\psi}(x,a|\bar{x}',\bar{a}') = \text{cst}.$$

3. Proof of (iii), Sec. IV E

Take $\bar{\psi}$ as in Eq. (C6) and calculate $\partial \psi / \partial u_\beta$ for the evolution given by Eq. (C2), to obtain, using the fact that $m_l = \partial F / \partial a_l$ is constant and equal to $m^{(0)}_l$,

$$\frac{\partial \psi}{\partial u_\beta} = \frac{1}{k_B T}\sum_i (\mu_i(x,a) - \mu_i(\bar{x},\bar{a})) \tau^i_\beta = \sum_i \tau^i_\beta \frac{\partial \bar{\psi}}{\partial x_i}.$$

Now, ψ satisfies

$$\sum_\beta \omega^+_\beta \left[\exp\left(\frac{\partial \psi}{\partial u_\beta} \right) - 1 \right] + \sum_\beta \omega^-_\beta \left[\exp\left(-\frac{\partial \psi}{\partial u_\beta} \right) - 1 \right] = 0$$

[provided in ω^+_β, ω^-_β, x, and a are replaced by the evolution of Eq. (C2)]. So this is

$$\sum_r w_r \left[\exp\left(\sum_i r_i \frac{\partial \bar{\psi}}{\partial x_i} \right) - 1 \right] = 0 \qquad (C7)$$

provided in this equation, x and a are replaced by their expressions of Eq. (C2). For a situation of partial equilibrium free energy, the previous properties are made more precise in Sec. III F.

4. Proof of (i′), Sec. IV F

We have seen in the assertion (i) of Sec. IV E that the condition of finding $(\bar{x},a)$ (thermodynamic equilibrium state) is a sufficient condition. To see that this condition is also necessary we come back to Eq. (C1). The function ψ comes from a state function $\bar{\psi}(x)$, if and only if $d\psi$ can be written as a linear combination of the dx_i. In Eq. (C1), we see that

$$\sum_{i,\beta} \mu_i \tau^i_\beta du_\beta = dF_1(x). \tag{C8}$$

The second sum in Eq. (C1) is a linear combination of the dx_i, if and only if can find γ_i with,

$$\sum_{l,\beta} m_l^{(0)} t^l_\beta du_\beta = -\sum \gamma_i \tau^i_\beta du_\beta$$

or for all β,

$$\sum_l m_\beta^{(0)} t^l_\beta + \sum \gamma_i \tau^i_\beta = 0. \tag{C9}$$

We can always find $(\bar{x}_i)$ such that

$$\gamma_i = \frac{\partial F_1}{\partial x_i}(\bar{x}) \quad \text{for all} \quad i,$$

while $m_l^{(0)} = \partial F_2 / \partial a_l(a)$.

Then Eq. (C9) means exactly that

$$\omega^+_\beta(\bar{x},a) = \omega^-_\beta(\bar{x},a)$$

which is the equilibrium condition. Then Eq. (5.26) is evident from Eq. (C6) in view of the fact that $F = F_1(x) + F_2(a)$.

The proofs of assertions (ii) and (iii), Sec. IV F are straightforward from the corresponding assertions (ii), (iii) of Sec. IV E but here $\sigma^l_\alpha = -t^l_\alpha$ so that the a_l keep a constant value, so Eq. (C10) is valid for all x in the space $E(x(0))$. But now, $\bar{\psi}$ depends on $x(0)$, only through an additive constant [see Eq. (5.26) for $\bar{\psi}$], so that Eq. (C10) is valid on every subspace $E(x(0))$ and thus, is valid everywhere in the space of the concentrations x.

5. Proof of (iii′), Sec. V F

We have seen in assertion (iii) that $\bar{\psi}$ satisfies the equation

$$\sum_r w_r(x,a)\left[\exp\left(\sum_i r_i \frac{\partial \bar{\psi}}{\partial x_i} \right) - 1 \right] = 0 \tag{C10}$$

provided one replaces in this equation the variables x and a by their expressions in term of the progress variables,

$$x_i = x_i(0) + \sum_\beta \tau^i_\beta u_\beta, \quad a_l = a_l(0) + \sum_\alpha (t^l_\alpha + \sigma^l_\alpha) u_\alpha.$$

6. Proof of (iv′), Sec. IV F

This is a consequence of Part I, where it is proven that the Hamilton–Jacobi equation associated with the Master equation has a unique smooth solution when there is at least one attracting zero of the deterministic vector field A_i.

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