

Variational nonequilibrium thermodynamics of reaction-diffusion systems.

I. The information potential

Bernard Gaveau^{a)}

*Université Pierre et Marie Curie, Laboratoire Equations aux Dérivées Partielles, Case courrier 172,
75252 Paris Cedex 05, France*

Michel Moreau

*Université Pierre et Marie Curie, Laboratoire Physique Théorique des Liquides,
75252 Paris Cedex 05, France*

Janos Toth

Agricultural University, Department of Computer Science, Gödöllő, Pater K. u.l, H-2103, Hungary

(Received 16 February 1999; accepted 2 August 1999)

In this work, we consider the nonequilibrium thermodynamics of a reaction-diffusion system at a given temperature, using the Master equation. The information potential is defined as the logarithm of the stationary state. We compare the approximations, given by the Fokker–Planck equation and the Wentzel–Kramers–Brillouin method directly applied to the Master equation, and prove that they lead to very different results. Finally, we show that the information potential satisfies a Hamilton–Jacobi equation and deduce general properties of this potential, valid for any reaction-diffusion system, as well as a unicity result for the regular solution of the Hamilton–Jacobi equation. A second article (Paper II), in the same series, will develop a path integral approach and an estimation of the chemical rate constants in this general context. © 1999 American Institute of Physics. [S0021-9606(99)50940-9]

I. INTRODUCTION

Most macroscopic systems are usually in a nonequilibrium state, and even far away from equilibrium. In fact, this is why they become interesting. How to describe them qualitatively, or even quantitatively, at least in the thermodynamic limit? This question has been asked since the beginning of thermodynamics (in fact, an engine following its Carnot cycle is already far away from equilibrium) and many approaches and answers to this question have been proposed without a general agreement concerning basic questions, like the definition of thermodynamic functions, the definition of dissipation, the characterization of the stationary state, the nature of phase transitions in nonequilibrium.^{1–9} New concepts applicable to chemical systems far from equilibrium have been recently developed.^{10–12} Recently, we have proposed an approach based on the Master equation and we have been able to define dissipation of information, relative entropy, fluctuation–dissipation relations, Onsager reciprocity coefficients currents matrices, and first order transitions.^{13,14}

Equilibrium situations are well understood, both from the thermodynamical and the statistical mechanical points of view. Everything can, in principle at least, be deduced from the partition function associated to the Boltzmann distribution on the state space. Then, the free energy can be deduced as the logarithm of the probability distribution (up to temperature) and the relaxation towards equilibrium and

fluctuation–dissipation relations, follow naturally. As usual, it is necessary to distinguish statistical equilibrium which is realized when the equilibrium distribution is established, from the equilibrium state which is the most probable state of the equilibrium distribution, i.e., the state which is observed macroscopically at equilibrium. Even if statistical equilibrium is established, it is possible to observe nonequilibrium macroscopic states due to fluctuations in the system, but these relax rapidly to the equilibrium state. The usual thermodynamic functions, such as entropy, or free energy can be defined from the probability distribution, either globally, as is the case on the well-known information entropy, or locally for individual states, as is the case for the Einstein entropy formula. For the most probable (or macroscopic equilibrium state), these local quantities become practically equal to the corresponding global or average quantities.

In nonequilibrium situations, it is impossible to use the partition function, in particular because the probability distribution on the state space is already given by the system without being related in any obvious manner to an energy on the state space. On the other hand, at least formally, every probability distribution can be considered as a Boltzmann distribution with an energy $H(x) = -k_B T \log p(x)$. What is important, is the dynamics which can distinguish between equilibrium and nonequilibrium situations.¹⁴ Nonequilibrium stationary situations are manifested by the existence of non-zero currents, or by net fluxes due to the fact that a nonequilibrium dynamics does not satisfy the principle of detailed balance, though the system is in a stationary state. On the contrary, for a system at thermal equilibrium there are no net

^{a)}Electronic mail: gaveau@ccr.jussieu.fr

fluxes, and the system appears, to a macroscopic observer, completely inert.¹⁴

Our aim is to develop systematically the Master equation approach as a foundation of nonequilibrium thermodynamics in the context of reaction diffusion systems. Moreover, we shall also assume that the volume of the system is macroscopic, i.e., large but not infinite, as in equilibrium situations¹⁵ (see Refs. 16 and 17 for difficulties with the infinite volume limit). For a system in a stationary state, the main quantity is the logarithm of the stationary probability distributions divided by the volume, namely $\Phi(x) = -V^{-1} \log p(x)$, x being a state of the system. For obvious reasons, we call this quantity the “information potential.” In an equilibrium situation, this would be the free energy, up to multiplication by $k_B T$. This series of articles will be centered around the information potential Φ . In the first part, we shall construct and study various properties of Φ . In the second part,¹⁸ we shall introduce path integrals and use Φ as a way to estimate rate constants and first exit time of domains. The third part of this series will compare free energy and information potential. We shall prove that the energy dissipation to transfer a system in a nonequilibrium situation is always larger than the information dissipation. Finally, we shall prove that our version of the information potential can be effective even for systems with several degrees of freedom where it leads to explicit analytic calculations.¹⁹

In Sec. II, we fix the basic notations which will be used in this series of articles, concerning Master equations or Fokker–Planck equations in the context of reaction diffusion systems. In Sec. III, we consider in detail the large volume approximation leading to the definition of Φ and the Hamilton–Jacobi equation associated to the Master equation, which was introduced in Refs. 4 and 20 as well as applications in Refs. 12 and 21. As was discussed,²¹ this Hamilton–Jacobi equation associated to the Master equation gives more sensible and precise results than the one associated to the Fokker–Planck equation. This is why, we shall systematically use the Master equation approach and its Hamilton–Jacobi theory, rather than the Fokker–Planck equation approach. Still, the Fokker–Planck equation and its Hamilton–Jacobi theory will be useful as technical tools to prove results concerning the more exact situation of the Hamilton–Jacobi equation of the Master equation. This is why we treat both Hamilton–Jacobi theories together. In Sec. IV, we derive a certain number of general results concerning the information potential which are valid for any reaction diffusion systems, relating the Hamilton–Jacobi equation to the standard variational method (minimization of a Lagrangian); the title of this series of articles is “variational nonequilibrium thermodynamics.” We prove that the positivity of the Lagrangian, gives a construction of the information potential, proves that it is unique up to a constant, and finally shows that its minima are the attracting points of the deterministic vector field of the macroscopic theory of the diffusion reaction system and vice versa. Proofs and several results to be used later are given in the Appendices.

II. MASTER EQUATIONS AND FOKKER–PLANCK EQUATIONS

A. Master equation

We consider a system formed of s different species labeled by $1 \leq i \leq s$ and we denote n_i the number of particles of species i . The total volume of the system is V . The system evolves by various processes and we call $W_r(\{n_i\})$ the total probability per unit time of a transition:

$$\{n_i\} \rightarrow \{n_i + r_i\} \quad (2.1)$$

with given integers $r_i \geq 0$. r denotes the s uplet $r = \{r_i\}$. It is clear that various different processes can contribute to a given transition Eq. (2.1) but presently we do not need this fact. The state of the system at time t is characterized by a probability distribution function $P(\{n_i\}, t)$ whose time evolution is given by a standard Master equation

$$\frac{\partial P(\{n_i\}, t)}{\partial t} = (LP)(\{n_i\}, t) \quad (2.2)$$

where L is the evolution operator^{2–7}

$$(LP)(\{x_i\}, t) = \sum_r [W_r(\{n_i - r_i\})P(\{n_i - r_i\}, t) - W_r(\{n_i\})P(\{n_i\}, t)]. \quad (2.3)$$

To define the large volume limit, we introduce the concentration variables

$$x_i = \frac{n_i}{V}, \quad dx_i = \frac{1}{V}, \quad (2.4)$$

and define the density of the probability distribution function $p(\{x_i\}, t)$ by

$$P(\{n_i\}, t) = p(\{x_i\}, t) \prod_{i=1}^s dx_i. \quad (2.5)$$

Since the chemical reactions are local phenomena, the corresponding overall transition rates W_r should be extensive quantities, and we redefine them as

$$W_r(\{n_i\}) = V w_r(\{x_i\}).$$

Using these notations, the Master equation [Eqs. (2.2) and (2.3)] can be rewritten for the function $p(x, t)$ as

$$\frac{\partial p(x, t)}{\partial t} = V \sum_r \left[w_r \left(\left\{ x_i - \frac{r_i}{V} \right\} \right) p \left(\left\{ x_i - \frac{r_i}{V} \right\}, t \right) - w_r(\{x_i\}) p(\{x_i\}, t) \right]. \quad (2.6)$$

This formalism can also describe reaction-diffusion processes: the total volume V is divided into N cells labeled k with the various numbers of particles in each cell as “chemical” species with rate processes of the type Eq. (2.1) for the exchange of particles by diffusion between adjacent cells.

B. Approximate Fokker–Planck equation

A standard approximation³ of the Master equation [Eq. (2.6)] in the large volume limit is obtained by the Taylor expansion the second member of Eq. (2.6) up to terms of order $0(1/V)$. This expansion gives the Fokker–Planck equation for p

$$\frac{\partial p(x,t)}{\partial t} = - \sum_{i=1}^s \frac{\partial}{\partial x_i} [A_i(x)p(x,t)] + \frac{1}{2V} \sum_{i,j=1}^s \frac{\partial^2}{\partial x_i \partial x_j} (D_{ij}p) \quad (2.7)$$

where

$$A_i(x) = \sum_r r_i w_r(x), \quad D_{ij}(x) = \sum_r r_i r_j w_r(x). \quad (2.8)$$

It is well known that higher approximation [keeping terms in $0(1/V^n)$] can lead to inconsistent results (as negative probabilities). On the other hand in general the present approximation does not respect the natural boundary conditions of the Master equation.

Both Master equations and Fokker–Planck equations are consistent with the usual deterministic equation

$$\frac{d\bar{x}_i}{dt} = A_i(\bar{x}), \quad i = 1, \dots, s, \quad (2.9)$$

which holds for the average \bar{x}_i of x_i , if all fluctuations are neglected.⁴ Here, the average of \bar{x}_i is the average of x_i with respect to the solution $p(x,t)$ of the Fokker–Planck equation.

C. Conservation laws and irreducibility

The Master equation is associated to a birth and death process $\{x_i(t)\}$.⁴ During a time interval Δt the variation $\Delta x_i(t)$ is

$$\Delta x_i(t) = \sum_r r_i \eta_r, \quad (2.10)$$

where the η_r are random variables (indexed by the r corresponding to nonzero transition rates w_r). The stochastic process $\{x_i(t)\}$ will then satisfy certain linear conservation laws. More precisely for each point $x(0)$ in the space X of concentrations, one defines a linear subspace

$$E[x(0)] = \left\{ x \in X \mid x_i = x_i(0) + \sum_r r_i \xi_r \right\}, \quad (2.11)$$

where the ξ_r are real numbers indexed by the r with $w_r \neq 0$. In general the various vectors $\{r_i\}$ are not linearly independent, so that a given x is not uniquely represented by the equations in Eq. (2.11). The whole space X is a union of all the subspaces $E[x(0)]$ and by definition, the birth and death process $\{x_i(t)\}$ remains in $E[x(0)]$ for all time. As a consequence, each subspace $E[x(0)]$ will support a stationary solution, which is the stationary distribution of $\{x_i(t)\}$ starting from $\{x_i(0)\}$. This stationary distribution can be denoted by $p[x|x(0)]$ and does not depend of the choice of $x(0)$ in $E[x(0)]$. Thus it contains various δ -functions factors ex-

pressing the fact that it is supported by $E[x(0)]$. The Master equation Eq. (2.6) induces on each $E[x(0)]$ a Master equation for a smaller number of variables, (the other variables being linear functions of these variables), but now, the stationary distribution is unique. The deterministic evolution given by Eq. (2.9) stays in $E[x(0)]$ also, because the variation in dt of $d\bar{x}_i$ is

$$d\bar{x}_i = \sum_r r_i w_r(\bar{x}) dt,$$

which is of the form of Eq. (2.10). The same remarks are also valid for the stochastic processes associated to the Fokker–Planck equation.

In Part I, we shall assume that the Master equation is irreducible, that is, there are no linear conservation laws. We can always assume that this situation holds, if one considers the reduced Master equation on a given subspace E . We shall also assume that the zeroes of the vector field $\{A_i(x)\}$ are isolated on each subspace E .

III. HAMILTON–JACOBI APPROXIMATION FOR THE MASTER EQUATION AND FOKKER–PLANCK EQUATION

We shall recall an approximation, originally introduced by Kubo *et al.*,²⁰ also Ref. 22 and more recently Ref. 12. This approximation is better than the usual Fokker–Planck approximation (see Sec. IV, as well as Ref. 21 in the sense that it gives more physical results).

A. Hamilton–Jacobi theory for the Master equation

The idea of the approximation is to write $p(x,t)$ as a Wentzel–Kramers–Brillouin (WKB) type expansion, valid for large V

$$p(x,t) = \exp[-V\Phi(x,t)] \left[U_0(x,t) + \frac{1}{V} U_1(x,t) + \dots \right] \quad (3.1)$$

where Φ , U_0 , U_1, \dots are unknown functions. Then, one replaces p in Eq. (2.6) by the expansion given in Eq. (3.1) and group together terms by decreasing powers of V . The highest order term in V , is of order $0(V)$ and contains U_0 in factor. It is zero if and only if, Φ satisfies the equation:

$$\frac{\partial \Phi}{\partial t} + \sum_r w_r(x) \left[\exp \left(\sum_{i=1}^s r_i \frac{\partial \Phi}{\partial x_i} \right) - 1 \right] = 0. \quad (3.2)$$

This is a Hamilton–Jacobi equation which can be integrated by the method of bicharacteristics.²³ The next term of order $0(1)$ in V , in Eq. (2.6) [after one has replaced p by the expansion Eq. (3.1)] is a first order linear equation for U_0 , called the transport equation

$$\frac{\partial U_0}{\partial t} + \sum_r \left[\exp \left(\sum_{i=1}^s r_i \frac{\partial \Phi}{\partial x_i} \right) \sum_{i=1}^s \frac{\partial}{\partial x_i} (r_i w_r U_0) \right] + U_0 \sum_r \exp \left(\sum_{i=1}^s r_i \frac{\partial \Phi}{\partial x_i} \right) \left(\frac{1}{2} \sum_{i,j} r_i r_j w_r \frac{\partial^2 \Phi}{\partial x_i \partial x_j} \right) = 0. \quad (3.3)$$

B. Hamilton–Jacobi theory of the Fokker–Planck equation

For large V , one can use WKB-type expansion for p in Eq. (2.7), namely

$$p(x,t) = \exp(-V\Phi^{(FP)}(x,t)) \times \left[U_0^{(FP)}(x,t) + \frac{1}{V} U_1^{(FP)}(x,t) + \dots \right]. \quad (3.4)$$

One obtains equations for $\Phi^{(FP)}$, $U_0^{(FP)}$, $U_1^{(FP)}$, inserting the expansion Eq. (3.4) in the Fokker–Planck Eq. (2.7) and identifying the various powers of V

$$\frac{\partial \Phi^{(FP)}}{\partial t} + \sum_i A_i \frac{\partial \Phi^{(FP)}}{\partial x_i} + \frac{1}{2} \sum_{i,j} D_{ij} \frac{\partial \Phi^{(FP)}}{\partial x_i} \frac{\partial \Phi^{(FP)}}{\partial x_j} = 0 \quad (3.5)$$

$$\frac{\partial U_0^{(FP)}}{\partial t} + \sum_i \frac{\partial}{\partial x_i} (A_i U_0^{(FP)}) + \sum_{i,j} \frac{\partial \Phi^{(FP)}}{\partial x_i} \frac{\partial}{\partial x_j} (D_{ij} U_0^{(FP)}) + \frac{1}{2} \left(\sum_{i,j} D_{ij} \frac{\partial^2 \Phi^{(FP)}}{\partial x_i \partial x_j} \right) U_0^{(FP)} = 0. \quad (3.6)$$

Equation (3.5) is a standard Hamilton–Jacobi equation (with a standard Hamiltonian, quadratic in the momentum) and Eq. (3.6) is a transport equation. One sees immediately that the system of Eqs. (3.5) and (3.6) is obtained from Eqs. (3.2) and (3.3) when one assumes that the derivatives ($\partial \Phi / \partial x_i$) are small, so that one can replace

$$\exp\left(\sum_{i=1}^s r_i \frac{\partial \Phi}{\partial x_i}\right) - 1,$$

by its Taylor expansion up to second order. Then Eq. (3.2) reduces immediately to Eq. (3.5) with the A_i and D_{ij} given as in Eq. (2.7). This indicates that the Hamilton–Jacobi and transport equations Eqs. (3.5)–(3.6) associated with the Fokker–Planck equation are less precise than the Hamilton–Jacobi and transport equations [Eqs. (3.2) and (3.3)] directly deduced from the Master equation. In fact, their range of validity is limited to neighborhoods of the stationary points of the action function Φ , i.e., points where $\nabla \Phi$ is zero.

C. Stationary solutions

We shall again write the stationary solution of the Master equation or of the Fokker–Planck equation as

$$p(x) \sim e^{-V\Phi(x)} \left[U_0(x) + \frac{1}{V} U_1(x) + \dots \right]. \quad (3.7)$$

Then Φ satisfies the stationary form of the time dependent Hamilton–Jacobi equations Eqs. (3.2) or (3.5) and U_0 satisfies the stationary form of the transport equations [Eqs. (3.3) or (3.6)]. In both cases, the stationary Hamilton–Jacobi equation can be written as

$$H(x, \nabla \Phi) = 0, \quad (3.8)$$

where $H(x, \xi)$ is of the form

$$H_M(x, \xi) = \sum_r w_r(x) \left[\exp\left(\sum_{i=1}^{s^-} r_i \xi_i\right) - 1 \right], \quad (3.9)$$

or

$$H_{FP}(x, \xi) = \sum_i A_i(x) \xi_i + \frac{1}{2} \sum_{i,j} D_{ij} \xi_i \xi_j, \quad (3.10)$$

for the Master equation or the Fokker equation, respectively, the variables ξ_i being the conjugate momenta of x . From Eq. (2.8), we deduce for small ξ

$$H_M(x, \xi) = H_{FP}(x, \xi) + O(|\xi|^3). \quad (3.11)$$

In this work, we shall only use the stationary form of the equations.

It is proved in Appendix A that in some neighborhood of some zero of the vector field $\{A_{ij}\}$, it is always possible to study the stationary solution of the Master equation by using the Fokker–Planck Hamiltonian.

D. The particular case of one chemical species

We consider the case when only one chemical concentration can vary (so $s=1$ in the previous section) and we assume that the system evolves only by transitions $n \rightarrow n \pm 1$. As before we go to the large volume limit, defining

$$x = \frac{n}{V}, \quad P(n) = p(x) \frac{1}{V}, \quad W_{\pm}(n) = V w_{\pm}(x),$$

so that one obtains the exact Master equation and the Fokker–Planck equation Eqs. (2.6) or (2.7), with

$$\begin{aligned} A(x) &= w_+(x) - w_-(x), \\ D(x) &= w_+(x) + w_-(x). \end{aligned} \quad (3.12)$$

The solution of the Master equation,^{21,22} Eq. (3.1), is

$$\begin{aligned} p(x) &= U_0(x) \exp[-V\Phi(x|a)] \\ &= \frac{C}{\sqrt{w_+(x)w_-(x)}} \exp\left(-V \int_a^x \log \frac{w_-(x')}{w_+(x')} dx'\right), \end{aligned} \quad (3.13)$$

where a is an arbitrary value and C is a normalization constant. When w_+ and w_- have no common zero, p given by Eq. (3.1) is normalizable with

$$\begin{aligned} C &= \left[\int_0^1 \frac{dx}{\sqrt{w_+(x)w_-(x)}} \right. \\ &\quad \left. \times \exp\left(-V \int_a^x \log \frac{w_+(x)}{w_-(x)} dx'\right) \right]^{-1}. \end{aligned} \quad (3.14)$$

The integral in Eq. (3.14) can be estimated by the saddle point method. The main contribution to the integral is obtained for a point x_s which is an absolute minimum of $\Phi(x|a)$. If we assume that there exists only one such point we have

$$p(x) \sim \frac{C_0}{\sqrt{w_+(x)w_-(x)}} \exp\left[-V \int_{x_s}^x \log \frac{w_-(x')}{w_+(x')} dx'\right], \quad (3.15)$$

where C_0 is now $0[(1/\sqrt{V})]$ if the minimum of Φ is not degenerate. When there are several attracting points of $A = w_+ - w_-$, $x_s^{(l)}, \dots, x_s^{(r)}$, one chooses $x_s^{(k)}$ such that

$$\Phi(x_s^{(\ell)} | x_s^{(k)}) \geq 0 \text{ for all } \ell,$$

and again, one obtains Eq. (3.15). In the same manner, the stationary solution of the Fokker–Planck equation can be written

$$p(x) \sim U_0^{(\text{FP})}(x) \exp[-V\Phi^{(\text{FP})}(x|a)] \\ = \frac{C}{D(x)} \exp\left(V \int_a^x \frac{2A(x')}{D(x')} dx'\right), \quad (3.16)$$

and is normalizable provided $D(x)$ has no zero (or w_+ and w_- have no common zero), with

$$C = \left[\int_0^1 \frac{dx}{D(x)} \exp\left(2V \int_a^x \frac{A(x')}{D(x')} dx'\right) \right]^{-1}.$$

Again, C can be evaluated by the saddle point method, the main contribution coming from the absolute minimum x_s of $\Phi^{\text{FP}}(a)$, which is an attracting point of the vector field $A(x)$:

$$p(x) \sim \frac{C_0}{\sqrt{VD(x_s)}} \exp\left(2V \int_{x_s}^x \frac{A(x')}{D(x')} dx'\right). \quad (3.17)$$

When w_+ and w_- have a common zero, p given above is not normalizable, indicating that the expression of Eq. (3.1) for p is not valid. This is exactly the case of criticality.

E. Comparison of asymptotic results

The two approximations given by Eqs. (3.15) and (3.16) are close to each other for small values of $(d\Phi/dx)$, or when A is small and in this case one has

$$\log \frac{w_-}{w_+} \sim -\frac{2A}{D}.$$

The approximation of Eq. (3.16) given by the Fokker–Planck equation is precise near a zero of $A(x)$. But when there are several zeroes, the approximation fails, because the eigenvalues and the mean exit times calculated by Fokker–Planck equation differ from the analog quantities given by the Master equation, by an exponentially large factor.²¹

This is also the indication that the limit theorems of the Kurtz²³ type are not valid in case A and has several zeros. These theorems state that the stochastic process $\{x_i(t)\}$ associated to the Master equation tend to the deterministic trajectory of $A(x)$ (starting from the same point), and that the deviation is Gaussian, but these theorems are valid uniformly on finite time intervals. They cannot describe the situation for times which are like $\exp(kV)$. In particular, these theorems cannot describe chemical activated events like the passage over a potential barrier, and they do not correctly describe the rate constants.

IV. CONSTRUCTION, UNIQUENESS, AND CRITICAL POINTS OF Φ

In this section and the following one, we shall derive general basic properties of the function Φ which is a solution of the Hamilton–Jacobi equation Eq. (3.8)

$$H(x, \nabla\Phi) = 0, \quad (4.1)$$

with H given by Eqs. (3.9) and (3.10). The traditional method²⁴ for constructing Φ does not work, but we shall show how to construct it and prove the uniqueness of smooth solution Φ . Finally, we study the critical point of Φ . We shall treat H_M and H_{FP} together (in fact, we need the results concerning H_{FP} to derive certain results for H_M).

A. Lagrangians

The Master equation and Fokker–Planck Hamiltonian are, respectively:

$$H_M(x, \xi) = \sum_r w_r(x) [\exp(\pi_r) - 1], \quad (4.2)$$

with

$$\pi_r = \sum_{i=1}^s r_i \xi_i, \quad (4.3)$$

and

$$H_{\text{FP}}(x, \xi) = \sum_{i=1}^s A_i(x) \xi_i + \frac{1}{2} \sum_{i,j} D_{ij} \xi_i \xi_j. \quad (4.4)$$

The corresponding velocities \dot{x}_i are

$$\dot{x}_i = \frac{\partial H_M}{\partial \xi_i} = \sum_r r_i w_r(x) \exp(\pi_r) \quad (4.5)$$

and

$$\dot{x}_i = \frac{\partial H_{\text{FP}}}{\partial \xi_i} = A_i(x) + \sum_{j=1}^s D_{ij}(x) \xi_j, \quad (4.6)$$

and the Lagrangians are

$$L_M(x, \dot{x}) = \sum_r w_r(x) [\pi_r \exp(\pi_r) - \exp(\pi_r) + 1], \quad (4.7)$$

and

$$L_{\text{FP}}(x, \dot{x}) = \frac{1}{2} (\dot{x} - A) D^{-1} (\dot{x} - A). \quad (4.8)$$

In this Fokker–Planck case [Eq. (4.8)] $\xi = D^{-1}(\dot{x} - A)$ provided D is nondegenerate, which is the case if we assume that there are no conservation laws.

The first result is that, under the hypothesis of no linear conservation laws, L_{FP} and L_M are ≥ 0 and L_{FP} or L_M are 0 if and only if $\xi = 0$.

In the case of L_{FP} , this is obvious because of Eq. (4.8). In the case of L_M , using Eq. (4.7) and the inequality $e^{-u} - 1 + u \geq 0$, for any u , we see that L_M is positive or 0, and is 0, if and only if, $\pi_r = 0$ for all r such that $w_r \neq 0$. When there is no conservation law, the vectors $r = \{r_i\}$ generate the whole space X , so that a vector $\{\xi_i\}$ orthogonal to all these r 's is 0, but the fact that $\pi_r = 0$ for all r is exactly equivalent to the fact that $\sum r_i \xi_i = 0$ for all r , so that $\xi_i = 0$.

We also notice that when there are conservation laws, D is necessarily degenerate, because $D_{ij} = \sum_r r_i r_j w_r(x)$ and there is ξ_i such that $\sum r_i \xi_i = 0$ for all r .

B. Special paths

(i) *Deterministic paths*: The deterministic paths

$$\begin{cases} \frac{d\bar{x}_i}{dt} = A_i(\bar{x}) \\ \bar{\xi}_i = 0 \end{cases}, \tag{4.9}$$

are obviously solutions of both Hamiltonian equations. Conversely a path $\{x_i(t), \xi_i(t)\}$ which is a solution of the Hamiltonian equations, such that $\xi_i(0) = 0$ for all i is the deterministic path, because of the unicity of paths under given initial conditions. Moreover, the Lagrangian is zero along a deterministic path and conversely, and as a consequence, the variation of the action Φ along a deterministic path is zero.

(ii) *Antideterministic paths*: Let us assume now that $\Phi(x)$ is a smooth solution of the Hamilton–Jacobi equation and define

$$\xi_i(x) = \frac{\partial \Phi}{\partial x_i}. \tag{4.10}$$

A solution $[x(s), \xi(s)]$ of the system

$$\begin{aligned} \frac{dx_i}{ds} &= \frac{\partial H}{\partial \xi_i}[x, \xi(x)] \\ \xi_i(s) &= \xi_i[x(s)], \end{aligned} \tag{4.11}$$

is a Hamiltonian path because

$$\begin{aligned} \frac{d\xi_i(s)}{ds} &= \sum_j \frac{\partial \xi_i}{\partial x_j} \frac{dx_j}{ds} = \sum_j \frac{\partial^2 \Phi}{\partial x_i \partial x_j} \frac{\partial H}{\partial \xi_j} \left(x, \frac{\partial \Phi}{\partial x} \right) \\ &= - \frac{\partial H}{\partial x_i} [x, \xi(x)] \end{aligned}$$

because $H[x, (\partial \Phi / \partial x)] = 0$ so that

$$\frac{\partial H}{\partial x_i} + \sum_j \frac{\partial H}{\partial \xi_j} \frac{\partial^2 \Phi}{\partial x_i \partial x_j} = 0.$$

Moreover, Φ is increasing along such paths because

$$\frac{d\Phi}{ds} = \sum_i \frac{\partial \Phi}{\partial x_i} \frac{dx_i}{ds} = \sum_i \xi_i(s) \frac{dx_i}{ds} = L \geq 0,$$

so that Φ is increasing along the path. The trajectories given by Eq. (4.11) will be called *antideterministic paths* (for reasons to follow).

C. Construction of Φ

Until now, we have not said how to construct the action Φ . The traditional method to construct a solution Φ of $H(x, \nabla \Phi = 0$ is the following.²⁴ One chooses a point $x^{(0)}$ and consider a path $[x(s), \xi(s)]$, solution of the Hamiltonian system

$$\dot{x}_i = \frac{\partial H}{\partial \xi_i}, \quad \dot{\xi}_i = - \frac{\partial H}{\partial x_i}, \tag{4.12}$$

with the conditions

$$x(0) = x^{(0)}, \quad \xi(0) = \xi^{(0)}, \quad x(t) = x, \quad H(x^{(0)}, \xi^{(0)}) = 0. \tag{4.13}$$

The unknowns are $\xi^{(0)}$ and t , which will be implicitly fixed by condition Eq. (4.13). Then the function

$$\Phi(x) = \int_0^t \sum_{i=1}^s \xi_i dx_i, \tag{4.14}$$

is the solution $\Phi(x|x^{(0)})$ of $H(x, \nabla \Phi) = 0$, where in Eq. (4.14) the integral is taken along the path $[x(s), \xi(s)]$ satisfying Eqs. (4.12) and (4.13). But the function $\Phi(x|x^{(0)})$ is not differentiable at $x^{(0)}$ since $\nabla_x \Phi = \xi \rightarrow \xi_0$ as $x \rightarrow x_0$; but ξ_0 depends on the path from x to x_0 , so that $\nabla_x \Phi$ is not defined at x_0 , in general. In our situation where

$$p(x) \sim U_0(x) \exp[-V\Phi(x)], \tag{4.15}$$

we expect $\Phi(x)$ to be regular everywhere and to be peaked at a point x_M (at least), so that one cannot take for our Φ a function $\Phi(x|x^{(0)})$ constructed by the traditional method as above.

We shall now describe the correct construction of Φ by a limiting process.

Let us consider a point x_s which is an attracting point of the vector field $\{A_i(x)\}$. We take another point $x^{(0)}$ and we construct the usual action $\Phi(x|x^{(0)})$ using Hamiltonian paths starting from $x^{(0)}$, with energy 0. For $x^{(0)} \neq x_s$, this function is nontrivial and is not differentiable at $x^{(0)}$. The function $\Phi(x|x_s)$ is now defined as

$$\Phi(x|x_s) = \lim_{x^{(0)} \rightarrow x_s} \Phi(x|x^{(0)}) = 0. \tag{4.16}$$

The function $\Phi(x|x_s)$ is not simply the function $\Phi(x|x^{(0)})$ for $x^{(0)} = x_s$. The reason is that if we choose $x^{(0)} = x_s$, ξ_0 must vanish in order that $H(x^{(0)}, \xi^{(0)}) = 0$. This is obvious for H_{FP} and is also valid for H_M using the inequality $e^a - 1 \geq a$, then the trajectory never moves away from $x^{(0)}$ and the traditional action is 0. In general, $\Phi(x|x_s)$ is a nontrivial function, which is differentiable at $x = x_s$, has a strict minimum at x_s , which is a nondegenerate minimum if x_s is a nondegenerate attracting point of the vector field $\{A_i\}$. We prove the existence of the limit in Eq. (4.16) in Appendix B. Moreover, we will consider a given point x and a trajectory with 0 energy starting from $x^{(0)}$ and arriving at x in a certain (unknown) time, t . This trajectory has an initial momentum ξ which is a function $\xi(x|x^{(0)})$. In the Fokker–Planck case, we have

$$H_{FP}[x^{(0)}, \xi(x|x^{(0)})] = 0.$$

Call

$$x^{(0)} = x_s + \delta x,$$

so that

$$A(x^{(0)}) \sim A(x_s) + A'(x_s) \delta x \approx A'(x_s) \delta x, \quad \text{for } \delta x \rightarrow 0,$$

then from the definition of H_{FP} , we have

$$\frac{1}{2} \xi D \xi \approx -A'(x_s) \delta x \cdot \xi. \tag{4.17}$$

Assuming that $A'(x_s) \neq 0$ and D is invertible at x_s , we deduce from Eq. (4.17) that

$$|\xi(x|x^{(0)})| = O(\delta x) \quad (4.18)$$

and from Eq. (4.18) $\xi(x|x^{(0)})$ tends to 0 when $x^{(0)} \rightarrow x_s$. From Eq. (4.18) and the definition of the velocity

$$\dot{x} = A(x) + D\xi,$$

we see that the initial velocity is

$$|\dot{x}(0)| = O(\delta x), \quad (4.19)$$

so that the time t needed to join $x^{(0)}$ to x along the Hamiltonian trajectory of energy 0 will tend to infinity when $x^{(0)}$ tends to x_s . It is precisely because the initial momentum is tending to zero, that the limiting function $\lim \Phi(x|x^{(0)})$ will be differentiable at x_s , when $x^{(0)}$ tends to x_s .

D. Unicity of Φ

We prove in Appendix C, the following fact:

If Φ is a smooth solution of the Hamilton–Jacobi equation (either H_M or H_{FP}) and x_0 is a minimum of Φ , the Taylor expansion of Φ at $x = x_0$ is uniquely determined up to an additive constant. In particular, if Φ is an analytic solution near x_0 , it is unique. As a consequence there exists at most one function Φ which is a global analytic solution of the Hamilton–Jacobi equation (up to an additive constant). Because of this latter fact, we can define the antideterministic path, by using the unique analytic solution Φ of the Hamilton–Jacobi equation as in Sec. IV B namely,

$$\begin{aligned} \frac{d\tilde{x}_i(s)}{ds} &= \frac{\partial H}{\partial \xi_i}[\tilde{x}(s), \tilde{\xi}(s)], \\ \tilde{\xi}_i(s) &= \xi_i[\tilde{x}(s)] \equiv \frac{\partial \Phi}{\partial x_i}[\tilde{x}(s)]. \end{aligned} \quad (4.20)$$

E. Limit of trajectories

In this section, we consider the linear Fokker–Planck Hamiltonian with D a constant invertible positive matrix and $A_i(x)$ a linear vector field as in Appendix B:

$$A_i(x) = \sum_{j=1}^s A_{ij}x_j. \quad (4.21)$$

Here A_{ij} are the coefficients of A_i as a linear function of the $\{x_j\}$. Let $[x(s), \xi(s)]$ be a trajectory with $H=0$ such that

$$x(0) = x^{(0)}, \quad x(t) = x,$$

where $x^{(0)}$ and x are both nonzero.

Then if $t \rightarrow \infty$, this trajectory has the following limit behavior: (i) for fixed s , $x(s)$ tends to the deterministic trajectory $\tilde{x}(s)$ starting from $x^{(0)}$; (ii) for fixed s , $x(t-s)$ tends to the antideterministic trajectory $\tilde{x}(t-s)$ defined by Eq. (4.20) ending at x .

These facts are proved in Appendix B for a Fokker–Planck Hamiltonian near an attracting point of the deterministic vector field. They remain valid for the Hamiltonian

H_M , in general, since we have proved that H_M can be approximated by H_{FP} in the neighborhood of a zero of the vector field A .

F. Critical points of Φ and zeros of the deterministic vector field

In Appendix C, we prove the following facts:

(i) a nondegenerate critical point of Φ is a zero of the deterministic vector field A (for both H_M and H_{FP}). A nondegenerate minimum of Φ is a stable attracting point of A . (ii) Conversely for H_{FP} , the zeroes of A are critical points of Φ and the stable attracting points of A are minima of Φ . (iii) Conversely for H_M , the stable attracting points of A are minima of Φ .

V. CONCLUSION

In this article, we have studied the stationary state of the Master equation for a reaction-diffusion system using a Hamilton–Jacobi equation adapted to the Master equation and which gives more precise results than the usual Fokker–Planck equations. We have proved that, nevertheless, the Hamilton–Jacobi equation for the Master equation can be approximated by the Hamilton–Jacobi theory for the associated Fokker–Planck equation near a zero of the deterministic vector field. We have constructed rigorously the corresponding action, without using the standard Hamilton–Jacobi theory, near a stable zero of the deterministic vector field and we have also proved the unicity of a smooth solution. Finally we have proved that the critical points of the action are the zeroes of the vector field. These results show that the stationary distribution is peaked exactly at the stable zero of the vector field. This Hamiltonian formalism and the related Lagrangian will be used in further works to estimate rate constants and exit times¹⁸ and to study exactly solvable models¹⁹ for transition to criticality.

ACKNOWLEDGMENTS

One of the authors (B.G.) thanks M. A. Gaveau and L. S. Schulman for inspiration and discussions. He was supported by a EU Grant No. 930096 of the program ‘‘Capital Humain et Mobilite.’’

APPENDIX A: APPROXIMATE HAMILTONIANS IN A NEIGHBORHOOD OF A ZERO OF THE DETERMINISTIC VECTOR FIELD

We shall use, as in Eq. (4.3), the notation

$$\pi_r = \sum_{i=1}^s r_i \xi_i, \quad (A1)$$

and will assume that $\{\pi_r\} = 0$ if and only if $\{\xi_i\} = 0$ (this assumption is discussed in Sec. IV A, and means that there are no conservation laws, which we can assume if we restrict the variables [(see also Sec. II C)].

If $\{\pi_r\}$ belongs to the image of the s -dimensional space of the ξ_i by the linear application defined by Eq. (A.1), this Eq. (A1) can be inverted in a unique way and gives a unique solution ξ such that

$$\max_i |\xi_i| \leq M \max_r |\pi_r|. \tag{A2}$$

We now consider a point (x, ξ) such that

$$H_M(x, \xi) = 0,$$

or

$$\sum_r w_r (e^{\pi_r} - 1) = 0.$$

Because $e^{\pi_r} - 1 - \pi_r \geq 0$, we have at that point, using $A_i = \sum_r r_i w_r$

$$0 \leq - \sum_r w_r \pi_r = - \sum_i A_i \xi_i. \tag{A3}$$

Presently we consider a zero x_s of the vector field $\{A_i\}$ and a neighborhood of x_s so that for x in that neighborhood

$$\sum_{i=1}^s |A_i(x)| < \epsilon,$$

ϵ being any positive number so that, by Eqs. (A3) and (A2):

$$0 \leq - \sum_i A_i \xi_i \leq \epsilon \sup_i |\xi_i| \leq \epsilon C \max_r |\pi_r|, \tag{A4}$$

where C is the norm of the linear application defined by Eq. (A1).

Let us assume that for all r

$$w_r(x_s) > 0, \tag{A5}$$

so that for x in a neighborhood of x_s , we have

$$w_r(x) > w > 0, \tag{A6}$$

where w is a positive number.

We then use Eq. (A6), $H_M = 0$, which implies

$$\begin{aligned} 0 &\leq w [\exp(\max_r |\pi_r|) - 1 - \max_r |\pi_r|] \\ &\leq \sum_r w_r(x) [\exp(\pi_r) - 1 - \pi_r] = - \sum_r w_r \pi_r \end{aligned}$$

so by Eqs. (A3) and (A4), this is

$$0 \leq w [\exp(\max_r |\pi_r|) - 1 - \max_r |\pi_r|] \leq \epsilon C \max_r |\pi_r|. \tag{A7}$$

However, the function $(e^u - 1 - u/u)$ increases from 0 to ∞ if u goes from 0 to infinity, so that Eq. (A7) proves that $\pi_r = 0$ for all r , because we can choose ϵ being as small as we want, and as a consequence $\xi_i = 0$ but this implies, in view of Eq. (3.11), that near zero of the deterministic vector field $\{A_i\}$, H_M can be replaced by H_{FP} .

APPENDIX B: EXISTENCE OF Φ AND LIMITS OF TRAJECTORIES NEAR AN ATTRACTING POINT OF THE DETERMINISTIC VECTOR FIELD

1. Trajectories

In this Appendix, we shall study the properties of the Hamiltonian trajectories and the construction of Φ for the case of a Fokker-Planck Hamiltonian H_{FP} such that $A(x)$ is a linear vector field having a zero at $x = 0$

$$A_i(x) = \sum_{j=1}^s A_{ij} x_j \tag{B1}$$

and D is a constant matrix. We assume that $x_s = 0$ is an attracting point of A , i.e. (A_{ij}) is a nondegenerate matrix such that the real parts of its eigenvalues are all negative. We shall call A the matrix (A_{ij}) and D the matrix (D_{ij}) . The Hamiltonian equations associated to H_{FP} are given as in Eq. (4.2), in matrix notations:

$$\frac{dx}{ds} = Ax + Dp \quad \frac{dp}{ds} = -{}^t A p,$$

(${}^t A$ is the transpose of A) which have solutions

$$\begin{aligned} p(s) &= \exp(-{}^t A s) p(0) \\ x(s) &= \exp(A s) x(0) \\ &+ \left(\int_0^s \exp[A(s-s')] D \exp({}^t A s') ds' \right) p(0). \end{aligned} \tag{B2}$$

The condition $x(t) = x$ (given), implies that

$$\begin{aligned} p(0) &= \left(\int_0^t \exp(-A s) D \exp(-{}^t A s) ds \right)^{-1} \\ &\times [\exp(-A t) x - x(0)] \end{aligned} \tag{B3}$$

and then the condition that the energy is equal to 0 (at time 0, and therefore at any time) determines t

$$H_{FP}[x(0), p(0)] = 0. \tag{B4}$$

2. Action

The action $\Phi[x|x(0)]$ is the integral along the trajectory given by Eq. (B2) with $t, p(0)$ given by Eqs. (B3) and (B4)

$$\Phi[x|x(0)] = \int_0^t p(s) dx(s).$$

Presently,

$$\begin{aligned} dx &= (Ax + Dp) ds \\ {}^t p dx &= {}^t p Ax + {}^t p Dp = H + \frac{1}{2} p Dp = \frac{1}{2} p Dp \end{aligned}$$

so that using Eqs. (B2) and (B3)

$$\begin{aligned} \Phi[x|x(0)] &= \frac{1}{2} [{}^t x \exp(-{}^t A t) - {}^t x(0)] \\ &\times \left(\int_0^t \exp(-A s) D \exp(-{}^t A s) ds \right)^{-1} \\ &\times [\exp(-A t) x - x(0)]. \end{aligned} \tag{B5}$$

We have proved in Sec. IV C that when $x(0)$ tends to 0, t should tend to infinity and it is clear that $\Phi[x|x(0)]$ has a limit

$$\begin{aligned} \Phi(x) &\equiv \lim_{x(0) \rightarrow 0} \Phi[x|x(0)] \\ &= \frac{1}{2} {}^t x \left(\int_0^\infty \exp(A s) D \exp({}^t A s) ds \right)^{-1} x, \end{aligned} \tag{B6}$$

where the integral is convergent because A has its eigenvalues with negative real parts and is nonzero because D is nondegenerate. We shall call

$$C = \int_0^\infty \exp(As)D \exp({}^tAs)ds, \quad (\text{B7})$$

C is a symmetric matrix and

$$AC + C'A = \int_0^\infty \frac{d}{ds} [\exp(As)D \exp({}^tAs)]ds = -D \quad (\text{B8})$$

so that the matrix C^{-1} which arises in the definition of Eq. (B6) for $\Phi(x)$ satisfies

$$C^{-1}DC^{-1} = -(C^{-1}A + {}^tAC^{-1}). \quad (\text{B9})$$

From this, it is easy to check directly that the function $\Phi(x)$ given by Eq. (B6) satisfies the Hamilton–Jacobi equation. We also notice the value of the momentum $p(s)$ as given by Eqs. (B2) and (B3):

$$p(s) = \exp(-{}^tAs) \left(\int_0^t \exp(-As')D \exp(-{}^tAs')ds' \right)^{-1} \times [\exp(-At)x - x(0)] \quad (\text{B10})$$

so that at time $t \rightarrow +\infty$, when $x(0) \rightarrow 0$, the final momentum is

$$p(t) = \exp(-{}^tAt) \left(\int_0^t \exp(-As')D \exp(-{}^tAs')ds' \right)^{-1} \times [\exp(-At)x - x(0)]$$

and

$$p(\infty) = \lim_{x(0) \rightarrow 0} p(t) = \left(\int_0^\infty \exp(As)D \exp({}^tAs)ds \right)^{-1} x = C^{-1}x, \quad (\text{B11})$$

which is exactly the gradient of Φ .

3. Limit of trajectories

In this section we prove the results of Sec. IV E. We will now consider the trajectory joining $x(0)$ at time $t=0$ to x at time t , but not necessarily at energy 0 so that we have from Eq. (B3)

$$p(0) = \exp({}^tAt) \left(\int_0^t \exp(As)D \exp({}^tAs)ds \right)^{-1} \times [x - \exp(At)x(0)]. \quad (\text{B12})$$

Call,

$$C(t) = \int_0^t \exp(As)D \exp({}^tAs)ds,$$

so that we can rewrite Eqs. (B2) using Eq. (B12)

$$p(s) = \exp[{}^tA(t-s)]C^{-1}(t)[(x - \exp(At)x(0))] \quad (\text{B13})$$

$$x(s) = \exp(As)x(0) + C(s)\exp[{}^tA(t-s)] \times C^{-1}(t)[x - \exp(At)x(0)].$$

Now, when t tends to infinity and s is fixed, then from Eq. (B13)

$$\lim_{\substack{t \rightarrow \infty \\ s \text{ fixed}}} x(s) = \exp(As)x(0), \quad (\text{B14})$$

because $C(s)$ has the finite limit C and A has its eigenvalues with negative real parts so that $\lim_{s \text{ fixed}}^{\infty} x(s)$ is exactly the deterministic path $\bar{x}(s)$ starting from $x(0)$, namely,

$$\frac{d\bar{x}}{ds} = A\bar{x}.$$

On the other hand, when t tends to infinity and s is fixed, one has from Eq. (B13),

$$\lim_{\substack{t \rightarrow \infty \\ s \text{ fixed}}} x(t-s) = C \exp({}^tAs)C^{-1}x. \quad (\text{B15})$$

From Eq. (B15) we obtain, for fixed s , and t tending to infinity

$$\frac{d \lim x(t-s)}{d(t-s)} = -C'A C^{-1} \lim x(t-s). \quad (\text{B16})$$

On the other hand

$$\frac{\partial H}{\partial p} = Ax + Dp.$$

When $p = \nabla\Phi$, or $p = C^{-1}x$

$$\frac{\partial H}{\partial p} = Ax + DC^{-1}x = -C'A C^{-1}x. \quad (\text{B17})$$

[see Eq. (B9)]. Equation (B16) shows that $\lim x(t-s)$ is the antideterministic path. Finally, we can study the behavior of the trajectory when both t and s tend to infinity.

We notice that

$$\begin{aligned} \frac{dC}{dt} &= \exp(At)D \exp({}^tAt) \\ &= -\exp(At)(AC + C'A)\exp({}^tAt) \\ &= -\frac{d}{dt} [\exp(At)C \exp({}^tAt)] \end{aligned}$$

so that

$$C(t) = C - \exp(At)C \exp({}^tAt) = [C \exp(-{}^tAt) - \exp(At)]\exp({}^tAt). \quad (\text{B18})$$

From Eq. (B13), we obtain

$$\begin{aligned} x(s) &= \exp(As)x(0) + [C \exp(-{}^tAs) - \exp(As)C] \\ &\quad \times [C \exp(-{}^tAt) - \exp(At)C]^{-1} \\ &\quad \times [x - \exp(At)x(0)] \end{aligned}$$

so that when t and s tend to infinity:

$$x(s) = \exp(As)x(0) + C \exp[{}^tA(t-s)]C^{-1}x.$$

Obviously $x(s) \rightarrow 0$ with the following asymptotic behavior

$$s < t/2 \quad x(s) \sim \exp(As)x(0)$$

$$s > t/2 \quad x(s) \sim C \exp[{}^tA(t-s)]C^{-1}x$$

$$s = t/2 \quad x(s) \sim \exp\left(\frac{At}{2}\right)x(0) + C \exp\left(\frac{{}^tAt}{2}\right)C^{-1}x.$$

In conclusion, we see that the limit behavior of the trajectory joining $x(0)$ at time 0, to x at time t , when t tends to infinity is the following:

(i) for finite s , $x(s)$ tends to the deterministic trajectory starting from $x(0)$; (ii) for finite s , $x(t-s)$ tends to the antideterministic trajectory ending at x ; (iii) when s is large, and tends to infinity, $x(s)$ tends to 0.

So essentially, for large times, the trajectory $x(s)$ starts like the deterministic trajectory, goes to a neighborhood of 0 (the attracting point of A) where it loses much time, and finally ends like the antideterministic trajectory.

Notice that if $C = Id$, and A is symmetric, the antideterministic trajectory is exactly the deterministic path, but with reverse speed, namely

$$\frac{d\tilde{x}}{dt} = -A\tilde{x}.$$

In general, the eigenvalues of the velocity matrix $-C^tAC^{-1}$ of the antideterministic trajectory are the opposite of the eigenvalues of the velocity matrix of the deterministic trajectory, namely A , but the eigenvectors are rotated by C (which is the matrix of Φ). We shall see, in a future publication, that in the case of detailed balance, C is the identity matrix and $A = {}^tA$, so that in the case of detailed balance, the antideterministic trajectory is the time reversal of the deterministic trajectory.

In Appendix A, we have seen that when $x(0)$ tends to x_s [stable point of the deterministic vector field $A(x)$], $p(0)$ tends to zero. If x is close to x_s as well, then the whole situation is well described by the linearized Fokker–Planck Hamiltonian for which we have proved that $\Phi[x|x(0)]$ has a limit.

APPENDIX C: CRITICAL POINTS OF THE ACTION

1. Critical points of Φ are zeros of A

Let x_0 be a critical point of Φ which is assumed to be nondegenerate. This means that one can choose coordinates $(x_i)_{i=1,\dots,s}$ around x_0 , so that x_0 has coordinate 0 and

$$\frac{\partial\Phi}{\partial x_i} = \sum_j \varphi_{ij}x_j + 0(|x|^2) \tag{C1}$$

where (φ_{ji}) is a nondegenerate symmetric matrix which we can assume to be diagonal.

We also write for the deterministic vector field

$$A_i(x) = A_i(0) + 0(|x|).$$

Now, we know that Φ satisfies the Hamilton–Jacobi equation $H_m(x, \nabla\Phi) = 0$ or $H_{FP}(x, \nabla\Phi) = 0$. We take the expansion of $H(x, \nabla\Phi)$ to first order in x around 0. In both cases, we obtain

$$\sum_i A_i(0)\varphi_{ij} = 0 \quad \text{for all } j,$$

so that $A_i(0) = 0$ because (φ_{ij}) is nondegenerate, and 0 is a zero of A . As a consequence, we can write

$$A_i(x) = \sum_j A_{ij}x_j + 0(|x|^2). \tag{C2}$$

Let us now expand the Hamilton–Jacobi equations $H(x, \nabla\Phi) = 0$ up to second order in x around 0. We obtain

$$\sum_{i,j} D_{ij}^{(0)}\varphi_{ik}\varphi_{j\ell} + \sum_i (A_{ij}\varphi_{i\ell} + A_{i\ell}\varphi_{ik}) = 0, \tag{C3}$$

for all (k, ℓ) .

2. Minima of Φ are stable attracting points of A

If $x_0 = 0$ is a nondegenerate minimum of Φ , we have Eq. (C3) above. Assume that φ_{ij} is diagonal, with diagonal elements $\varphi_i > 0$. Then for all k, ℓ we have

$$D_{k\ell}^{(0)}\varphi_k\varphi_{\ell} + A_{\ell k}\varphi_{\ell} + A_{k\ell}\varphi_k = 0. \tag{C4}$$

Now, if D is nondegenerate (so that it is a positive definite symmetric matrix), Eq. (C4) shows that $A_{\ell k}\varphi_{\ell} + A_{k\ell}\varphi_k$ is symmetric definite negative. Let V become an eigenvector of $A_{\ell k}$ (in general complex), so that

$$AV = \lambda V \quad AV^* = \lambda^*V^*,$$

then

$$0 > \sum_{\ell,k} V_{\ell}^*(A_{\ell k}\varphi_{\ell} + A_{k\ell}\varphi_k)V_k,$$

or

$$0 > \left(\sum_{\ell} \varphi_{\ell}|V_{\ell}|^2 \right) (\lambda + \lambda^*),$$

Then $\text{Re } \lambda < 0$, so that 0 is attracting point of the vector field.

3. For H_{FP} , zeroes of A are critical points of Φ

In the case of H_{FP} , the Hamilton–Jacobi equation at a point x_0 such that $A(x_0) = 0$, is

$$0 = H_{FP}[x_0, \nabla\Phi(x_0)] = \frac{1}{2} \sum_{i,j} D_{ij} \frac{\partial\Phi}{\partial x_i}(x_0) \frac{\partial\Phi}{\partial x_j}(x_0),$$

and if $D_{ij}(x_0)$ is nondegenerate, $(\partial\Phi/\partial x_i)(x_0) = 0$ for all i . If x_0 attracts A , x_0 is a critical point Φ , but then the proof of (ii) proves that x_0 is a minimum of Φ .

APPENDIX D: UNICITY OF ANALYTIC SOLUTIONS OF THE HAMILTON–JACOBI EQUATIONS

In this Appendix, we prove the unicity of the Taylor expansion of Φ around a minimum x_0 . We choose coordinates (x_i) , $i=1,\dots,s$ which vanish at x_0 and write as Eq. (C1), assuming $\Phi(x_0)=0$:

$$\Phi = \frac{1}{2} \sum_{i,j} \varphi_{ij} x_i x_j + 0(|x|^3), \quad (\text{D1})$$

$$A_i(x) = \sum_j A_{ij} x_j + 0(|x|^2). \quad (\text{D2})$$

We know that φ_{ij} satisfies Eq. (C3)

$$\sum_{i,j} D_{ij}(0) \varphi_{ik} \varphi_{j\ell} + \sum_i (A_{ik} \varphi_{i\ell} + A_{i\ell} \varphi_{ik}) = 0 \quad (\text{all } k, \ell). \quad (\text{D3})$$

1. Unicity of the solution of Eq. (D3)

Let us define the vector field $A_i^{(0)}$ and the diffusion matrix $D_{ij}^{(0)}$

$$A_i^{(0)} = \sum_j A_{ij} x_j, \quad D_{ij}^{(0)} = D_{ij}(x_0)$$

as well as

$$\Phi^{(0)} = \frac{1}{2} \sum_{i,j} \varphi_{ij} x_i x_j.$$

Then Eq. (D3) is exactly the Hamilton–Jacobi equation associated to the Hamiltonian $H_{\text{FP}}^{(0)}$

$$H_{\text{FP}}^{(0)}(x, \nabla \Phi^{(0)}) = 0, \quad (\text{D4})$$

where

$$H_{\text{FP}}^{(0)}(x, p) = \sum_i A_i^{(0)} p_i + \frac{1}{2} \sum_{i,j} p_i D_{ij}^{(0)} p_j.$$

Moreover, $\exp[-V\Phi^{(0)}(x)]$ is, up to a constant prefactor a Gaussian probability distribution, which is the stationary solution of the Fokker–Planck equation:

$$-\sum_i \frac{\partial}{\partial x_i} (A_i^{(0)} p) + \frac{1}{2V} \sum_{i,j} D_{ij}^{(0)} \frac{\partial^2 p}{\partial x_i \partial x_j} = 0. \quad (\text{D5})$$

This implies that the solution of Eq. (D4) which is analytic, and as a consequence the solution of Eq. (D3), is unique and in fact the matrix (φ_{ij}) is equal to C^{-1} defined in Eq. (C7).

2. Unicity of the Taylor expansion of Φ around x_0

We now consider the full Hamilton–Jacobi equation $H(x, \nabla \Phi) = 0$ where H is either H_{FP} or H_M and a smooth solution Φ and a minimum x_0 of Φ . We expand Φ in Taylor series around x_0 , as in Eq. (D1) as well as $A_i(x)$, $D_{ij}(x)$, and $w_r(x)$. In $H_M(x, \nabla \Phi)$ we also expand the $\exp[\sum_i r_i (\partial \Phi / \partial x_i)]$.

When we compute the Taylor expansions of $H(x, \nabla \Phi)$ around x_0 , we notice, obviously, that only monomials in the coordinates (x_i) $i=1,\dots,s$ of degree ≥ 2 arise and we must

equate to zero all the coefficient of these monomials. When we equate to zero the coefficients of the monomials of degree 2, in $H(x, \nabla \Phi)$, i.e., the monomial $x_k x_\ell$, we recover Eq. (D3) which has been proven to have a unique solution, just above. Again, we consider the equation $H(x, \nabla \Phi) = 0$ and a monomial $x_1^{n_1} \dots x_s^{n_s}$ of total degree $n \geq 3$, in $H(x, \nabla \Phi)$. We write

$$\Phi = \sum a_{n_1 \dots n_s} x_1^{n_1} \dots x_s^{n_s}.$$

We choose coordinates x_i so that A_{ij} is diagonal. Then the equation expressing the fact that the monomial $x_1^{n_1} \dots x_s^{n_s}$ in $H(x, \nabla \Phi)$ has a zero coefficient, for $n = n_1 + \dots + n_s \geq 3$, is of the type:

$$\left(\sum_{i=1}^s n_i A_i \right) a_{n_1 \dots n_s} = \dots, \quad (\text{D6})$$

where the dots in the second member of Eq. (D6) are polynomials of the $a_{k_1 \dots k_s}$ where $k_1 + \dots + k_s < n$ but the real parts of the A_i are all < 0 , so that none of the $\sum n_i A_i$ vanishes (for $n \geq 1$). As a consequence, $a_{n_1 \dots n_s}$ is uniquely expressed in terms of the coefficients of Φ of the monomials of degree $< n$ and by recursion all coefficients are uniquely determined.

3. The attracting points of A are minima of Φ

If x_s is an attracting point of A , one can construct the unique Φ by the limiting process of Sec. V C (up to a constant)

$$\Phi(x|x_s) = \lim_{x(0) \rightarrow x_s} \Phi[x|x(0)],$$

but, using the result of Sec. V B, Φ is the action computed along antideterministic paths

$$\Phi(x|x_s) = \int \sum \frac{\partial \Phi}{\partial x_i} dx_i = \int \sum p_i dx_i = \int L ds.$$

The Lagrangian being positive, x_s is a minimum.

¹L. D. Landau and E. M. Lifschitz, *Statistical Physics* (Pergamon, Oxford, 1980).

²I. Prigogine, *Nonequilibrium Statistical Mechanics* (Wiley, New York, 1962).

³I. Prigogine and G. Nicolis, in *From Theoretical Physics to Biology*, edited by M. Marois (Karger, Basel, 1973).

⁴G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley, New York, 1977).

⁵J. Keizer, *Statistical Thermodynamics of Nonequilibrium Processes* (Springer, New York, 1987).

⁶R. Kubo, *Statistical Mechanics* (North-Holland, Amsterdam, 1988).

⁷R. Kubo, M. Toda, and N. Hashitsume, in *Statistical Physics II* (Springer, New York, 1986).

⁸S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover, New York, 1984).

⁹D. Forster, *Frontiers in Physics* (Benjamin Cummings, New York, 1975), Vol. 47.

¹⁰J. Ross, K. L. C. Hunt, and P. M. Hunt, *J. Chem. Phys.* **96**, 618 (1992).

¹¹Q. Zheng, J. Ross, K. L. C. Hunt, and P. M. Hunt, *J. Chem. Phys.* **96**, 630 (1992).

¹²M. O. Vlad and J. Ross, *J. Chem. Phys.* **100**, 7268 (1994); **100**, 7279 (1994); **100**, 7295 (1994).

- ¹³M. Moreau, *J. Math. Phys.* **19**, 2494 (1978).
- ¹⁴B. Gaveau and L. S. Schulman, *J. Math. Phys.* **37**, 3897 (1996); *Phys. Lett. A* **229**, 347 (1997); *J. Math. Phys.* **39**, 1517 (1998); (see, also Refs. 16 and 17 concerning the problems posed by the thermodynamic limit in phase transitions).
- ¹⁵D. Ruelle, *Statistical mechanics* (Benjamin, New York, 1970).
- ¹⁶L. S. Schulman, in *Finite Size Scaling and Numerical Simulation of Statistical Systems*, edited by V. Privman (World Scientific, Singapore, 1990).
- ¹⁷B. Gaveau and L. S. Schulman, *J. Phys. A* **20**, 2865 (1987); *J. Stat. Phys.* **70**, 613 (1993).
- ¹⁸B. Gaveau, M. Moreau, and J. Toth, *J. Chem. Phys.* **111**, 7748 (1999), following paper.
- ¹⁹B. Gaveau, M. Moreau, and J. Toth, *Physica A* (to be published).
- ²⁰R. Kubo, K. Matsuo, and K. Kitahara, *J. Stat. Phys.* **9**, 51 (1973).
- ²¹B. Gaveau, M. Moreau, and J. Toth, *Lett. Math. Phys.* **37**, 285 (1996); **40**, 101 (1997).
- ²²H. Lemarchand, *Physica (Utrecht)* **101**, 518 (1980).
- ²³T. Kurtz, *J. Chem. Phys.* **57**, 2976 (1972).
- ²⁴R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience, New York, 1953); L. Landau and E. Lifschitz, *Mécanique* (Mir, Moscow).