Journal of Statistical Physics, Vol. 29, No. 2, 1982

Thermodynamic Criteria Governing Irreversible Processes under the Influence of Small Thermal Fluctuations

B. H. Lavenda[1] and E. Santamato[2]

Received April 29, 1982

The Ventsel'–Freidlin probability estimates for small random perturbations of dynamical systems are used to generalize and justify the Onsager–Machlup irreversible thermodynamic variational description of Gaussian statistical distributions in the limit where Boltzmann's constant tends to zero for non-Gaussian diffusion processes. A Hamiltonian formulation is used to determine the maximum likelihood paths for the growth and decay of nonequilibrium fluctuations, in the same limit, subject to the imposed constraints. The paths of maximum likelihood manifest a symmetry in past and future and are the stationary conditions of the constrained thermodynamic variational principle of least dissipation of energy. The power balance equations supply the required constraints and the most likely path for the growth of a fluctuation is characterized by a negative entropy production. The entropy plays the role of the quasipotential of Ventsel' and Freidlin and exit from a bounded domain containing a deterministically stable steady state is made at that state on the boundary with maximum entropy.

KEY WORDS: Thermodynamic variational principles; maximum likelihood paths; stochastic exit; thermodynamic evolutionary criteria.

1. INTRODUCTION

The pioneering work of Onsager and Machlup[1] has led to the introduction of thermodynamic variational expressions into the statistical description of *linear* irreversible thermodynamical processes under the influence of

[1] Istituto Chimico, Università de Camerino, Via Sant' Agostino 1, Camerino 62032 (MC) Italy.
[2] Istituto di Fisica Sperimentale, Università di Napoli, Via Antonio Tari 3, Napoli 80138 Italy.

0022-4715/82/1000-0345$03.00/0

random thermal fluctuations. The Onsager and Machlup analysis was restricted to the important, but special, case of Gaussian nonequilibrium fluctuations which are impervious to the mathematical problems of nonlinear processes.[2]

More recently, Ventsel' and Freidlin[3] have considered the behavior of dynamical systems under the influence of small random perturbations of the white noise type. They studied the motion of a particle diffusing against the flow in an analogous way that the WKB aproximation is applied to the Schrödinger equation in the classical limit where Planck's constant $h\downarrow 0$. They showed that an estimate of the probability for a trajectory of the perturbed motion not to deviate from a smooth path, for small noise intensities, has the form $\exp[-\frac{1}{2}\Theta(\phi)/k]$ where $\Theta(\phi)$ is identical to the Onsager–Machlup (OM) functional which is independent of the small, positive parameter k that is a measure of the noise intensity. In irreversible thermodynamics, k is identified as Boltzmann's constant.

The asymptotic behavior of the solutions of diffusion equations has also been studied by Friedmann.[4] Ludwig[5] applied a ray method to the asymptotic solution of the Fokker–Planck equation and interpreted the rays as paths of maximum likelihood in the spirit of Ventsel' and Freidlin. However, Ludwig did not go into the detailed differences between the classical mechanical variational formulation and the Hamiltonian type of formulation that is required when the equations of motion are of first rather than second order in time.

The probability estimates derived by Ventsel' and Freidlin have been applied to the problem of reflection on hitting the boundary of a domain enclosing a stable stationary state by Anderson and Orey,[6] Matkowsky and Schuss[7] used singular perturbation techniques to predict asymptotically the mean exit time. Williams,[8] again using singular perturbation methods, constructed the probability densities of exit positions in the case where there is no unique point on the boundary which minimizes the OM functional.

Equipped with the Ventsel'–Friedlin probability estimates we generalize and justify the Onsager–Machlup irreversible thermodynamic variational description of linear irreversible processes. This also applies to the further developments of the Onsager–Machlup formulation made by one of us.[9] The generalization to nonlinear irreversible processes can be made only in the "thermodynamic" limit $k\downarrow 0$. Morover, it will be appreciated that the domain of validity of irreversible thermodynamics is restricted to this limit; any corrections to the Ventsel'–Freidlin probability estimate, in terms of the OM functional, explicitly takes into account the nature of the random thermal fluctuations and requires a stochastic analysis which is beyond the realm of irreversible thermodynamics. This fact was camouflaged in the Onsager–Machlup analysis of Gaussian nonequilibrium fluctuations since their properties (e.g., stability) are analogous to those of the unperturbed system. For instance, qualitative differences regarding the nature of the critical point of nonequilibrium phase transitions occur between the macroscopic Landau–Ginsburg theory and a stochastic analysis containing the effects of random thermal fluctuations. In the critical region, the importance of random thermal fluctuations becomes predominant and the Landau–Ginsberg theory arises, like irreversible thermodynamics, in the thermodynamic limit $k \downarrow 0$.[10]

2. IRREVERSIBLE PROCESSES IN THE PRESENCE OF SMALL RANDOM THERMAL FLUCTUATIONS

The omnipresence of random thermal fluctuations in irreversible processes makes it necessary to modify the deterministic criteria of stability. Suppose that an irreversible thermodynamic process in R^n is described by the set of rate equations

$$\dot{x}_t = b(x_t), \qquad x_{t=0} = x_0 \tag{1}$$

in which the origin O of the generalized coordinates x is a stable stationary state. Let Ω be any bounded region containing the stationary state and $\partial\Omega$ be the boundary of Ω. Then any trajectory beginning at $x_0 \in \Omega$ will asymptotically approach the stationary state without ever leaving Ω. Moreover, denoting ν as the unit outer normal vector to $\partial\Omega$ at y, the drift vector b satisfies the inequality

$$b(y) \cdot \nu(y) < 0, \qquad y \in \partial\Omega \tag{2}$$

The presence of random thermal fluctuations gives rise to a diffusion "against the flow." Random thermal fluctuations are accounted for by adding a statistically defined term w_t to the right-hand side of (1), viz.,

$$\dot{x}_t^k = b(x_t^k) + (2k)^{1/2}\sigma(x_t^k)w_t, \qquad x_{t=0} = x_0 \tag{3}$$

where w_t is a continuous process which is only an approximation to white noise. In contrast to the solution of the deterministic equation (1), the trajectories of the perturbed system (3) will, sooner or later, leave any bounded domain containing the deterministically stable stationary state O with probability 1. The strength of the random thermal fluctuations is measured by Boltzmann's constant k and σ is related to the diffusion matrix (D^{ij}) by $(D^{ij}) = \sigma(x)\sigma^+(x)$, where σ^+ is the transpose of the matrix σ. We shall be concerned with the behavior of the process x_t^k as $k \downarrow 0$.

Since w_t is a continuous process, the solution of (3) is not a Markov process but, under certain conditions,[11] it converges to one in mean square as $qm - \lim \int_0^T w_t \, dt = W_T$, where W_T is an n-dimensional standard Brownian motion. This implies that x_t^k is a solution of the Fisk–Stratonovich stochastic differential equation[12]:

$$(S) - dx_t^k = b(x_t^k)\,dt + (2k)^{1/2}\sigma(x_t^k) \circ dW_t \tag{4}$$

where the circle denotes symmetric (forward) multiplication:

$$\sigma(x_t^k) \circ dW_t = \sigma(x_t^k)\,dW_t + \tfrac{1}{2} d\sigma(x_t^k)\,dW_t = \sigma(x_t^k)\,dW_t + (\tfrac{1}{2}k)^{1/2}\sigma\partial_x\sigma\,dt \tag{5}$$

Upon introducing (5) into (4), we obtain the Itô stochastic differential equation[13]:

$$(I) - dx_t^k = b^k(x_t^k)\,dt + (2k)^{1/2}\sigma(x_t^k)\,dW_t \tag{6}$$

where

$$b^k(x_t^k) = b(x_t^k) + k\hat{b}(x_t^k) \tag{7}$$

and

$$\hat{b}^i = \left[\det(D^{ij})\right]^{1/2}\partial_j\left(D^{ij}/\left[\det(D^{ij})\right]^{1/2}\right) \tag{8}$$

The solution of Eq. (6) is a Markov process with an infinitesimal generator $\mathrm{G}^k = k\Delta + (b(x), \nabla)$, where Δ is the Laplace–Beltrami operator corresponding to the metric $D_{ij}(x)\,dx^i\,dx^j$, (D_{ij}) is the matrix inverse to (D^{ij}), and ∇ is the Riemannian gradient. In the thermodynamic limit $k \downarrow 0$, Eq. (6) goes over into the macroscopic rate equations (1) and consequently, x_t^k can be viewed as the result of small random thermal fluctuations imposed upon otherwise macroscopic rate equations.

Albeit there is an overwhelming probability for the system to evolve in time to within any small neighborhood of the deterministically stable stationary state, where it will spend an unlimited amount of time, there will, nevertheless, be a finite probability for motion, in one form or another, against the flow, no matter how small Boltzmann's constant may be.[3] Sooner or later, the system will make its exit from any bounded domain containing O. We now address ourselves to the problem of determining thermodynamic criteria for the paths of maximum likelihood of a fluctuation subject to the imposed constraints in the limit $k \downarrow 0$.

3. BASIC PROBABILITY ESTIMATES

Following the general development of Ventsel' and Freidlin,[3] we determine the probability that the perturbed trajectory x_t^k does not deviate by more than δ from a smooth curve ϕ_t. We do so by enclosing ϕ_t in a δ tube and ask for the probability that $d_T(\phi, x^k) = \max_{0 \leqslant s \leqslant T} d(\phi_s, x_s^k) < \delta$ where $d(\cdot, \cdot)$ is the Riemannian distance.

With this goal in mind, we compare the actual diffusion process $\tilde{x}_t^k$, with drift $b^k(\tilde{x}_t^k)$, to a hypothetical diffusion process x_t^k which is driven by a drift $\dot{\phi}_t$ that it would have were it to follow the smooth trajectory ϕ_t in the absence of thermal fluctuations. The hypothetical diffusion process is then governed by the stochastic equation:

$$x_T^k = x_0 + \int_0^T \left[\dot{\phi}_t + k\hat{b}\left(x_t^k\right)\right] dt + (2k)^{1/2} \int_0^T \sigma\left(x_t^k\right) dW_t \tag{9}$$

while the actual diffusion process is given by

$$\tilde{x}_T^k = x_0 + \int_0^T b^k\left(\tilde{x}_t^k\right) dt + (2k)^{1/2} \int_0^T \sigma\left(\tilde{x}_t^k\right) dW_t \tag{10}$$

Writing

$$x_t^k = z_t^k + \phi_t \quad \text{and} \quad \tilde{x}_t^k = \tilde{z}_t^k + \phi_t \tag{11}$$

the pair of stochastic equations (9) and (10) are transformed into

$$z_t^k = z_0 + k\int_0^T \hat{b}\left(z_t^k + \phi_t\right) dt + (2k)^{1/2} \int_0^T \sigma\left(z_t^k + \phi_t\right) dW_t \tag{12}$$

and

$$\tilde{z}_t^k = z_0 + \int_0^T \left[b^k\left(\tilde{z}_t^k + \phi_t\right) - \dot{\phi}_t\right] dt + (2k)^{1/2} \int_0^T \sigma\left(\tilde{z}_t^k + \phi_t\right) dW_t \tag{13}$$

respectively, where $z_0 = x_0 - \phi_0$. The actual diffusion process $\tilde{z}_t^k$ is, in a certain sense, close to the hypothetical diffusion process z_t^k and its corresponding probability measure $\tilde{\mu}$ is close to the probability measure μ of the hypothetical diffusion process. The two diffusion processes possess the same sample functions but are considered as distinct stochastic processes with respect to their different probability measures.

Since the local variance matrices of the two measures are equal on the entire interval $[0, T]$ the probability measure $\tilde{\mu}$ is absolutely continuous with respect to the probability measure μ so that the Radon–Nikodym derivative

$$\frac{d\tilde{\mu}}{d\mu}(z.) = \rho(z.) \tag{14}$$

exits where ρ is the probability measure density given by the Girsanov formula[14]:

$$\rho(z.) = \exp\left[\int_0^T \beta\left(z_t^k + \phi_t\right) dW_t - \tfrac{1}{2}\int_0^T \beta^2\left(z_t^k + \phi_t\right) dt\right] \tag{15}$$

β being proportional to the difference in the two drifts:

$$\beta(z_t^k + \phi_t) = \left[(2k)^{1/2}\sigma(z_t^k + \phi_t)\right]^{-1}\left[b(z_t^k + \phi_t) - \dot{\phi}_t\right] \tag{16}$$

since the common term $k\hat{b}(z_t^k + \phi_t)$ cancels out.

The probability that $d_T(z^k) < \delta$ is thus given by

$$\mathsf{P}_{z_0}\{d_T(z^k) < \delta\} = \mathsf{E}_{z_0}\left\{\chi_{\{d_T(z^k)<\delta\}}\frac{d\tilde{\mu}}{d\mu}\right\} \tag{17}$$

where χ is the indicator function and E_{z_0} is the conditional expectation with respect to the probability measure μ. Using the Chebyshev inequality to obtain an upper bound on the Itô stochastic integral in (15) and estimating the upper bound about the path ϕ_t we obtain the inequality[3]

$$\mathsf{P}_{x_0}\{d_T(\phi, x^k) < \delta\} > \exp\{-(2k)^{-1}[\Theta_T(\phi) + h]\} \tag{18}$$

for any $h > 0$ where $k \leqslant \min(h, \delta)/C(T, K)$ and $C(T, K)$ is a constant depending on T, $K = \Theta_T(\phi) + T$ and positive parameters that place bounds on the magnitudes of the drift vector and the local variance matrix. Inequality (18) stresses the fundamental role of the additive OM functional[1]

$$\Theta_T(\phi) = \tfrac{1}{2}\int_0^T \|\dot{\phi}_t - b(\phi_t)\|^2\,dt \tag{19}$$

as far as probabilistic estimates are concerned in the $k\downarrow 0$ limit. In fact, the probability that $x_t^k \in A$, where A is a Borel set, is given by

$$\lim_{k\downarrow 0} 2k \log \mathsf{P}_{x_0}\{x_t^k \in A\} = -\inf\{\Theta_T(\phi) : \phi_0 = x_0, \phi_T \in A\} \tag{20}$$

Similar argumentation leads to the inequality[3,4]

$$\mathsf{P}_{x_0}\{\tau_\Omega^k < T\} > \mathsf{P}_{x_0}\{d_T(\phi, x^k) < \delta\} \geqslant \exp\{-(2k)^{-1}[\Theta_T(x_0, \partial\Omega) + h']\} \tag{21}$$

for the probability that the system will make its first exit from Ω at a time $\tau_\Omega^k < T$ for any $h' > 0$, provided k is sufficiently small. The exit time is defined as $\tau_\Omega^k \equiv \inf\{t : \phi_t \notin \Omega\}$ and

$$\Theta_T(x_0, \partial\Omega) = \inf\{\Theta_T(\phi) : \phi_0 = x_0, \phi_T \in \partial\Omega\} \tag{22}$$

In the $k\downarrow 0$ limit there results

$$\lim_{k\downarrow 0} 2k \log \mathsf{P}_{x_0}\{\tau_\Omega^k < T\} = -\min_{y\in\partial\Omega} \Theta_T(x_0, y) \tag{23}$$

Furthermore, the transition probability for the process $\tilde{x}_t^k$,

$$P(A, T \mid x_0) = \mathsf{P}_{x_0}(x_T^k \in A) \tag{24}$$

has a density p which in the thermodynamic limit $k\downarrow 0$ is given by[3,4]

$$\lim_{k\downarrow 0} 2k \log p(x, T \mid x_0) = -\Theta_T(x_0, x) \tag{25}$$

where

$$\Theta_T(x_0, x) = \inf\{\Theta_T(\phi) : \phi \in \Omega, \phi_0 = x_0, \phi_T = x\} \tag{26}$$

The results of Ventsel' and Freidlin suggest a variational formulation in which the paths of maximum likelihood minimize the OM functional subject to given endpoint conditions. This has been carried out by Ludwig[5] using a ray method in which Ω is covered by a family of rays, obtained from a Hamiltonian that is associated with an eikonal equation. Ludwig's analysis is based on an asymptotic expansion of the Fokker–Planck equation in which the eikonal equation arises at order (k^{-1}). This method avoided the variational problem of specifying the end-point conditions: the paths of maximum likelihood which render the OM functional stationary satisfy first-, rather than second-, order differential equations so that one cannot specify both end points of the transition. Nevertheless, implicit in Ludwig's analysis is the criterion that correctly determines the paths of maximum likelihood which Onsager and Machlup took for granted since their starting point was the phenomenological equations of irreversible thermodynamics. In the next section we derive the paths of maximum likelihood from a variational principle and discuss the differences encountered with variational principles of classical mechanics.

4. VARIATIONAL FORMULATION FOR PATHS OF MAXIMUM LIKELIHOOD

The results of the last section indicate that

$$\mathsf{P}_{x_0}\{\tilde{x}_T^k \in A\} = \int \chi_A \mathsf{E}_{x_T^k}\{\rho\} \mathsf{P}_{x_0}\{x_T^k \in dx\}$$

tends to

$$\text{const} \times \exp\{-(2k)^{-1} \inf[\Theta_T(\phi) : \phi_0 = x_0, \phi_T \in A]\}$$

in the limit $k\downarrow 0$. In the thermodynamic limit, the distribution functions of the diffusion process become exceedingly sharp so that means and modes coincide. Therefore, in this limit, the paths of maximum likelihood can be obtained from the stationary points of the "action" functional

$$\Theta_{T_1T_2}(\phi) = \tfrac{1}{2} \int_{T_1}^{T_2} D_{ij}(\phi_t)\{\dot{\phi}_t^i - b^i(\phi_t)\}\{\dot{\phi}_t^j - b^j(\phi_t)\} \tag{27}$$

The integrand of (27) plays the role of a Lagrangian and it is well known that the Lagrangian is invariant up to an exact differential. This term may be extracted out by writing[3]

$$D_{ij}b^j = \partial_i S + A_i \tag{28}$$

where S is some scalar potential and A is a vector field. The properties of A shall be specified below [cf. Eq. (37)]. Introducing (28) into (27) results in

$$\Theta_{T_1T_2}(\phi) = \mathsf{A}_{T_1T_2}(\phi) - \{S(\phi_{T_2}) - S(\phi_{T_1})\} \tag{29}$$

Introducing (29) into (25), the expression for the transition probability density becomes

$$\lim_{k\downarrow 0} 2k \log p(x, T_2 \mid x_0, T_1) = S(x) - S(x_0) - \mathsf{A}_{T_1T_2}(x_0, x) \tag{30}$$

where

$$\mathsf{A}_{T_1T_2}(x_0, x) = \inf\{\Theta_{T_1T_2}(\phi) : \phi_{T_1} = x_0, \phi_{T_2} = x\} + S(x) - S(x_0) \tag{31}$$

and plays a role analogous to Hamilton's principal function. Expression (31) is the kinetic analog of Boltzmann's principle in the thermodynamic limit.[15]

Since the transition probability satisfies both the forward and backward Kolmogorov equations, A satisfies the pair of Hamilton–Jacobi equations

$$\partial_{T_2}\mathsf{A} + \tfrac{1}{2}D^{ij}(\partial_i\mathsf{A} + A_i)(\partial_j\mathsf{A} + A_j) - \Psi(x) = 0 \tag{32}$$

and

$$-\partial_{T_1}\mathsf{A} + \tfrac{1}{2}D^{ij}(\partial_{0_i}\mathsf{A} - A_i)(\partial_{0_j}\mathsf{A} - A_j) - \Psi(x_0) = 0 \tag{33}$$

which can be derived at order (k^{-1}) in a formal expansion of the solution of the Kolmogorov equations in powers of k. The subscript 0 means partial differentiation with respect to the initial coordinates of the transition. The Hamilton–Jacobi equations (32) and (33) indicate that

$$\mathsf{H}(x, \partial\mathsf{A}) = \tfrac{1}{2}D^{ij}(\partial_i\mathsf{A} + A_i)(\partial_j\mathsf{A} + A_j) - \Psi(x) \tag{34}$$

has the role of a Hamiltonian with a potential which is the negative of

$$\Psi(x) = \tfrac{1}{2}D_{ij}b^i b^j \tag{35}$$

known in statistical thermodynamics as the "generating" function.[16]

In addition, the time-dependent Fokker–Planck equation for the invariant probability density must be satisfied to order (k^{-1}) in an asymptotic expansion of the invariant probability density in powers of k. In the thermodynamic limit $k\downarrow 0$, Boltzmann's principle

$$\lim_{k\downarrow 0} k \log p_\infty(x) = S(x) + \text{const} \tag{36}$$

relates the invariant probability density p_∞ to the entropy $S(x)$. Thus at order (k^{-1}) we obtain the transversality condition

$$v^i \partial_i S = 0 \tag{37}$$

where $v^i = D^{ij}A_j$. Note that the rotational probability current $J^i = p_\infty v^i$ vanishes in isolated systems since rotational motion must be sustained by external sources. The transversality condition was also required by Ventsel' and Freidlin in the drift decomposition (28).

The thermodynamic action functional is[17]

$$\mathsf{A}_{T_1T_2}(\phi) = \int_{T_1}^{T_2} \mathsf{L}(\phi_t, \dot{\phi}_t)\, dt \tag{38}$$

where L is the thermodynamic Lagrangian

$$\mathsf{L}(\phi_t, \dot{\phi}_t) = \tfrac{1}{2} D_{ij}\dot{\phi}_t^i \dot{\phi}_t^j - A_i \dot{\phi}_t^i + \tfrac{1}{2} D_{ij} b^i b^j \tag{39}$$

We may say that the thermodynamic Lagrangian (39) differs from the Lagrangian of the OM functional (27) by a gauge transformation. The thermodynamic Lagrangian (39) has the appearance of a Lagrangian of a charged particle in a scalar potential $-\Psi$ which is acted upon by a vector potential $-A$. Provided the transversality condition (37) holds, L is invariant under time reversal since $A_i \to -A_i$ under $t \to -t$. Defining the dissipation function Φ and the rate of working of the external forces Π by[9]

$$\Phi = \tfrac{1}{2} D_{ij} \dot{\phi}_t^i \dot{\phi}_t^j \tag{40}$$

$$\Pi = A_i \dot{\phi}_t^i \tag{41}$$

the thermodynamic Lagrangian can be written in the form of a difference between the sum of dissipation functions and the external power, viz.,

$$\mathsf{L} = \Phi + \Psi - \Pi \tag{42}$$

It should be noted that Ψ like Φ is a dissipation function with the difference that whereas Ψ is a function of state, Φ is a function of its rate of change.[1] In the analysis of Onsager and Machlup, they are always assumed to be numerically equal by virtue of the phenomenological relations. We shall now see that their numerical equivalence is the criterion for determining paths of maximum likelihood.

Allowing for both a variable time of transit and variations in the end points of transition, the variational principle

$$\Delta\Theta_{T_1T_2}(\phi) = \Delta\int_{T_1}^{T_2} \mathsf{L}\, dt - \partial_i S \Delta\phi^i|_{T_1}^{T_2} = \delta\int_{T_1}^{T_2} \mathsf{L}\, dt + \mathsf{L}\Delta t|_{T_1}^{T_2} - \partial_i S \Delta\phi^i|_{T_1}^{T_2} = 0 \tag{43}$$

determines the paths of maximum likelihood for both the growth and decay of nonequilibrium fluctuations. The Δ variation is related to the virtual δ

variation by $\Delta\phi = \delta\phi + \dot{\phi}\Delta t$. Introducing the conjugated generalized momenta

$$\pi_i = \partial_i \mathsf{A} = \partial_{\dot{\phi}^i}\mathsf{L} = D_{ij}\dot{\phi}^j + A_i \tag{44}$$

the Hamiltonian (34) becomes

$$\mathsf{H}(\phi, \pi) = \tfrac{1}{2}D^{jm}(\pi_j + A_j)(\pi_m + A_m) - \tfrac{1}{2}D_{jm}b^j b^m \tag{45}$$

and so (43) can be written in canonical form as

$$\Delta\Theta_{T_1T_2}(\phi) = \int_{T_1}^{T_2}\left[\left(\dot{\phi}^i - \partial_{\pi_i}\mathsf{H}\right)\delta\pi_i - \left(\dot{\pi}_i + \partial_i\mathsf{H}\right)\delta\phi^i\right]dt$$

$$+ \left\{(\pi_i - \partial_i S)\Delta\phi^i - \mathsf{H}\Delta t\right\}\Big|_{T_1}^{T_2} = 0 \tag{46}$$

where the momenta in the integrated part refer to the end points of the transition. Since $\delta\phi^i$ and $\delta\pi_i$ are arbitrary virtual variations, we obtain the following three conditions:

$$\text{(A)} \quad \dot{\phi}^i = \partial_{\pi_i}\mathsf{H} = D^{ij}(\pi_j + A_j)$$

$$\dot{\pi}_i = -\partial_i\mathsf{H} = -\Big\{\tfrac{1}{2}\partial_i D^{kj}\big[(\pi_k + A_k)(\pi_j + A_j) - (\partial_k S + A_k)(\partial_j S + A_j)\big] + D^{kj}\big[\partial_i A_k(\pi_j - \partial_j S) - \partial_i\partial_k S(\partial_j S + A_j)\big]\Big\}$$

$$\text{(B)} \qquad \mathsf{H}(\phi, \pi) = 0 \qquad \text{if} \quad \Delta t\big|_{T_1}^{T_2} \neq 0$$

$$\text{(C)} \qquad \pi_i = \partial_i S \qquad \text{if} \quad \Delta\phi^i\big|_{T_1}^{T_2} \neq 0$$

It is apparent that condition (C) satisfies both (A) and (B); it determines the *absolutely* most probable path, $\hat{\phi}$. This path is the deterministic path which is the solution of Eq. (1). We have called this path the "thermodynamic" path[17] and along $\hat{\phi}$, $\Theta(\hat{\phi}) = 0$. Since Θ is positive semidefinite, this is its absolute minimum. Condition (B) is, however, more general and the class of maximum likelihood paths $\bar{\phi}$ can be determined by the dissipation balance condition

$$\mathsf{H}(\bar{\phi}, \bar{\pi}) = \Phi(\bar{\pi}) - \Psi(\bar{\phi}) = 0 \tag{47}$$

provided the transversality condition (37) holds. By virtue of the dissipation balance condition (47), which provides a numerical equivalence of the dissipation functions along the paths of maximum likelihood $\bar{\phi}$, $\mathsf{A}(x_0, x)$ ceases to be an explicit function of time along these paths.

Following Ventsel' and Freidlin,[3] we can show that $\Theta(\phi) \geqslant \Theta(\bar{\phi})$ for any other path not belonging to the class of maximum likelihood paths $\bar{\phi}$. Along the extreme path, the speed is $\|\dot{\bar{\phi}}^i\| = \{\|D^{ij}\partial_j S\|^2 + \|v^i\|^2\}^{1/2}$

$= \|b^i(\bar{\phi})\|$. Suppose that $\bar{\phi}_t$ is obtainable from another curve ϕ_t by a change in the time scale, viz., $\tau = \tau(t)$, $\bar{\phi}_t = \phi_{\tau(t)}$. Then

$$\Theta_{T_1T_2}(\phi) = \tfrac{1}{2}\int_{T_1}^{T_2}\|\dot{\phi}_\tau - b(\phi_\tau)\|^2\,d\tau = \tfrac{1}{2}\int_{\tau^{-1}(T_1)}^{\tau^{-1}(T_2)}\|\dot{\bar{\phi}}_t/\dot{\tau}(t) - b(\bar{\phi}_t)\|^2\dot{\tau}(t)\,dt$$

$$\geqslant \int_{\tau^{-1}(T_1)}^{\tau^{-1}(T_2)}\|\dot{\bar{\phi}}_t\|\,\|b(\bar{\phi}_t)\|\,dt - \int_{\tau^{-1}(T_1)}^{\tau^{-1}(T_2)}\left[b(\bar{\phi}_t),\dot{\bar{\phi}}_t\right]dt = \Theta_{T_1T_2}(\bar{\phi}) \quad (48)$$

on account of the inequality $ax^2 + y^2/a \geqslant 2xy$ for any $a > 0$.

In contrast to variational principles of classical mechanics, the extremum paths satisfy first order differential equations so that only one end condition in the variational expression can be specified. The thermodynamic path satisfies condition (C) and the problem of specifying the endpoint conditions does not arise. If, on the other hand, (C) is not satisfied then it will be possible to reach $\inf\Theta(\phi)$ only for $T_1 \to -\infty$ when the final state of transition x is specified at time T_2.[3] As $T_1 \to +\infty$, the system will reach any neighborhood of the stable stationary state. This was already recognized by Onsager and Machlup, who used the initial condition to eliminate the exponentially falling solution in the case of Gaussian fluctuations: "the aged system was certainly at equilibrium some time long ago".[1] Physically, this conforms to our intuition that an arbitrary nonequilibrium state cannot be realized in a finite time if the system is found in a small neighborhood of the stationary state $x_0 = 0$ where it spends an unlimited portion of its time. Also in this case, the time of transit is variable so condition (B) applies to these paths of maximum likelihood for the system to follow in making the transition from the stationary state to any fixed terminal state x in the limit $k\downarrow 0$. Again the thermodynamic action is not an explicit function of time along these paths of maximum likelihood.

The distinction between the paths of maximum likelihood for the growth and decay of fluctuations in the limit $k\downarrow 0$ can be seen in terms of the different forms that the variational principle (46) assumes. The minimization of the OM functional to obtain the most likely path for the decay of a nonequilibrium fluctuation is analogous to d'Alembert's principle in classical mechanics[9]; it makes an independent statement at each instant in time during the motion. This is precisely the content of condition (C). Alternatively, the minimization of the OM functional to obtain the most likely path for the growth of a fluctuation is analogous to Hamilton's principle which considers the motion as a whole. However, the specification of both end points is incompatible with the first-order differential equation for the path of maximum likelihood. This requires letting $T_1 \to -\infty$, which ensures that the system will arrive at any neighborhood of the stationary state. Only in this case will $\Theta(\phi)$ reach a minimum.

Since H is not an explicit function of time, the thermodynamic action can be written in the separated form

$$\mathsf{A}_{T_1T_2}(x_0, x) = \mathsf{W}_\alpha(x_0, x) - \alpha(T_2 - T_1) \tag{49}$$

where the parameter $\alpha \geqslant 0$. W_α is analogous to Hamilton's characteristic function in classical mechanics. Paths of maximum likelihood are characterized by $\alpha = 0$ and consequently W_0 satisfies the pair of time-independent Hamilton–Jacobi equations:

$$\tfrac{1}{2}D^{ij}(\partial_i\mathsf{W}_0 + A_i)(\partial_j\mathsf{W}_0 + A_j) - \Psi(x) = 0 \tag{50}$$

$$\tfrac{1}{2}D^{ij}(\partial_{0_i}\mathsf{W}_0 - A_i)(\partial_{0_j}\mathsf{W}_0 - A_j) - \Psi(x_0) = 0 \tag{51}$$

By virtue of the form of the generating function (35) one particular solution to Eqs. (50) and (51) is

$$\hat{\mathsf{W}}_0(x_0, x) = S(x) - S(x_0) \tag{52}$$

Consequently, $\hat{\pi}_i = \partial_i S$ and introducing this into the first of Hamilton's equations gives

$$\dot{\hat{\phi}}_t^i = D^{ij}\partial_j S(\hat{\phi}_t) + v^i(\hat{\phi}_t), \qquad \hat{\phi}_0 = x_0 \tag{53}$$

which will be recognized as the equation of motion for absolutely most probable path for the regression of a fluctuation. The second of Hamilton's equations in (A) is satisfied identically.

Now, provided the transversality condition (37) holds, there is another particular solution to the time-independent Hamilton–Jacobi equations (50) and (51), viz.,

$$\tilde{\mathsf{W}}_0(x_0, x) = -\{S(x) - S(x_0)\} \tag{54}$$

According to (44) and (49) we now find $\tilde{\pi}_i = -\partial_i S$ and introducing this into the first of Hamilton's equations we have

$$\dot{\tilde{\phi}}_t^i = -D^{ij}\partial_j S(\tilde{\phi}_t) + v^i(\tilde{\phi}_t), \qquad \tilde{\phi}_{T_2} = x, \ t \in [-\infty, T_2] \tag{55}$$

Equation (54) specifies a unique extremal of $\Theta(\phi)$ on the set

$$\bigcup_{-\infty \leqslant T_1 < T_2} \{\phi : \phi_{T_1} = 0, \phi_{T_2} = x\}$$

Recalling that $v^i \to -v^i$ under $t \to -t$, it will be apppreciated that (54) is the mirror image in time of the deterministic equation (53) for the absolutely most probable path. For this reason, we have referred to $\tilde{\phi}$ as the "antithermodynamic" path.[17] In the next section, we shall see that this path of maximum likelihood, in the limit $k\downarrow 0$, is intimately connected with the most probable path of exit in any bounded domain containing the stationary state.

5. THERMODYNAMIC CRITERIA FOR STOCHASTIC EXIT

Although the deterministic system is asymptotically stable and $b \cdot \nu < 0$ on the boundary $\partial\Omega$ of the domain Ω containing the unique stationary state, there will, with probability 1, be trajectories of the system which reach the boundary and induce on it a probability distribution. Assuming that there exits a unique position on $\partial\Omega$ at which the system makes its first exit from Ω, we can, following Ventsel' and Freidlin, obtain a thermodynamic criterion for the state of exit.

If the system does not leave Ω on the the interval $[T_1, T_2]$, then the entropy is a function of state, viz.,

$$S(\phi_{T_2}) - S(\phi_{T_1}) = \int_{T_1}^{T_2} \partial_i S \dot{\phi}_t^i \, dt \tag{56}$$

The OM functional can then be written as

$$\begin{aligned} \Theta_{T_1T_2}(\phi) &= \tfrac{1}{2}\int_{T_1}^{T_2} D_{ij}\left(\dot{\phi}_t^i + D^{ik}\partial_k S - v^i\right)\left(\dot{\phi}_t^j + D^{jk}\partial_k S - v^j\right) dt \\ &\quad - 2\int_{T_1}^{T_2} \partial_i S \dot{\phi}_t^i \, dt \\ &\geqslant 2\left\{ S(\phi_{T_1}) - S(\phi_{T_2}) \right\} \end{aligned} \tag{57}$$

provided the transversality condition (37) holds. Hence $\Theta_{T_1T_2}(\phi) \geqslant 2\{S(\phi_{T_1}) - S(\phi_{T_2})\}$ for any curve ϕ_t' that connects the stationary state $\phi_{T_1} = 0$ with an arbitrary nonequilibrium state $\phi_{T_2} = x$. If, on the other hand, ϕ_t exits from Ω at some intermediate time $\tau \in [T_1, T_2]$, it will do so at that state $x \in \partial\Omega$ for which $S(x) = \max_{y \in \partial\Omega} S(y)$. By virtue of the fact that the OM functional is additive and non-negative, we have

$$\Theta_{T_1T_2}(\phi) \geqslant \Theta_{T_1\tau}(\phi) \geqslant 2\left\{ S(\phi_{T_1}) - S(\phi_\tau) \right\} \tag{58}$$

from which it follows that $S(\phi_s) \geqslant S(\phi_\tau)$ for $s \leqslant \tau$. This means that the system does not pass through states in which the entropy is strictly smaller than the maximum entropy at the boundary, with probability 1, as $k \downarrow 0$.

In our formulation, the entropy plays the role of the quasipotential introduced by Ventsel' and Freidlin.[3] Thus, the expected exit time is related to the minimum entropy change by

$$\lim_{k \downarrow 0} k \log \mathsf{E}_0\left\{ \tau_\Omega^k \right\} = S(0) - \max_{y \in \partial\Omega} S(y) \tag{59}$$

provided there is a unique state on the boundary with maximum entropy. The final lap, before reaching the boundary, occurs within a δ tube enclosing the extremal path $\tilde{\phi}$, with probability close to 1, for $k \downarrow 0$. Ventsel' and Freidlin have pointed out that although this is the most probable mode of exit, there are nevertheless infinitely other modes of exit. And although each of these modes has an infinitely smaller probability of occurrence, their sum may, however, be greater.

6. THERMODYNAMIC VARIATIONAL PRINCIPLES AND EVOLUTIONARY CRITERIA

As we have already mentioned, in the limit $T_1 \to -\infty$, $\inf \Theta(\phi)$ is achieved along the antithermodynamic path. The first integral in (57) vanishes and we obtain

$$\tfrac{1}{2}\Theta_{-\infty T_2}(\tilde{\phi}) = -\int_{-\infty}^{T_2} \partial_i S \dot{\tilde{\phi}}_t^i \, dt = S(0) - S(\phi_{T_2}) \geqslant 0 \tag{60}$$

where we have used $\lim_{t \to -\infty} \tilde{\phi}_t = 0$, which is a consequence of the fact that

$$\dot{S}(\tilde{\phi}_t) = -\partial_i S \dot{\tilde{\phi}}_t^i = -D^{ij} \partial_i S \partial_j S \leqslant 0 \tag{61}$$

provided the transversality condition (37) holds.

Inequality (60) attests to the fact that the entropy is a strictly monotonically decreasing function along the antithermodynamic path. In other words, the entropy production (61) is negative semidefinite along $\tilde{\phi}$. The integrand in (57) can be written as a power inequality, viz.,

$$\Phi + \Psi \geqslant \Pi - \dot{S} \tag{62}$$

which expressed in words states that the rate of energy dissipation must prevail over the rate of energy input and its generation in the system. Along the antithermodynamic path (62) reduces to

$$2\Phi(\dot{\tilde{\phi}}) - \Pi(\dot{\tilde{\phi}}) = -\dot{S}(\dot{\tilde{\phi}}) \geqslant 0 \tag{63}$$

where we have used the dissipation balance condition (47) for paths of maximum likelihood. In the particular case of an isolated ($\Pi \equiv 0$) system, (63) corresponds to the Onsager–Machlup result.[1] Note that the dissipation balance condition (47) is implicit in their analysis since their starting point was the phenomenological equations of irreversible thermodynamics.

Using the fact that the OM functional semidefinite we obtain the power inequality

$$\Phi + \Psi \geqslant \Pi + \dot{S} \tag{64}$$

If the trajectory ϕ_t coincides on $[T_1, T_2]$ with a trajectory of the thermodynamic path $\hat{\phi}_t$, the increment in the OM functional on the entire interval vanishes. We then obtain the power balance relation[18]:

$$2\Phi(\dot{\hat{\phi}}) - \Pi(\dot{\hat{\phi}}) = \dot{S}(\dot{\hat{\phi}}) = D^{ij} \partial_i S \partial_j S \geqslant 0 \tag{65}$$

where the second equality follows from (53) and the transversality condition (37). Along $\hat{\phi}_t$, the entropy production is positive semidefinite; the entropy of an unconstrained nonequilibrium process will, in general, be a strictly monotonically increasing function of time. Alternatively, if it is known that the entropy was a maximum at some distant time in the past, then there will be a finite probability to observe states with lower entropy in the course of time. The most probable path for the growth of a spontaneous fluctuation is, with probability 1, the antithermodynamic path in the limit $k \downarrow 0$.

The paths of maximum likelihood for the growth and decay of fluctuations can be derived from the *constrained* thermodynamic variational principle of least dissipation of energy[19]:

$$\Phi(\dot{\phi}) \to \inf \tag{66}$$

subject to the power balance constraints, (63) and (65), respectively. Let λ be a Lagrange undetermined multiplier; the free variational principles are:

$$\delta_{\dot{\phi}}\left\{\Phi(\dot{\phi}) - \lambda\left[2\Phi(\dot{\phi}) - \Pi(\dot{\phi}) \pm \dot{S}(\dot{\phi})\right]\right\} = 0 \tag{67}$$

where the $\pm$ refers to the growth and decay of fluctuations, respectively, and the variations are taken with respect to the independent velocities for a given configuration. Explicitly we find

$$\left\{(1 - 2\lambda)D_{ij}\dot{\phi}^j - \lambda(\pm\partial_i S - A_i)\right\}\delta\dot{\phi}^i = 0 \tag{68}$$

Since the variations are arbitrary, we obtain $\lambda = 1$ in both cases upon multiplying through by $\dot{\phi}^i$ and using the power balance constraints (63) and (65). The free thermodynamic variational principles are

$$\Phi - \Pi \pm \dot{S} \to \text{extremum} \tag{69}$$

for the most probable paths of the growth and decay of fluctuations, respectively.

The principle of minimum dissipation of energy has an additional probabilistic significance. The joint probability density, $p(x, T_2; x_0, T_1) = p(x, T_2 \mid x_0, T_1) \cdot p_\infty(x_0)$, in the limit $k \downarrow 0$ is given by the expression

$$\lim_{k \downarrow 0} 2k \log p(x, T_2; x_0, T_1) = S(x) + S(x_0) - \mathsf{A}_{T_1 T_2}(x_0, x) \tag{70}$$

where the thermodynamic action is given by

$$\mathsf{A}_{T_1 T_2}(x_0, x) = \inf\left\{\int_{T_1}^{T_2}\left[\Phi(\dot{\phi}_t) + \Psi(\phi_t) - \Pi(\dot{\phi}_t)\right]dt : \phi_{T_1} = x_0, \phi_{T_2} = x\right\} \tag{71}$$

Integrating the power balance equation (63) on the integral $[-\infty, T_2]$ and the power balance equation (65) on the interval $[T_1, \infty]$ we obtain

$$S(0) - S(x) = \int_{-\infty}^{T_2}\left\{2\Phi(\dot{\tilde{\phi}}_t) - \Pi(\dot{\tilde{\phi}}_t)\right\}dt = \mathsf{A}_{-\infty T_2}(0, x) \tag{72}$$

and

$$S(0) - S(x_0) = \int_{T_1}^{\infty} \left\{ 2\Phi(\overset{\lambda}{\phi}_t) - \Pi(\overset{\lambda}{\phi}_t) \right\} dt = \mathsf{A}_{T_1\infty}(x_0, 0) \tag{73}$$

respectively. Introducing (72) and (73) into (70) leads to

$$\lim_{k \downarrow 0} k \log p(x, T_2; x_0, T_1) = S(0) - \tfrac{1}{2} \mathsf{A}_{-\infty,\infty}(x_0, x) \tag{74}$$

where

$$\mathsf{A}_{-\infty,\infty}(x_0, x) = \inf\left\{ \int_{-\infty}^{\infty} \left\{ \Phi(\dot{\phi}_t) + \Psi(\phi_t) - \Pi(\dot{\phi}_t) \right\} dt : \phi_{T_1} = x_0, \phi_{T_2} = x \right\} \tag{75}$$

Expressions (73) and (74) show that a complete statistical description is afforded by the time integral of the thermodynamic Lagrangian. We shall now show that the thermodynamic Lagrangian characterizes the rate of decay of statistical correlations between nonequilibrium states that are not well separated in time. An expression analogous to (74) has been previously derived by Onsager and Machlup,[1] in the case of Gaussian fluctuations occurring in an isolated system ($\Pi \equiv 0$), using arguments based on symmetry in past and future (see also Ref. 20).

An evolutionary criterion can be derived that is analogous to the generalized Boltzmann H theorem.[21] We define the function

$$\begin{aligned} \Sigma_{T_1T_2}(x_0, x) &\equiv -\lim_{k \downarrow 0} 2k \log\{ p(x, T_2 \mid x_0, T_1)/p_\infty(x) \} \\ &= \mathsf{A}_{T_1T_2}(x_0, x) + S(x) + S(x_0) \end{aligned} \tag{76}$$

In the thermodynamic limit, $k \downarrow 0$, the thermodynamic action coincides with the negative of the joint entropy,[15] as shown by (76). The joint entropy accounts for the statistical correlations between nonequilibrium states that are not well-separated in time.[15,21] Along the thermodynamic path, $\hat{\Sigma}(x_0, x) = 2S(x)$, while along the antithermodynamic path $\tilde{\Sigma}(x_0, x) = 2S(x_0)$.

The total time derivative of Σ is

$$d_T\Sigma = \Phi + \Psi - \Pi + \dot{S} \geqslant 0 \tag{77}$$

In the thermodynamic limit, the thermodynamic Lagrangian ($\Phi + \Psi - \Pi$) describes the rate of decay of the statistical correlations between nonequilibrium states. From the power inequalities, (62) and (64), we conclude that the rate of change of the entropy associated with the decay of the statistical correlations is always greater than or equal to the absolute value of the entropy production. Moreover, along the thermodynamic path, $d_T\hat{\Sigma} = 2\dot{S} \geqslant 0$, and consequently Σ provides a criterion of evolution. In contrast, $d_T\tilde{\Sigma} = 0$ along the antithermodynamic path and Σ does not provide any evolutionary criterion along this path.

REFERENCES

1. L. Onsager and S. Machlup, *Phys. Rev.* **91**:1505 (1953); S. Machlup and L. Onsager, *Phys. Rev.* **91**:1512 (1931).
2. B. H. Lavenda, *Found. Phys.* **9**:405 (1979).
3. A. D. Ventsel' and M. I. Freidlin, *Russ. Math. Surv.* **25**:1 (1970); *Theory Probab. Appl.* **17**:269 (1972).
4. A. Friedmann, *Stochastic Differential Equations and Applications*, Vol. 2, Academic Press, New York (1976), Chap. 14.
5. D. Ludwig, *SIAM (Soc. Ind. Appl. Math.) Rev.* **17**:605 (1975).
6. R. F. Anderson and S. Orey, *Nagoya Math. J.* **60**:189 (1976).
7. B. J. Matkowsky and Z. Schuss, *Bull. Am. Math. Soc.* **82**:321 (1976); *SIAM (Soc. Ind. Appl. Math.) J. Appl. Math.* **33**:365 (1977); see also Z. Schuss, *Theory and Applications of Stochastic Differential Equations*, Wiley, New York (1980), Chap. 7.
8. R. G. Williams, *SIAM (Soc. Ind. Appl. Math.) J. Appl. Math.* **40**:208 (1981).
9. B. H. Lavenda, *Thermodynamics of Irreversible Processes*, Macmillan, London/Halsted, New York (1978).
10. B. H. Lavenda, in preparation.
11. E. Wong and M. Zakai, *Int. J. Eng. Sci.* **3**:213 (1965).
12. R. L. Stratonovich, *SIAM (Soc. Ind. Appl. Math.) J. Control* **4**:362 (1966); see also R. L. Stratonovich, *Conditional Markov Processes and Their Application to the Theory of Optimal Control*, American Elsevier, New York (1968), Chap. 2.
13. K. Itô, *Memoir Am. Math. Soc.* **4**:1 (1951).
14. I. V. Girsanov, *Theory Prob. Appl.* **5**:285 (1960).
15. B. H. Lavenda and E. Santamato, *J. Math. Phys.* **22**:2926 (1981).
16. L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Pergamon Press, Oxford (1959), p. 377.
17. B. H. Lavenda, *Rivista Nuovo Cimento* **7**:229 (1977).
18. Ref. 9, Chap. V.
19. Ref. 9, Chap. VI.
20. B. H. Lavenda and E. Santamato, *Lett. Nuovo Cimento* **26**:27 (1979).
21. E. Santamato and B. H. Lavenda, *The stochastic H theorem*, submitted to *J. Math. Phys.*