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On the principle of minimal correlational entropy†

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Abstract. The Onsager-Machlup approximation for a discrete Markov chain, representing multistationary state transitions, is formulated in the limit of small thermal fluctuations. The principle of minimal correlational entropy is used to determine the state in which the invariant probability measure tends to concentrate as the intensity of the fluctuations tends to zero. It is this principle, rather than that of maximum entropy, which is valid in open systems without microscopic reversibility. In systems characterised by microscopic reversibility, the two principles give the same predictions. The principle of minimal correlational entropy is shown to be the statistical analogue of the thermodynamic principle of least dissipation of energy. The principle of minimal correlational entropy is applied to the problem of stochastic exit from domains enclosing multistationary states; it reduces to a minimum entropy difference principle for systems satisfying microscopic reversibility.

1. Introduction

Thermodynamic evolutionary criteria are couched in the concavity of thermodynamic potentials. The second law asserts that the entropy of an isolated system will tend to increase in time and the final state of thermodynamic equilibrium possesses maximum entropy. However, in the absence of the 'fourth law', which affirms that the entropy is extensive, the principle that '*states of maximum entropy as obtained by the use of calculus are stable equilibrium states of the system*' also fails (Landsberg and Tranah 1980a). Landsberg and Tranah (1980b) have further shown that it is the superadditive, rather than the concave, property of the entropy which is the essence of the second law. In particular, positive specific heats are no longer necessary for a stable equilibrium state (Landsberg and Tranah 1980b).

The situation is further aggravated far from equilibrium where a multiplicity of non-equilibrium stationary states can appear for a given non-equilibrium constraint as opposed to the equilibrium transformation from a more to a less constrained state by the removal of a partition. The most obvious extension would be to carry over a maximum entropy principle in a more general non-equilibrium setting. Then, one could associate the most thermodynamically stable state with that non-equilibrium state which maximises the entropy subject to the given non-equilibrium constraint that prevents the system from relaxing back to equilibrium. The main result of our paper will be to show that this conjecture is, in general, incorrect.

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Thermodynamics does not provide a physical mechanism for the transitions between non-equilibrium stationary states so that if a system is in a state of a relative maximum of the entropy, it would have no way of knowing that a state corresponding to the absolute maximum of the entropy exists. In order to invoke such a mechanism we have to take into consideration random thermal fluctuations. In order not to overshadow the deterministic behaviour, the fluctuations must necessarily have a small intensity. Also, in order for them to affect the deterministic behaviour of the system, we must wait sufficiently long for there to be a non-vanishing probability for even rare events to occur. Some of these events will be more improbable while others will be less improbable. And it is precisely the latter which will determine the evolution of the system over infinitely long time intervals (Freidlin and Wentzell 1984).

On account of the smallness of the random thermal fluctuations, non-equilibrium multistationary state transitions can be modelled as a positive, recurrent Markov chain (Wentzell and Freidlin 1970). We can argue that on account of the smallness of the fluctuations and the extremely large time interval considered, the system will spend an overwhelmingly larger portion of its time in the immediate vicinity of a stationary state than between them. Non-equilibrium transitions appear as rare jumps and these jumps comprise the Markov chain. The pertinent transition probability estimates are due to Wentzell and Freidlin (1970) to which we now turn our attention.

2. Markov chain formulation of the Onsager–Machlup theory

Consider a non-equilibrium process in $\mathbb{R}^n$ which is described by the set of macroscopic rate equations:

$$\dot{x}_t = b(x_t); \qquad x_0 = y \tag{2.1}$$

with a drift vector $b(x) = \{b^1(x), b^2(x), \ldots, b^n(x)\}$. Near equilibrium, the law of detailed balance guarantees the uniqueness of thermodynamic equilibrium while far from equilibrium there may be more than one physically acceptable branch solution to the rate equations (2.1). The (stable) stationary states are a set of ω-limit sets (Nemytskii and Stepanov 1960) of solutions x_t to (2.1) as $t \to \infty$. Let us assume that every limit set of (2.1) is found in one of a finite number of compacta K_i ($i = 1, \ldots, l$). Since the non-equilibrium stationary states are stable, they will act as basins to the dynamical flow (2.1) and correspond to states of relative entropy maxima. Some of these states will have a larger entropy than others and our problem is to predict the behaviour of the motion in large time intervals.

Transitions from one stable compactum to another cannot occur along trajectories of the dynamical flow since the system must go 'against the flow', at least for some distance between the stable compacta. This necessitates the introduction of random thermal fluctuations which we model as Brownian motion. The perturbed process will then be described by the set of stochastic differential equations:

$$\dot{X}_t = b(X_t) + (2kL)^{1/2}\dot{W}_t; \qquad X_0 = y \tag{2.2}$$

where kL is the molecular diffusion matrix and k is Boltzmann's constant. The reason for the appearance of k is that it will play the role of the small parameter regulating the size of the thermal fluctuations (Lavenda and Santamato 1982). $\dot{W}_t$ is a 'white' noise process which is the formal derivative of the standard n-dimensional Wiener process $W = \{W^1, W^2, \ldots, W^n\}$. As $k\downarrow 0$, the perturbed process X_t will converge in probability to x_t and asymptotically $(X_t - x_t)$ will converge to a Gaussian process, analogous to the law of large numbers (Schilder 1966, Ellis and Rosen 1980, Lavenda 1984).

In the small-k limit, which we shall refer to as the 'thermodynamic' limit (Lavenda and Santamato 1982), it is more informative to take the thermal fluctuations into account implicitly rather than explicitly solving the stochastic differential equations (2.2) or their corresponding diffusion equations. In other words, we would like to obtain asymptotic estimates for the transition probability and stationary-limit distribution that are valid in the small-k limit. This has been accomplished by Wentzell and Freidlin (1970) who generalised the Gaussian fluctuation theory of Onsager and Machlup (1953) to the small-k limit (Lavenda and Santamato 1982). We now need a Markov chain description of the Onsager and Machlup theory.

The invariant probability measure of a Markov chain of events can be expressed in terms of the transition probabilities $p(i, j)$. A well known method for solving for the invariant measure is the maximal directed tree graph method developed by Kirchhoff (1847). Let L denote the set of indices $\{1, 2, \ldots, l\}$, each index corresponding to one of the compacta K_i. A maximal directed tree graph or $\{i\}$-graph consists of connecting the L vertices by arrows, $m \to n$, such that $m \neq n$ and $m \neq i$ with precisely one arrow coming from each vertex other than i and there are no closed graphs. Let us designate the entire set of $\{i\}$-graphs by $G\{i\}$ and its elements by the letter g. Kirchhoff's method expresses the invariant probability measure $\mu(i)$ of the ith vertex as the ratio of $\{i\}$-graphs to the total maximal directed tree graphs, namely

$$\mu(i) = \sum_{g \in G\{i\}} P(g) \Big/ \sum_i \sum_{g \in G\{i\}} P(g) \tag{2.3}$$

where $P(g)$ denotes the product $\Pi_{(m \to n) \in g}\, p(m, n)$ of individual transition probabilities, $p(m, n)$.

In the small-k limit Wentzell and Freidlin (1970) have estimated that the transition $m \to n$ over a long time T converges to 0 with a rate:

$$p(m, n) \asymp \exp[-(1/2k)\Omega(K_m, K_n)] \tag{2.4}$$

where $\asymp$ denotes a logarithmic equivalence as $k \downarrow 0$ and

$$\Omega(y, x) = \inf[\Omega_{0T}(\phi) \colon \phi_0 = y \text{ and } \phi_T = x], \tag{2.5}$$

provided that $y \in K_m$ and $x \in K_n$. For perturbations of the white noise type, the functional $\Omega_{0T}(\phi)$ coincides with the Onsager–Machlup functional:

$$\Omega_{0T}(\phi) = (1/2) \int_0^T \|\dot{\phi} - b(\phi)\|^2_{L^{-1}}\, \mathrm{d}t \tag{2.6}$$

over smooth functions ϕ that connect K_m to K_n on an arbitrarily long time interval T and $\| \cdot \|^2_{L^{-1}}$ denotes the quadratic form associated with the symmetric resistance matrix, L^{-1}.

The Onsager–Machlup function (2.5) has been referred to as a 'quasi-potential' by Freidlin and Wentzell (1984). Using this, they introduce the following equivalence relation: 'if y and x belong to the same compactum, $x \sim y$, then $\Omega(y, x) = \Omega(x, y) = 0$'. It is important to bear in mind that this equivalence relation is based on the asymptotic form of the dynamical flow (2.1), irrespective of the random thermal fluctuations. Moreover, the Onsager–Machlup function can take on values $0 \leqslant \Omega(K_m, K_n) \leqslant \infty$. If $\Omega(K_m, K_n) > 0$, then the compactum K_m is judged to be stable. It is unstable when

$\Omega(K_m, K_n) = 0$, implying that a transition to the stable compactum K_n occurs with probability 1. Alternatively, if K_m is stable and K_n unstable, then we set $\Omega(K_m, K_n) = \infty$. The property that the Onsager-Machlup function be positive definite will shortly be converted into a realisability condition for a graph.

In the $k\downarrow 0$ limit, we can therefore evaluate (2.3) with the aid of the probability estimate (2.4):

$$\mu(i) \asymp \sum_{g\in G\{i\}} \exp\left(-(1/2k) \sum_{(m\to n)\in g} \Omega(K_m, K_n)\right)\left[\sum_{g\in G} \exp\left(-(1/2k) \times \sum_{(m\to n)\in g} \Omega(K_m, K_n)\right)\right]^{-1}. \tag{2.7}$$

Now, on account of the smallness of Boltzmann's constant, the main contribution to the sums in (2.7) will come from that graph which renders the Onsager-Machlup function a minimum. In an analogous manner to the Gaussian case, we can replace the average

$$\sum_{g\in G\{i\}} \exp\left(-(1/2k) \sum_{(m\to n)\in g} \Omega(K_m, K_n)\right)$$

by its most probable value:

$$\exp\left(-(1/2k) \min_{g\in G\{i\}} \sum_{(m\to n)\in g} \Omega(K_m, K_n)\right) := \exp[-(1/2k)\mathbb{C}(K_i)] \tag{2.8}$$

in the limit as $k\downarrow 0$. As a result, the invariant probability measure can be estimated as:

$$\mu(i) \asymp \exp\{-(1/2k)[\mathbb{C}(K_i) - \min_i \mathbb{C}(K_i)]\} \tag{2.9}$$

in the limit as $k\downarrow 0$.

The single-step transition probabilities are estimated by the Wentzell and Freidlin expression (2.4) in the $k\downarrow 0$ limit. Since the process is Markov, the multi-step transition probabilities will simply be products of the individual transition probabilities (2.4). Now, in the $k\downarrow 0$ limit, Wentzell and Freidlin implicitly converted a maximal directed tree graph problem into a discrete optimisation problem by singling out some subset W of the state space chain such that the system will make a transition from some state $i \in L\setminus W$, which is the complement of W, to a state $j \in W$. Denote by $G_{ij}(W)$ the set of such W-graphs. The normalised multi-step transition probabilities can thus be expressed as:

$$\sum_{g\in G_{ij}(W)} P(g) \Big/ \sum_{g\in G} P(g) \asymp \exp\{-(1/2k)[\mathbb{C}(K_i, K_j) - \min_{i,j} \mathbb{C}(K_i, K_j)]\}$$

in the limit as $k\downarrow 0$ where $\mathbb{C}(K_i, K_j)$ is the correlational entropy:

$$\mathbb{C}(K_i, K_j) := \min_{g\in G_{ij}(W)} \sum_{(m\to n)\in g} \Omega(K_m, K_n). \tag{2.10}$$

The minimum of the correlational entropy (2.10) with respect to all initial states of transition gives us back the quantity defined in (2.8), namely,

$$\mathbb{C}(K_j) = \min_i \mathbb{C}(K_i, K_j). \tag{2.11}$$

In the thermodynamic limit, the Onsager-Machlup function can be decomposed into the difference between the 'thermodynamic' action, A, which is the time integral of the net rate of energy dissipation, and the difference in entropy between the end states of transition (Lavenda 1977, Lavenda and Santamato 1982):

$$\Omega(K_i, K_j) = A(K_i, K_j) - [S(K_j) - S(K_i)]. \tag{2.12}$$

In general, a difference in a function of state can always be extracted from the Onsager-Machlup function. However, in the general case of non-Gaussian fluctuations, the thermodynamic action loses its significance as being the time integral of the net rate of energy dissipation (cf Lavenda and Santamato 1981). According to the stability criteria given in terms of the Onsager-Machlup function, we have the realisability condition:

$$A(K_m, K_n) > S(K_n) - S(K_m) \tag{2.13}$$

for a transition from a stable compactum K_m to a compactum K_n. The realisability condition (2.13) states that the weight of an edge, $A(K_m, K_n)$ cannot be inferior to the entropy difference, $S(K_n) - S(K_m)$, of the two vertices which it connects. The additional entropy, implied by inequality (2.13) is generated by the statistical correlations between the two vertices. As $T \to \infty$, all physically realisable processes tend to 'forget' their past; in other words, the statistical correlations between the two states wear off in a sufficiently long interval of time. This leads to the interpretation of the correlational entropy (2.10) as the largest amount by which the thermodynamic action, or the time integral of the net rate of energy dissipation, can be decreased in a W-graph, (i.e. with fixed endpoints of transition), without violating the realisability condition (2.13).

The thermodynamic action can now be shown to satisfy a classical Hamilton-Jacobi equation. To this end, let us assume that the drift field admits the orthogonal decomposition:

$$b(x) = L(\partial S/\partial x) + v(x) \tag{2.14}$$

where the non-conservative vector field, v, satisfies the orthogonality condition (Wentzell and Freidlin 1970)

$$v(\partial S/\partial x) = 0. \tag{2.15}$$

Since the transition probability (2.4) satisfies the Fokker-Planck equation to leading order in k, the decomposition of the Onsager-Machlup function (2.12) implies that the thermodynamic action will satisfy the *classical* Hamilton-Jacobi equation:

$$\partial A(K_i, x)/\partial T + \tfrac{1}{2}\|\partial A(K_i, x)/\partial x + B\|_L^2 - \Psi(x) = 0 \tag{2.16}$$

where the non-conservative external force field $B = (L^{-1})v$ and Ψ is known as the 'generating' function (Landau and Lifschitz 1969):

$$\Psi(x) = \tfrac{1}{2}\|b(x)\|^2_{L^{-1}}, \tag{2.17}$$

which is a state-dependent dissipation function (Onsager and Machlup 1953, Lavenda 1978). The continuous variable x assumes values *only* in the domain of attraction of the stable compactum, K_i. As $T \to \infty$, the thermodynamic action tends to a stationary value which is the solution of the time-independent equation:

$$\tfrac{1}{2}\|\partial A(K_i, x)/\partial x + B(x)\|_L^2 - \Psi(x) = 0. \tag{2.18}$$

In the asymptotic time limit, the statistical correlations between the two states have had ample time to have worn off. This is confirmed by the solution:

$$A^\circ(K_i, x) = S(K_i) - S(x) \tag{2.19}$$

to the time-independent Hamilton-Jacobi equation (2.18). On the strength of the decomposition of the Onsager-Machlup function (2.12), the asymptotic solution (2.19) implies that the correlational entropy (2.10) reduces to:

$$\mathbb{C}^{\circ}(K_i, x) = 2[S(K_i) - S(x)] \tag{2.20}$$

in the asymptotic time limit. We shall refer to (2.20) as the 'static' correlational entropy in order to distinguish it from the 'dynamic' correlational entropy (2.10) which accounts for the statistical correlations between states of the Markov chain that are not well separated in time. In the next section, we shall show that it is the correlational entropy and not the entropy in the general case that determines the state in which the invariant probability measure tends to concentrate in the thermodynamic limit.

3. Multistationary state evolutionary criteria

We shall consider an example in one dimension which follows Freidlin and Wentzell (1984). The reason for considering the one-dimensional case is that it allows an explicit calculation to be made. In the one-dimensional case, the non-conservative velocity field is superfluous and it suffices to consider the case where the entropy is the potential for the drift, *b*.

Suppose that the entropy curve has the form shown in figure 1 where the units are entirely arbitrary. States 1, 3, 5 correspond to relative maxima in the entropy, corresponding to stable compacta. In addition, state 5 is allowed to 'communicate' with state 1 directly since the manifold consisting of the interval 0 to 6 is closed into a circle (Freidlin and Wentzell 1984).

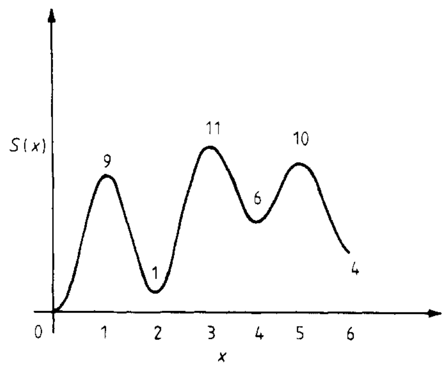

Figure 1.

If we were to ask where the invariant probability measure tends to concentrate in the limit as $k\downarrow 0$, the maximum entropy formulation would indicate state 3 since it corresponds to the *absolute* maximum of the entropy. We now show that this example contradicts this conclusion and in the following example show why it does.

The minima of the correlational entropy are determined by the minimisation of the correlational entropy (2.10) with respect to the initial state of the transition. This will give us the minimal correlational entropy (2.11) which determines the invariant probability measure according to (2.9) in the limit as $k\downarrow 0$. The curve $\mathbb{C}(x)$ in each of the domains of attraction of the stable stationary states is the sum of the dynamic correlational entropy for the transition to the stationary state and the static correlational entropy (2.20) for a spontaneous fluctuation to other states x in its domain of attraction, namely,

$$\mathbb{C}(x) = \min_i \mathbb{C}(K_i, K_j) + \mathbb{C}^\circ(K_j, x) \tag{3.1}$$

where x assumes values in the domain of attraction of the stable compactum K_j. In other words, the static correlational entropy is related to the probability of a spontaneous fluctuation from the stationary state which cannot occur along a trajectory of the deterministic motion (2.1). The relation between $\mathbb{C}^\circ(x)$ and Einstein's formula for the probability of a spontaneous fluctuation from a non-equilibrium stationary state in terms of the entropy decrease should be appreciated. The graphs which have the minimal correlational entropies for the stable stationary states 1, 3, and 5 have a rectangle drawn around them in figure 2. The minimal correlational entropies for these states are $\mathbb{C}(1) = 18$, $\mathbb{C}(3) = 24$, and $\mathbb{C}(5) = 28$. Subtracting from (3.1) its minimum, namely $\min_i \mathbb{C}(K_i) = \mathbb{C}(1)$, and calling this normalised quantity $\mathbb{C}^*(x)$ (i.e., normalisation with regard to the expression for the invariant probability distribution (2.9)), we find that:

$$\mathbb{C}^*(x) = 18 - 2S(x) \qquad \text{for } 0 \leq x \leq 2$$

$$\mathbb{C}^*(x) = 28 - 2S(x) \qquad \text{for } 2 < x \leq 4$$

$$\mathbb{C}^*(x) = 30 - 2S(x) \qquad \text{for } 4 < x \leq 6.$$

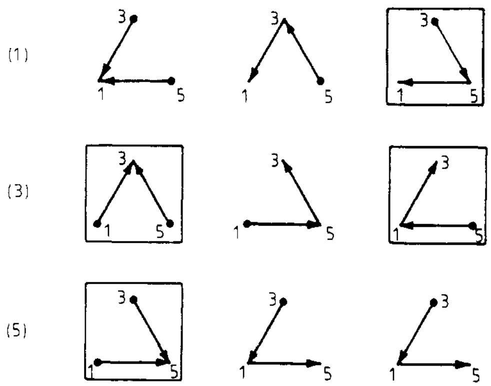

Figure 2.

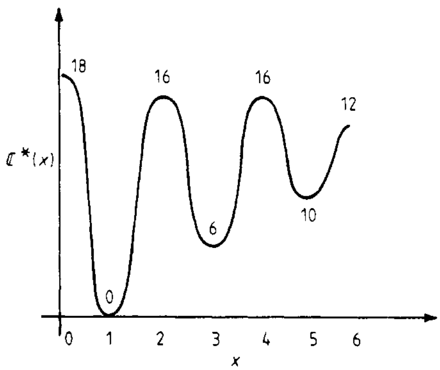

Figure 3.

The curve $\mathbb{C}^*(x)$, in figure 3, shows the unexpected and surprising fact that the absolute minimum of $\mathbb{C}^*(x)$ coincides with state 1 rather than state 3 which is the absolute maximum of the entropy. Apart from the fact that the height of the barrier which separates any two stable stationary states is determined by the statistical correlations and thermodynamics cannot tell us how high the barrier is, the example violates the principle of microscopic reversibility:

$$p(i, j)\mu(i) = p(j, i)\mu(j) \tag{3.2}$$

for the transitions $1 \leftrightarrow 5$.

In the limit as $k\downarrow 0$, the principle of microscopic reversibility (3.2) can be stated as:

$$A(K_i, K_j) - A(K_j, K_i) + 2[S(K_i) - S(K_j)] = \mathbb{C}(K_j) - \mathbb{C}(K_i) \tag{3.3}$$

where we have made use of (2.4), (2.9), and (2.12). The question is under what condition will (3.3) be valid. The principle of microscopic reversibility states that, under equilibrium conditions, any molecular process and the reverse of that process will be taking place on average at the same rate (Tolman 1938). To see what this implies, let us consider the corresponding continuous diffusion process. Let ϕ_t denote an arbitrary path on the time interval $[T_1 \leq t \leq T_2]$ and let ϕ_t^* be the reverse of this path on the interval $[-T_2 \leq t \leq -T_1]$. On the one hand, the thermodynamic action along the forward path ϕ_t of the motion is:

$$A_{T_1 T_2}(\phi) = \int_{T_1}^{T_2} [\mathcal{O}(\dot{\phi}_t) + \Psi(\phi_t) - B\dot{\phi}_t]\,\mathrm{d}t \tag{3.4}$$

where $\mathcal{O}(\dot{\phi}_t) = \frac{1}{2}\|\dot{\phi}_t\|^2_{L^{-1}}$ is the Rayleigh-Onsager dissipation function which is a homogeneous second-order function of the velocities. The last term in (3.4) is the net rate of working of the external forces, $\Pi := B\dot{\phi}_t$. On the other hand, along the time reversal path ϕ^*_{-t} we have:

$$A_{-T_2 -T_1}(\phi^*) = \int_{-T_2}^{-T_1} [\mathcal{O}(\dot{\phi}_t^*) + \Psi(\phi_t^*) - B\dot{\phi}_t^*]\,\mathrm{d}t$$

$$= \int_{T_1}^{T_2} [\mathcal{O}(\dot{\phi}_t) + \Psi(\phi_t) + B\dot{\phi}_t]\,\mathrm{d}t. \tag{3.5}$$

Only in the case where the non-conservative force field vanishes will

$$A_{T_1 T_2}(\phi) = A_{-T_2 -T_1}(\phi^*) \qquad (B \equiv 0) \tag{3.6}$$

hold or in terms of our discrete Markov chain:

$$A(K_i, K_j) = A(K_j, K_i). \tag{3.7}$$

This implies that the condition for microscopic reversibility (3.3) is really given by:

$$\mathbb{C}(K_j) - \mathbb{C}(K_i) = 2[S(K_i) - S(K_j)]. \tag{3.8}$$

Provided this condition holds, we have

$$\mu(i)/\mu(j) \asymp \exp\{(1/k)[S(K_i) - S(K_j)]\}, \tag{3.9}$$

showing that the invariant probability measure tends to concentrate on the absolute maximum of the entropy in the thermodynamic limit as $k\downarrow 0$. The relaxation time τ_{ji} for the transition $j \to i$ is:

$$\tau_{ji} \asymp \exp\{(1/k)[S(K_j) - S(K_i)]\}. \tag{3.10}$$

We can verify the foregoing result by allowing the entropy of state 6 in our example tend to zero so that states 0 and 6 become identical, as shown in figure 4. The maximal directed graphs which minimise the correlational entropy are shown in figure 5. The normalised minimal correlational entropy curve,

$$\mathbb{C}^*(x) = 22 - 2S(x) \qquad \text{for } 0 \leq x \leq 6$$

in figure 6, shows that the principle of minimal correlational entropy coincides with

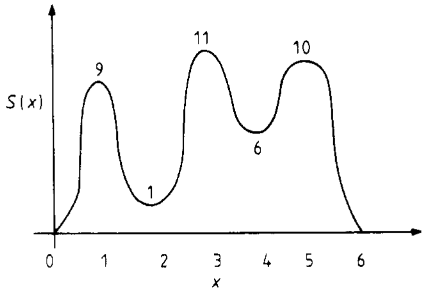

Figure 4.

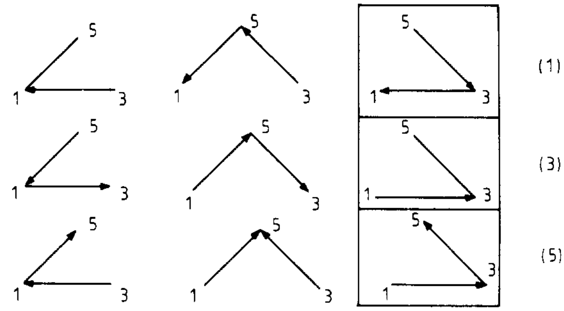

Figure 5.

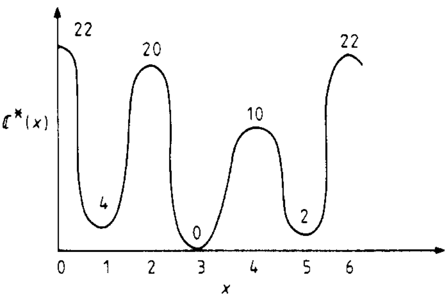

Figure 6.

maximum entropy in predicting that the invariant probability measure tends to concentrate in state 3.

Therefore, the principle of minimal correlational entropy will give the same prediction as the maximum entropy formulation only when microscopic reversibility holds and the non-conservative force field B vanishes identically. In our one-dimensional case, the 'discontinuity' in the end conditions, in figure 1, actually leads to a breakdown in microscopic reversibility which would occur in a multi-dimensional case in the presence of an external, non-conservative force field. In both cases, the principle of minimal correlational entropy gives the correct results whereas only in the potential case, where the microscopic reversibility holds, do the two coincide.

4. The principle of minimum dissipation of energy

With the decreasing size of Boltzmann's constant, the correlational entropy must likewise diminish so that in the limit as $k \downarrow 0$, the phenomenological laws of non-equilibrium thermodynamics emerge. In this limit, the set of $G_{ij}(W)$ of W-graphs shrinks to a single 'critical' graph consisting of a single, unstable transition from one compactum, K_i, to another, K_j, where the system will remain for ever after. The transition is unstable since $\Omega(K_i, K_j)$ vanishes and hence will occur with probability 1. The critical graph corresponds to the most probable behaviour which is governed by the macroscopic rate equations (2.1) and therefore lies beyond the domain of validity of the Markov chain description. The 'freezing-in' of the system into a stable compactum, K_j, is a manifestation of the diminished importance of random thermal fluctuations in creating a diffusion 'against the flow'. In contrast to our perspective in § 2, where we have given the system ample time to evolve to within any arbitrary small neighbourhood of the stationary state which became our initial condition, we now consider the system to be initially perturbed from a given stationary state. The asymptotic behaviour is again determined by the stationary value of the thermodynamic action which is the solution to equation (2.18). Since we are considering the relaxation of the system to the given stationary state, we find that the asymptotic form of the thermodynamic action will be given by the entropy difference of the final and initial stationary states. The static correlational entropy vanishes and we regain the thermodynamic evolutionary criterion based on the entropy difference of the two stationary states.

For the proof of these statements, it suffices to consider the Onsager-Machlup approximation for the corresponding Markov diffusion process. On the strength of the orthogonal decomposition of the drift, (2.14), the Onsager-Machlup functional can be written as (cf (3.4)):

$$\Omega_{0T}(\phi) = \int_0^T [L(\phi_t, \dot{\phi}_t) - \dot{S}(\dot{\phi}_t)]\, \mathrm{d}t \tag{4.1}$$

where the thermodynamic Lagrangian

$$L(\phi, \dot{\phi}) = \varnothing(\dot{\phi}) + \Psi(\phi) - \Pi(\dot{\phi}) \tag{4.2}$$

is the net rate of energy dissipation in the system. By virtue of the fact that Ω is positive semi-definite,

$$L(\phi, \dot{\phi}) \geqslant \dot{S}(\dot{\phi}) \tag{4.3}$$

which is our 'realisability' condition in the continuous limit. In contrast to inequality (2.13), we now have the possibility for an equality without violating the stability properties. In other words, in the thermodynamic limit, the vanishing of the Onsager-Machlup functional is not related to an instability criterion.

In the thermodynamic limit, the principle of minimal correlational entropy transforms into the *unconstrained* principle of least dissipation of energy (Lavenda 1978):

$$\mathbb{D}(\dot{\phi}) = \min_{\phi}[L(\phi, \dot{\phi}) - \dot{S}(\dot{\phi})]. \tag{4.4}$$

In contrast to the discrete, *global* variational principle (2.10), the continuous, *local* variational principle (4.4) employs the thermodynamic convention of varying the velocities for a fixed configuration of the system (Onsager 1931). In terms of an analogy with graph theory, we can say that whereas (2.10) is analogous to a 'shortest path' problem, (4.4) is analogous to an 'extremum flow' problem in network theory for which inequality (4.3) acts as the 'capacity' constraint (cf Bondy and Murty 1977).

The minimum dissipation of energy occurs along path $\hat{\phi}$ which is a solution of the non-equilibrium phenomenological equations:

$$L^{-1}[\hat{\phi}_t - v] = (\partial S / \partial \hat{\phi}). \tag{4.5}$$

The inner product of (4.5) with the velocity vector, $\dot{\hat{\phi}}$, gives the thermodynamic power relation:

$$2\varnothing(\dot{\hat{\phi}}) - \Pi(\dot{\hat{\phi}}) = \dot{S}(\dot{\hat{\phi}}). \tag{4.6}$$

In addition, the sum of the inner products of (4.5) and the orthogonal components of the drift vector is:

$$2\Psi(\hat{\not{o}}) - \Pi(\hat{\not{o}}) = \dot{S}(\dot{\hat{\not{o}}}). \tag{4.7}$$

Upon comparing the two power relations, we obtain:

$$\varnothing(\hat{\not{o}}) = \Psi(\hat{\not{o}}) \tag{4.8}$$

which is the *dissipation balance* condition that determines a family of optimal paths subject to given boundary conditions (Lavenda and Santamato 1982). Introducing the optimal path $\hat{\not{o}}$ into the principle of minimum dissipation of energy, (4.4), we find

$$\mathbb{D}(\dot{\hat{\not{o}}}) = 0 \tag{4.9}$$

and on account of (4.3), this is its absolute minimum.

The optimal path $\hat{\not{o}}$ is, in addition, characterised by a vanishing correlational entropy. The Onsager–Machlup functional

$$\Omega_{0T}(\not{o}) = A_{0T}(\not{o}) - [S(\not{o}_T) - S(\not{o}_0)] \tag{4.10}$$

vanishes along $\hat{\not{o}}$ since the dissipation balance condition (4.8) and the thermodynamic power relation (4.6) imply that the action functional reduces to a difference in a function of state, namely,

$$\begin{aligned} A_{0T}(\hat{\not{o}}) &= \int_0^T [2\varnothing(\dot{\hat{\not{o}}}_t) - \Pi(\dot{\hat{\not{o}}}_t)]\,\mathrm{d}t \\ &= S(\not{o}_T) - S(\not{o}_0). \end{aligned} \tag{4.11}$$

This, in turn, implies that the correlational entropy (2.10) vanishes since

$$\min_{g \in G_{ij}(\hat{W})} \sum_{(m \to n) \in g} A(K_m, K_n) = S(K_j) - S(K_i) \tag{4.12}$$

for the critical graph $\hat{W}$. This critical graph can now be appreciated as the discrete state space analogue of the optimal path $\hat{\not{o}}$ for the regression of a fluctuation. It is 'critical' insofar as it violates the realisability condition (2.13). Yet, we must bear in mind that we are at the limits of a probabilistic theory where 'most probable' events become 'certain' events. The evolutionary criterion reduces to determining the entropy differences of the stationary states in the absence of a non-conservative force field B. In fact, in the presence of small thermal fluctuations, which drive the system out of any bounded domain in a long enough period of time, the principle of minimal correlational entropy reduces to a minimum relative entropy principle for stochastic exit when $B \equiv 0$.

5. The minimum relative entropy principle for stochastic exit

We can now approach the problem of stochastic exit from our time reversal Markov chain description which is valid for systems in which microscopic reversibility holds. It is now assumed that the system has had ample time to have evolved to within an arbitrarily small domain of one of a finite number of stable compacta, $K_1, K_2, \ldots, K_l$. The presence of unstable compacta will not alter our results since they can only increase the thermodynamic action or, at least, leave it unchanged.

Suppose that several of the compacta are found in a domain D with a smooth boundary ∂D which we assume does not intersect with any of the compacta in D. Now, the system cannot leave D along any trajectory of the dynamical flow (2.1) since

$$b(y)\cdot n(y)<0 \qquad \text{for all } y\in\partial D \tag{5.1}$$

where n is the outward normal to ∂D. Nevertheless, on account of small thermal fluctuations, the system will leave any bounded domain containing a multiplicity of stationary states sooner or later. In the thermodynamic limit, this will occur in the most likely way. The problem we are faced with is to determine the most likely path to the boundary and the place where exit is most likely to occur.

Evaluating the Onsager-Machlup functional on the reverse path:

$$\Omega_{-T_2-T_1}(\phi^*)=\int_{-T_2}^{-T_1}[L(\phi_t^*,\dot\phi_t^*)-\dot S(\dot\phi_t^*)]\,\mathrm{d}t \tag{5.2}$$

we find that it will be equal to

$$\int_{T_1}^{T_2}[L(\phi_t,\dot\phi_t)+\dot S(\dot\phi_t)]\,\mathrm{d}t \tag{5.3}$$

only when $\Pi\equiv 0$. The principle of least dissipation of energy for an optimal path of the reverse motion is

$$\mathbb{D}^*(\dot\phi)=\min_{\dot\phi}[L(\phi,\dot\phi)+\dot S(\dot\phi)] \tag{5.4}$$

which is the mirror image in time of the principle of least dissipation of energy for a path of the forward motion, (4.4). The extremum of the integrand in (5.2) occurs along the path $\tilde\phi$ which is a solution of:

$$L^{-1}\dot{\tilde\phi}=-(\partial S/\partial\tilde\phi) \qquad (v\equiv 0). \tag{5.5}$$

The inner product of (5.5) with the velocity vector gives the power relation:

$$2\Phi(\dot{\tilde\phi})=-\dot S(\dot{\tilde\phi})\geqslant 0 \tag{5.6}$$

where the inequality follows from the positive semidefiniteness of the dissipation function Φ. Hence, the laws of non-equilibrium thermodynamics predict a negative entropy production along $\tilde\phi$. In the presence of small thermal fluctuations, this should be interpreted in a *probabilistic* sense in that such types of the motion are highly improbable. Yet, the path $\tilde\phi$ will be less improbable than other paths.

The extremal path $\tilde\phi$ satisfies the dissipation balance relation (4.8). Along this path, the dissipative energy flow (5.4) vanishes and this, in turn, implies that the Onsager-Machlup functional (5.3) vanishes. Also, because it is positive semidefinite,

$$\Omega_{T_1T_2}(\phi)\geqslant 2[S(\phi_{T_1})-S(\phi_{T_2})]=\Omega_{T_1T_2}(\tilde\phi). \tag{5.7}$$

The symmetry in the most probable paths for forward and reverse motions, in the thermodynamic limit, is now apparent: along the optimal path $\hat\phi$ the Onsager-Machlup functional for the forward motion vanishes and

$$\Omega_{-T_2-T_1}(\phi^*)\geqslant 2[S(\phi_{-T_2})-S(\phi_{-T_1})]=\Omega_{-T_2-T_1}(\hat\phi) \tag{5.8}$$

while along its mirror image in time, $\tilde\phi$, the Onsager-Machlup functional for the reverse motion vanishes and (5.7) applies.

The system must have surely been at some stationary state in some distant time in the past. Suppose that for $T_1 \to -\infty$, the system is found in compactum K_i and a trajectory is launched at some point $x \in K_i$. Denote by $i(x)$ the index of the compactum and let l denote the set of all indices of the (stable) compactum in D. Suppose that there exists a unique state $y_i \in \partial D$ for each $i \in l$ such that:

$$\Omega(x, y) = \min_{y \in \partial D} A(x, y) + S(x) - \max_{y \in \partial D} S(y) \qquad (x \in K_i), \tag{5.9}$$

then this state will possess maximum entropy. This constitutes a minimum relative entropy principle for stochastic exit. Along the extremal path:

$$\min_{y \in \partial D} A(x, y) = S(x) - \max_{y \in \partial D} S(y) \tag{5.10}$$

and the Onsager–Machlup function reduces to twice the minimum entropy difference. Let us now consider this in greater detail.

We now enlarge the index set L to include points ∂ on the boundary. A ∂-graph consists of a sequence of arrows leading from any stable compactum to a state ∂ on the boundary. The minimal correlational entropy is (cf (2.10)):

$$\mathbb{C}(x, \partial) = \min_{g \in G_i\{\partial\}} \sum_{(m \to n) \in g} \Omega(K_m, K_n) \qquad (x \in K_i), \tag{5.11}$$

where $G_i\{\partial\}$ is the set of ∂-graphs which start in compactum K_i. Since the system must overcome the dynamical flow to reach the boundary, the entropy on the boundary cannot be greater than the entropy of compactum K_i. Consequently, there is no realisability condition for ∂-graphs. In other words, ∂-graphs do not fall in the domain of validity of non-equilibrium thermodynamics since there is no deterministic lower bound to the energetics of the process. In fact, the macroscopic laws negate the possibility of such a process occurring.

The absolute minimum of the sum in (5.11) occurs along the critical $\tilde{\partial}$-graph. This critical $\tilde{\partial}$-graph is the discrete state space analogue of the optimal path $\tilde{\phi}$. The $\tilde{\partial}$-graph has a minimal correlation entropy which is twice the minimum entropy difference:

$$\mathbb{C}(x, \tilde{\partial}) = 2[S(x) - \max_{y \in \partial D} S(y)] \qquad (x \in K_i). \tag{5.12}$$

It consists of a single, unstable transition from the state x, belonging to the stable compactum K_i, to the state of maximum entropy on the boundary. The minimisation of (5.12) with respect to the initial state gives (cf (2.11))

$$\mathbb{C}(\tilde{\partial}) = \min_{x} \mathbb{C}(x, \tilde{\partial}) \tag{5.13}$$

which in view of (2.8) shows that (5.12) is none other than Boltzmann's principle which determines the invariant probability measure in terms of the entropy difference.

The ∂-graphs for which

$$\min_{g \in G_i\{\partial\}} \sum_{(m \to n) \in g} A(K_m, K_n) \tag{5.14}$$

is attained are, with probability tending to 1 as $k \downarrow 0$, such that the last arrow, in the sequence of arrows leading from $i(x)$ to ∂, lies in a small neighbourhood of the state y_i that possesses maximum entropy. Furthermore, if we delete the last arrow, $j \to \partial$, we obtain a j-graph whose sum cannot be superior to (5.14):

$$\min_{g\in G_i\{\partial\}} \sum_{(m\to n)\in g} A(K_m, K_n) \geq \min_{g\in G_i\{j\}} \sum_{(m\to n)\in g} A(K_m, K_n). \tag{5.15}$$

Since the equality holds for the absolute minimum of (5.14), which is one-half the correlational entropy (5.12), and the right-hand side of (5.15) cannot be inferior to $[S(x)-S(K_j)]$, it follows that:

$$S(K_j) \geq \max_{y\in\partial D} S(y). \tag{5.16}$$

Since this inequality must be true for all j, we conclude that the system will not make trips to neighbourhoods of those compacta which have an entropy strictly inferior to the maximum entropy on the boundary in the limit as $k\downarrow 0$.

In conclusion, we consider the case where there is no unique state on the boundary with maximum entropy and/or where there is more than one distinguished ∂-graph which minimises the correlational entropy. Let $J(i)$ denote the set of all states j in the final transition to the boundary, $j\to\partial$. It is apparent that by deleting this last arrow and replacing it by $j\to k\to\partial$, we cannot obtain a sum less than (5.14) since according to the triangle inequality we have:

$$A(K_j, K_k) + A(K_k, \partial) \geq A(K_j, \partial). \tag{5.17}$$

The only way that the sum cannot exceed the original one is when the equality holds. For then the existence of such a minimising ∂-graph would mean that $k\in J(i)$. This requires us to replace the single state of maximum entropy by the set $\bigcup_{j\in J(i)} \partial_j$ which possesses maximum entropy. In fact, Wentzell and Freidlin (1970) prove that the trajectory of the process, which is launched from any point $x\in D$, will reach the boundary in a small neighbourhood of the set $\bigcup_{j\in J(i)} \partial_j$ with a probability tending to one as $k\downarrow 0$. We have shown that this set is characterised by maximum entropy provided microscopic reversibility holds. This then constitutes a minimum relative entropy difference for stochastic exit when there is not a unique state of maximum entropy on the boundary.

References

Bondy J A and Murty U S R 1977 *Graph Theory with Applications* (London: Macmillan)
Ellis R S and Rosen J S 1980 *Bull. Am. Math. Soc.* **3** 705
Freidlin M I and Wentzell A D 1984 *Random Perturbations of Dynamical Systems* (New York: Springer)
Kirchhoff G 1847 *Ann. Phys. Chem.* **72** 497
Landau L D and Lifshitz E M 1969 *Statistical Physics* (Oxford: Pergamon)
Landsberg P T and Tranah D 1980a *Collect. Phenom.* **3** 73
—— 1980b *Phys. Lett.* **78A** 219
Lavenda B H 1977 *Riv. Nuovo Cimento* **7** 229
—— 1978 *Thermodynamics of Irreversible Processes* (London: Macmillan)
Lavenda B H 1984 *J. Phys. A: Math. Gen.* **17** 3353
Lavenda B H and Santamato E 1981 *J. Math. Phys.* **22** 2926
—— 1982 *J. Stat. Phys.* **29** 345
Nemytskii V V and Stepanov V V 1960 *Qualitative Theory of Differential Equations* (Princeton, NJ: Princeton University Press)
Onsager L 1931 *Phys. Rev.* **37** 405
Onsager L and Machlup S 1953 *Phys. Rev.* **91** 1505
Schilder M 1966 *Trans. Am. Math. Soc.* **125** 63
Tolman R 1938 *The Principles of Satistical Mechanics* (London: OUP)
Wentzell A D and Freidlin 1970 *Russ. Math. Surv.* **25** 1