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On the persistence of irreversible processes under the influence of random thermal fluctuations

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Abstract. A thermodynamic criterion for the persistence of an irreversible process is derived from the method of associative distributions applied to the probability of large deviations in stochastic processes. Paths of relative maximum likelihood are determined from the condition that the distribution and associated distribution be non-defective. The latter predicts the threshold value of the noise strength and the paths are mirror images in time of one another. Based on the analogy with the central limit theorem and the method of associated distributions, the technique is used to estimate the error in approximating the actual distribution by one that is obtained in the diffusion limit, analogous to the normal distribution, for large deviations. The maximum power of the deviation is discussed in terms of the fractal dimension.

1. Introduction

Regardless of how small random thermal fluctuations may be, their cumulative effects over long time intervals will eventually cause an irreversible process to leave the domain of attraction of a stable equilibrium or stationary state. The fact that the expected time of exit is finite means that the system will almost certainly leave the domain of attraction of the time-independent state. The deterministic concept of stability no longer makes any sense and it must be replaced by some stochastic notion of 'persistence' of an irreversible thermodynamic process (Ludwig 1975). The aim of this paper is to obtain a thermodynamic criterion of persistency based on the method of associated distributions which is commonly used in the analysis of large deviations of sums of independent random variables (Feller 1971).

The problem may appear superficially to be related to the problem of delineating the range of validity of the principle of minimum entropy production (Prigogine 1949, Denbeigh 1952, Klein and Meijer 1954, Klein 1955). This principle asserts that the stationary state of a system in which an irreversible process occurs is that state for which the rate of entropy production has its minimum value, compatible with the external constraints which prevent the system from relaxing back to equilibrium (Prigogine 1947, de Groot 1951). Apart from the fact that the principle is known not to apply to stationary states far from equilibrium (Klein 1958), the entire perspective in associating a 'maximum persistency' criterion with a stationary criterion of 'minimum entropy production' (Kikuchi 1961, Kikuchi and Gottlieb 1961) is contorted. For small thermal fluctuations, there is an overwhelming probability that an irreversible process

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which is displaced from its stationary state will tend to evolve to it in the course of time. There it will spend the greater part of its time, making only rare excursions to neighbouring states. However small such probabilities may be, they may ultimately govern the evolution of the irreversible process over long time intervals (Wentzell and Freidlin 1970, Lavenda 1985a). Therefore the concept of persistency must be related to the probability of large deviations and, being a statistical concept, it cannot be defined within the framework of the macroscopic thermodynamics of irreversible processes to which the principle of minimum entropy production is necessarily confined.

Denote by $\mathscr{F}_n$ the common distribution of a sequence of normalised sums, x, namely $\mathscr{F}_n(x) = P\{S_n/\sigma\sqrt{n} \leqslant x\}$ where $S_n = X_1 + X_2 + \ldots + X_n$, $n \geqslant 1$ and the X_j are independent (Bernoullian) random variables. For $n \to \infty$, $\mathscr{F}_n(x)$ tends to the normal distribution $\mathscr{R}(x)$. Although such information is useful for moderate values of x, it becomes an empty statement for large values of x since then both $\mathscr{F}_n(x)$ and $\mathscr{R}(x)$ are approximately unity. The proof that

$$[1 - \mathscr{F}_n(x)]/[1 - \mathscr{R}(x)] \to 1$$

as both x and n tend to infinity depends on whether the integral

$$E[\exp(sx)] < \infty$$

for all s in some interval $|s| < s^*$ (Feller 1971 and § 3). This is known as Cramér's condition (Cramér 1938) and the proof is based upon the method of associated distributions.

Such theorems on large deviations of independent and identically distributed random variables have been generalised to stochastic processes. Wentzell (1973, 1976) noticed that even when one is dealing with large deviations and improbable events, the major part of the realisations will occur within the immediate proximity of some well behaved function ϕ, and he obtained estimates of the form

$$P\{\rho[X(\cdot), \phi(\cdot)] < \delta\} > \exp\{-\Omega[\phi(\cdot)] - R[\delta, \phi(\cdot)]\}$$

for any $\delta > 0$, where ρ denotes the distance in the space of functions. Provided the remainder term R is small compared with the functional Ω, then the latter is a measure of the difficulty that the process has in passing close to the function ϕ. For diffusion processes, Ω is known as the Onsager-Machlup functional (Onsager and Machlup 1953, Lavenda 1985a). But can the diffusion approximation be used to determine the probabilities of large deviations? In this paper, we shall show that the diffusion approximation does not work for large deviations and we obtain an estimate for its validity. Nevertheless, there is an 'action' functional which can be used to determine the probabilities for large deviations.

2. The action functional for the two-level atom problem

We shall analyse the simple model of Klein (1958), who used it to show that the entropy production does not decrease monotonically with time in the approach to the stationary state, to derive the action functional and its relation to a persistency condition. Consider a system comprising N atoms which can be in either of two energy states, 0 or E. The system is placed in contact with a heat bath at temperature T and it can also absorb monochromatic radiation at a frequency $\nu = E/h$. The conversion of the radiation energy into thermal energy of the heat bath constitutes the irreversible process.

Denote by $p_u(t)$ and $p_l(t)$ the probabilities of finding an atom in the upper and lower states at time t, respectively, with the restriction $p_u(t)+p_l(t)=1$. An atom may make a transition between the two states by either absorbing or emitting a photon of energy E or by exchanging this energy with the heat bath. Let θ_r and θ_b be the quantum mechanical transition probabilities per unit time for the transition from the lower to the upper state due to radiation and the heat bath, respectively. Regarding the heat bath, the transition from upper to lower states will be more favourable than the reverse transition by a factor $\exp(E/T)$ in units where Boltzmann's constant is equal to unity.

If an atom is initially in the lower state, then three different kinds of events can occur in a small time Δt: an atom can remain in the lower state with probability $(1-\theta_l\Delta t)$ where $\theta_l=\theta_r+\theta_b$, or transitions to the upper state can take place with the *a priori* probabilities $\theta_r\Delta t$ and $\theta_b\Delta t$, due to radiative and thermal sources, respectively. The probability that out of Np_l atoms in the lower level at time t, NP_1 will remain there while NP_2 and NP_3 will jump to the upper level by absorbing radiation or thermal energy from the heat bath, respectively, is given by the well known multinomial expression (Kikuchi 1961)

$$\mathscr{P}_l\{P_i(t,\,t+\Delta t)\}=[(Np_l)!/(NP_1)!(NP_2)!(NP_3)!](1-\theta_l\Delta t)^{NP_1}(\theta_r\Delta t)^{NP_2}(\theta_b\Delta t)^{NP_3}. \tag{2.1}$$

The 'path' probability $\mathscr{P}_l$ is a function of the 'path' parameters $\{P_i\}$ for a given initial state p_l (Kikuchi 1961). It is a product of two factors: one factor gives the number of different possible paths which are consistent with the compatibility condition

$$p_l(t)=P_1+P_2+P_3$$

and the other factor is the *a priori* probability for an individual path which is characterised by the path parameters $\{P_i\}$.

In an entirely analogous way, we can construct the path probability $\mathscr{P}_u$ for transitions from the upper to the lower states. The transition probabilities from upper to lower states are $\theta_b\exp(E/T)\Delta t$ and $\theta_r\Delta t$, since downward transitions are more probable than upward transitions by a factor $\exp(E/T)$, when the transitions occur through the exchange of energy with the heat bath, while the transition probabilities due to the coupling to the radiation field are symmetric. The probability that an atom will remain in the upper state in a small time interval Δt is $(1-\theta_u\Delta t)$ where $\theta_u=\theta_r+\theta_b\exp(E/T)$. Out of Np_u events, the probability that these will occur NP_4, NP_5, and NP_6 times, respectively, is

$$\begin{aligned}\mathscr{P}_u\{P_i(t,\,t+\Delta t)\}&=[(Np_u)!/(NP_4)!(NP_5)!(NP_6)!]\\&\quad\times[\theta_b\exp(E/T)\Delta t]^{NP_4}(\theta_r\Delta t)^{NP_5}(1-\theta_u\Delta t)^{NP_6}\end{aligned} \tag{2.2}$$

subject to the restriction that

$$p_u(t)=P_4+P_5+P_6.$$

Since the path probabilities for upward, (2.1), and downward, (2.2), transitions are statistically independent of one another, their joint probability distribution is simply their product $\mathscr{P}=\mathscr{P}_l\mathscr{P}_u$ whose logarithm is

$$\begin{aligned}(1/N)\ln\mathscr{P}\{P_i(t,\,t+\Delta t)\}&=\sum_i p_i\ln p_i-\sum_i P_i\ln P_i+(P_3+P_4)\ln(\theta_b\Delta t)+(P_2+P_5)\ln(\theta_r\Delta t)\\&\quad+P_1\ln(1-\theta_l\Delta t)+P_6\ln(1-\theta_u\Delta t)+(E/T)P_4,\end{aligned} \tag{2.3}$$

for N sufficiently large to justify the use of Stirling's formula. In fact for N arbitrarily large, we expect a type of law of large numbers to hold similar to a central limit theorem. In the limit as $N \to \infty$, the path of maximum likelihood is obtained by maximising (2.3) with respect to the path parameters $\{P_i\}$ subject to the condition that the probability be conserved, which for the lower state reads

$$p_l(t+\Delta t) - p_l(t) = P_4 + P_5 - P_2 - P_3.$$

This procedure is entirely analogous to the derivation of the equilibrium Boltzmann distribution under the constraints that the energy and number of particles be conserved. Hence, the constraint can be introduced explicitly into the variational principle $\ln \mathcal{P}\{P_i(t, t+\Delta t)\} = \max$ by the method of Lagrange multipliers. In this way we obtain the expressions for the maximum values of the independent path parameters as

$$P_2^* = p_l \theta_r \Delta t \, e^s + O(\Delta t^2), \qquad P_3^* = p_l \theta_b \Delta t \, e^s + O(\Delta t^2),$$
$$P_4^* = p_u \theta_b \Delta t \, e^{(E/T-s)} + O(\Delta t^2), \qquad P_5^* = p_u \theta_r \Delta t \, e^{-s} + O(\Delta t^2),$$

where s is the Lagrange undetermined multiplier. In the derivation of the maximum independent path parameters, $\{P_i^*\}$, we have assumed that the dependent path parameters $P_1 \approx p_l$ and $P_6 \approx p_u$ since the time interval Δt is small. Moreover, their variations are related to the independent transition probabilities by $\delta P_1 = -(\delta P_2 + \delta P_3)$ and $\delta P_6 = -(\delta P_4 + \delta P_5)$ since p_l and p_u were held constant in the variation (Kikuchi 1960). Upon introducing these maximum transition probabilities into the original expression to be maximised, we obtain

$$(1/N) \ln \mathfrak{P}\{p(t), p(t+\Delta t)\} = -[s\dot{p}_u - H(s, p)]\Delta t + O(\Delta t^2) \tag{2.4}$$

where $H(s, p)$ is the Hamiltonian

$$H(s, p) = [r_l(e^s - 1) + r_u(e^{-s} - 1)] \tag{2.5}$$

with $r_j = p_j \theta_j$ and we have put

$$\dot{p}_u = (1/\Delta t)[p_u(t+\Delta t) - p_u(t)].$$

The probability $\mathfrak{P}\{p(t), p(t+\Delta t)\}$ is the maximum of the path probability on going from $\{p_i(t)\}$ to $\{p_i(t+\Delta t)\}$ in a short time interval Δt and it is a function of this time interval as well as the initial and final states of transition. By breaking up the small, but finite, time interval Δt into a sequence of subintervals, the right-hand side of (2.4) has the form of the negative of an action whose total time derivative is the Lagrangian

$$L(p, \dot{p}) = s\dot{p}_u - H(s, p). \tag{2.6}$$

This is the motivation for calling (2.5) a Hamiltonian since it is the Legendre transform of (2.6). In order to obtain a more symmetric form, we can write $s = s_u - s_l$ so that (2.6) becomes

$$L(p, \dot{p}) = (s, \dot{p}) - \{r_l[\exp(s_u - s_l) - 1] + r_u[\exp(s_l - s_u) - 1]\} \tag{2.7}$$

where $(s, \dot{p})$ denotes the scalar product $\Sigma_i s_i \dot{p}_i$.

Thus, beginning with the path probability, we have a succession of variational problems (Kikuchi 1961) which characterise the paths of maximum likelihood in the limit of an arbitrarily large number of systems, N. Maximising the path probability with respect to the path parameters, under the subsidiary condition that the probability be conserved, we have obtained the probability for the transition between initial and final states in a small time Δt along the path of maximum likelihood. Then, by using

the Markov property, we can divide the time interval into a finite number of subintervals and the variation of all intermediate states will give the equations of motion of the paths of maximum likelihood as well as a physical interpretation of the Lagrange multiplier, s. This procedure differs from the equilibrium statistical mechanical method of identifying the Lagrange multipliers through the association of average values with the thermodynamic values of the relevant physical quantities such as energy and work (cf Cox 1950). Therefore, it is the Markov property which allows us to formulate a path integral approach, and in the 'thermodynamic' limit as $N \to \infty$, the exact average values can be replaced by their most probable values.

In order to construct a path, we would consider a sequence of states $\{p_i(t)\}$, $\{p_i(t+\Delta t)\}$, $\{p_i(t+2\Delta t)\}, \ldots$, and integrate over all possible values of the intermediate states between the fixed endpoints of transition. This would lead us to the familiar path integral formulation of non-equilibrium statistical thermodynamics (Lavenda 1985a), except for the fact that we are considering the limit as $N \to \infty$ which allows us to replace average values by most probable values (Lavenda 1985b), since in the limit of weak thermal fluctuations the fluctuating paths tend to coalesce about the most probable path given by the macroscopic laws of irreversible thermodynamics. Hence, over arbitrary time intervals, expression (2.4) will generalise to (Kikuchi 1961, Wentzell and Freidlin 1970, Lavenda and Santamato 1982)

$$(1/N) \ln \mathfrak{P}\{p^{(0)}, p^{(n)}\} = -\left\{ \int_{t_0}^{t_n} [(s, \dot{p}) - H(s, p)] \, \mathrm{d}t \right\}_{\min} \tag{2.8}$$

as $N \to \infty$ subject to $p(t_0) = p^{(0)}$ and $p(t_n) = p^{(n)}$. In the Gaussian case, (2.8) was first derived by Onsager and Machlup (1953) by making use of the equivalence between means and modes of the distribution. We are thus led to minimise the functional in braces, subject to given end conditions, and this will provide a physical interpretation of the Lagrange multiplier, s.

The Hamilton equations for the functional in (2.8) are

$$\dot{p}_u = (\partial H/\partial s_u) = r_l \exp(s_u - s_l) - r_u \exp(s_l - s_u), \tag{2.9}$$

$$\dot{s}_u = -(\partial H/\partial p_u) = -\theta_u[\exp(s_l - s_u) - 1], \tag{2.10}$$

which are to be solved subject to the prescribed boundary conditions. Hamilton's equations furthermore imply that

$$(\mathrm{d}/\mathrm{d}t)H = \sum_i (\partial H/\partial s_i)\dot{s}_i + (\partial H/\partial p_i)\dot{p}_i = 0 \tag{2.11}$$

which means that H is a constant of the motion. It would then follow that any $H =$ constant would be acceptable. However, we will now show that $H = 0$ is the only physically acceptable solution which determines two paths of maximum likelihood.

3. Criterion of persistency

Let us turn our attention to what may appear to be a completely unrelated problem. In problems related to random walk and renewal theory it sometimes turns out that a distribution may be defective. If $\mathscr{F}$ is a defective distribution then $\mathscr{F}(\infty) < 1$ and the defect $q = 1 - \mathscr{F}(\infty)$ is the probability of termination before the process can be renewed.

In such a case one introduces the assumption (Feller 1971) that there exists a number s^* such that

$$\int_{-\infty}^{\infty} \exp[(s^*, \beta)]\mathcal{F}(d\beta) = 1. \tag{3.1}$$

A proper distribution

$$\mathcal{F}^{\#}(d\beta) = e^{(s^*,\beta)}\mathcal{F}(d\beta), \tag{3.2}$$

can be defined if there exists a real root to the integral equation (3.1). Stochastic processes generated by $\mathcal{F}^{\#}$ and $\mathcal{F}$ are said to be 'associated' with each other. Suppose that the integral

$$f(s) = \int_{-\infty}^{\infty} e^{(s,\beta)}\mathcal{F}(d\beta) \tag{3.3}$$

exists for $0 \leqslant s \leqslant s^*$. In this interval f is differentiable, and since its second derivative is positive, f is a convex function. So too will be its logarithm

$$H(s) := \ln f(s) = \ln E\{\exp[(s, \beta)]\}. \tag{3.4}$$

To make contact with our preceding development, we identify the function $H(s)$ in (3.4). Consider two independent random impulse processes, β_u and β_l, which have a bivariate Poisson distribution

$$P\{\beta_u = k, \beta_l = j\} = [e^{-r_u}(r_u)^k/k!][e^{-r_l}(r_l)^j/j!] \tag{3.5}$$

with average rates r_u and r_l, respectively. (Note that the intensity parameters are $r_i\Delta t$ rather than r_i. Since the moments are all proportional to Δt, this would have the effect of multiplying the left-hand side of (3.4) by Δt. We shall come back to this point in § 4.) Thus, the expectation in (3.4) is

$$E\{e^{(s,\beta)}\} = \exp[-(r_u + r_l)]\sum_{k,j}[(e^{s_l}r_l)^j/j!][(e^{s_u}r_u)^k/k!]. \tag{3.6}$$

Furthermore, if the strengths, s_u and s_l, are equal in magnitude and opposite in sign, namely, $s_l = -s_u := s$, then (3.6) simplifies to

$$E\{e^{(s,\beta)}\} = e^{H(s)} \tag{3.7}$$

where $H(s)$ is precisely the Hamiltonian given in (2.5).

Since $\mathcal{F}$ itself is a bona fide distribution, a process with vanishing strength

$$s^{\pm} = 0 \tag{3.8}$$

renders $H(0) = 0$ and the first of Hamilton's equations, (2.9), reduces to the deterministic rate equation

$$\dot{p}_u^{\pm}(t) = r_l^{\pm} - r_u^{\pm}. \tag{3.9}$$

The causal or 'thermodynamic' path $p^{\pm}(t)$, which is the solution of (3.9), is absolutely the most probable one since

$$\mathfrak{P}^{\pm}[p^{(0)}, p^{(n)}] = 1 \tag{3.10}$$

for $N \to \infty$. It is not surprising that the causal path arises in the limit where the strength of the noise source vanishes. The causal path maximises absolutely the probability distribution.

Considering the (convex) function $H(s)$, rather than the functional in (2.8), we can apply a Legendre transform (Gelfand and Fomin 1963)

$$L(\beta) = \sup_s \{(s, \beta) - H(s)\} \tag{3.11}$$

to obtain the conjugate function $L(\beta)$ which is of the same class as H. Since $(\partial H/\partial s_i) = \beta_i$, we have that for the particular choice $s = s^\dagger$, the random impulse processes β_i coincide with the deterministic rates of transitions.

The novel and interesting point is that even though the distribution $\mathscr{F}$ is a proper distribution, the associated distribution $\mathscr{F}^\#$ can also be a proper distribution for $s \neq 0$. Indeed for

$$s^* = \ln(r_u/r_l) \tag{3.12}$$

$H(s^*) = H(s^\dagger) = 0$ and $f(s^*) = 1$ which implies that the associated distribution $\mathscr{F}^\#$ is a proper distribution. Now since $H(s)$ is convex and $(\partial H/\partial s)|_{s=s^*}$ exists, it follows that $(\partial H/\partial s)$ will have opposite signs at $s = 0$ and $s = s^*$. From the first of Hamilton's equations, (2.9), we conclude that the two random processes induced by $\mathscr{F}$ and $\mathscr{F}^\#$ will have drifts in opposite directions.

The critical strength s^* of the random process satisfies both of Hamilton's equations of motion (2.9),

$$\dot{p}_u^*(t) = r_u^* - r_l^* \tag{3.13}$$

and (2.10). We can appreciate equation (3.13) as the mirror image in time of the causal equation of motion (3.9). The path $p^*(t)$ is therefore referred to as the anticausal or 'antithermodynamic' path and it is also a path of maximum likelihood (Lavenda and Santamato 1982, Lavenda 1985b). The novel point here is that this path is the result of a critical or threshold value of the strength of the underlying noise process. Although s can take on values between 0 and s^*, it is only the latter value of the noise strength which generates a path of relative maximum likelihood and whose drift is opposite to that of the absolutely most probable path. In other words, only these processes are generated by proper distributions: the original distribution, $\mathscr{F}$, and its associated one, $\mathscr{F}^\#$.

Since $H(s^*) = 0$, the Lagrangian (2.7) simplifies to

$$\begin{aligned} L[p^*(t), \dot{p}^*(t)] &= \sum_i \dot{p}_i^*(t) \ln r_i^* \\ &= (\mathrm{d}/\mathrm{d}t) \sum_i \{p_i^*(t) \ln r_i^*\} =: (\mathrm{d}/\mathrm{d}t)\mathscr{W}[p^*(t)] \end{aligned} \tag{3.14}$$

or

$$\mathscr{W}[p^*(t)] = \sum_i p_i^*(t) \ln r_i^* + \text{constant}. \tag{3.15}$$

Consequently, for any two states $p^{(0)}$ and $p^{(n)}$ that are connected by the anticausal path, $p^*(t)$, the transition probability (2.8) reduces to a difference in a function of state

$$\mathfrak{P}^*\{p^{(0)}, p^{(n)}\} = \exp[\![N\{\mathscr{W}[p^*(t_0)] - \mathscr{W}[p^*(t_n)]\}]\!], \tag{3.16}$$

subject to $p^{(0)} = p^*(t_0)$ and $p^{(n)} = p^*(t_n)$. The stationary state $\{p_i^\infty\}$ is characterised by the detailed balance condition

$$\theta_l/\theta_u = p_u^\infty/p_l^\infty \tag{3.17}$$

which is obtained by letting $t \to \infty$ in the equation for the causal path (3.9), or in the limit as $t \to -\infty$ in the equation for the anticausal path, (3.13). This condition allows us to write (3.16) in the more suggestive form

$$\mathfrak{P}^*\{p^{(0)}, p^{(n)}\} = \prod_i [p_i^*(t_n)/p_i^\infty]^{Np_i^*(t_n)} [p_i^\infty / p_i^*(t_0)]^{Np_i^*(t_0)}. \tag{3.18}$$

By letting $t_0 \to -\infty$, we can assure ourselves that the aged system must have been in a steady state at some distant time in the past. In this limit, expression (3.18) reduces to the probability of a spontaneous fluctuation from the steady state along the anticausal path, namely

$$\mathfrak{P}_\infty^*\{p^{(n)}\} = [(N)!/(Np_l)!(Np_u)!](p_l^\infty)^{Np_l}(p_u^\infty)^{Np_u} \tag{3.19}$$

where we have used Stirling's formula. The logarithm of the first factor is precisely the entropy of the non-equilibrium state $p^{(n)}$. The second factor is, however, not so simply related to the entropy of the stationary state.

The negative of the scalar potential, (3.15), has been referred to as the 'pseudo-entropy' (Kikuchi 1961) since it depends on a knowledge of the steady state $\{p_i^\infty\}$. For this reason, it has been argued that the 'principle of minimum pseudo-entropy production' cannot replace the 'principle of minimum entropy production' (Klein 1958). However, such knowledge is necessary in order that $\mathcal{W}$ be related to a persistency criterion.

The foregoing analysis of a two-level system can easily be extended to a many-level system (Mathews *et al* 1960, Kikuchi and Gottlieb 1961). This will illustrate the generality of our criterion $H(s) = 0$ for determining paths of relative maximum likelihood. Suppose a system has r states $i = 1, 2, 3, \ldots, r$ which are characterised by the state probability parameters $\{p_i(t)\}$. We consider an assembly of N such systems. The expression for the maximum transition probabilities (2.4) generalises to

$$(1/N) \ln \mathfrak{P}[\{p_i(t)\}, \{p_i(t+\Delta t)\}] = -[(s, \dot{p}) - H(s, p)]\Delta t + O(\Delta t^2). \tag{3.20}$$

The Hamiltonian is a generalisation of that appearing in (2.7), namely

$$H(s, p) = \sum_i \sum_j{}' p_i \theta_{ij} [\exp(s_j - s_i) - 1] \tag{3.21}$$

where θ_{ij} are the quantum mechanical transition probabilities per unit time that depend upon the specific mechanisms which induce transitions among the states of the system, and the prime on the sum means to exclude the state i.

The variational principle (2.8) now gives the canonical equations

$$\dot{p}_i = (\partial H/\partial s_i) = \sum_j{}' p_j \theta_{ji} \exp(s_i - s_j) - p_i \theta_{ij} \exp(s_j - s_i), \tag{3.22}$$

$$\dot{s}_i = -(\partial H/\partial p_i) = -\sum_j{}' \theta_{ij} [\exp(s_j - s_i) - 1], \tag{3.23}$$

as the conditions of stationarity of the integral. It is easily seen that the zero noise strength vector $s^+ = 0$ satisfies both canonical equations (3.22) and (3.23). The method of determining the critical vector, s^*, is analogous to that of determining the characteristic form of an equation with $r-1$ independent variables (cf Whitham 1974). There, one considers a function $\mathcal{W}(p_1, \ldots, p_{r-1})$ which satisfies the differential equation

$$H(s, p) = 0 \tag{3.24}$$

where s denotes a vector with components

$$s_i = \partial \mathcal{W}/\partial p_i. \tag{3.25}$$

The problem is to determine those curves in p space, $p = p(t)$, which are analogous to the characteristics of quasilinear equations. The total derivative of $\mathcal{W}$ along p is

$$(\mathrm{d}/\mathrm{d}t)\mathcal{W} = \sum_i (\partial \mathcal{W}/\partial p_i)\dot{p}_i = \sum_i s_i \dot{p}_i. \tag{3.26}$$

Condition (3.24) determines the modulus of the vector s; there remain $(r-1)$ parameters which determine the characteristics or rays (Ludwig 1975). If these parameters are known we can construct the solution $\mathcal{W}$ from equation (3.24). Differentiating (3.24) with respect to p_i yields

$$\sum_j \partial^2 \mathcal{W}/\partial p_j \partial p_i (\partial H/\partial s_j) + \partial H/\partial p_i = 0. \tag{3.27}$$

If we choose the special curves defined by

$$\dot{p}_i = \partial H/\partial s_i \tag{3.28}$$

then

$$\dot{s}_i = -\partial H/\partial p_i \tag{3.29}$$

because

$$\dot{s}_i = (\mathrm{d}/\mathrm{d}t)(\partial \mathcal{W}/\partial p_i) = \sum_j (\partial^2 \mathcal{W}/\partial p_j \partial p_i)\dot{p}_j. \tag{3.30}$$

Equations (3.28) and (3.29) are precisely Hamilton's equations (3.22) and (3.23). The vector s^* with components

$$s_i^* = \ln[p_i^*(t)/p_i^\infty] \tag{3.31}$$

will satisfy both of Hamilton's equations provided detailed balance (cf equation (3.17)),

$$\theta_{ij} p_i^\infty = \theta_{ji} p_j^\infty, \tag{3.32}$$

holds. In this case both of Hamilton's equations coalesce into the single set of equations

$$\dot{p}_i^* = \sum_j{}' \theta_{ij} p_i^* - \theta_{ji} p_j^* \tag{3.33}$$

which are the equations of motion for the anticausal path (cf equation (3.13)).

Detailed balance guarantees the existence of a scalar potential

$$\mathcal{W}[p^*(t)] = \sum_i p_i^*(t)\{\ln[p_i^*(t)/p_i^\infty] - 1\} \tag{3.34}$$

where the constant of integration has been chosen so that definition (3.25) gives (3.31). This inherent connection between detailed balance and the existence of a scalar potential failed to be appreciated by Kikuchi and Gottlieb (1961). They assumed detailed balance to be an auxiliary condition which would ensure the time symmetry between the causal and anticausal path. While it is true that detailed balance is responsible for the time inversion symmetry, it is not an auxiliary condition. Alternatively, if (3.34) exists then it is tantamount to requiring detailed balance to hold, since s^* is the gradient of $\mathcal{W}$ and the circulation around a closed curve $p^*(t)$ $(0 \leqslant t \leqslant T)$ with $p^*(0) = p^*(T)$ vanishes,

$$\oint (s^*, \mathrm{d}p^*) = \mathcal{W}[p^*(T)] - \mathcal{W}[p^*(0)] = 0, \tag{3.35}$$

and this implies detailed balance (3.32) (Ito 1984).

Let $p(t)$, $t_0 \leq t \leq t_n$ be any curve, in the space of independent variables, R^{r-1}, that connects a subset Δ, containing the stationary state, of an arbitrary domain D, having a smooth boundary ∂D, to a state y lying in the closure of D. The curve is contained entirely in the closure of D and the function $\mathcal{W}$ is continuous there, vanishing only in Δ. Once the domain has been chosen, $t_n - t_0$ becomes the time required for the passage.

Call

$$\mathcal{A}_{t_0 t_n}(p) := \int_{t_0}^{t_n} L[p(t), \dot{p}(t)]\,\mathrm{d}t \geq \int_{t_0}^{t_n} [(s, \dot{p}) - H(s, p)]\,\mathrm{d}t \tag{3.36}$$

the action, where the (Young's) inequality (Gelfand and Fomin 1963) follows from (3.11), and set

$$\mathcal{V}(\Delta, y) = \inf\{\mathcal{A}_{t_0 t_n}(p): p(t_0) \in \Delta, p(t_n) = y; -\infty \leq t_0 < t_n \leq \infty\}. \tag{3.37}$$

Suppose that $\mathcal{W}$ is a solution of

$$H(\nabla \mathcal{W}(y), y) = 0 \tag{3.38}$$

for any state y in the closure. Then $\mathcal{V}(\Delta, y) = \mathcal{W}(y)$ for all y for which the inequality $\mathcal{W}(y) \leq \min\{\mathcal{W}(x): x \in \partial D\}$ holds. Along the extremal $p^*(t)$ connecting any state in Δ with y, the second integral in (3.36) vanishes. We then have

$$L[p^*(t), \dot{p}^*(t)] = (\mathrm{d}/\mathrm{d}t)\mathcal{W}[p^*(t)] \geq 0. \tag{3.39}$$

The equality sign can only occur along the causal path where L vanishes. Hence, $\mathcal{W}[p^*(t)]$ is a monotonically increasing function of time. In general then $\mathcal{A}_{t_0 t_n}(p) \geq \mathcal{W}(y)$ where the equality holds along the extremal curve and $\mathcal{W}(y)$ can be interpreted as the minimal action necessary to bring the system from any state in Δ to that state on the boundary for which the inequality $\mathcal{W}(y) \leq \min\{\mathcal{W}(x): x \in \partial D\}$ holds.

For $t_0 = -\infty$, the trajectory $p^*(t)$ will enter the domain Δ of the stationary state. This is guaranteed by the fact that there is no finite, positive limit to $\mathcal{W}[p(t)]$ as $t \to -\infty$ (Freidlin and Wentzell 1984). If such a limit did exist, then it would contradict the strict inequality in (3.39) everywhere outside Δ. Hence, the trajectory $p^*(t)$ enters Δ as $t_0 \to -\infty$ for which there is no finite, positive limit to $\mathcal{W}[p^*(t)]$.

4. Large deviations

The method of associated distributions is commonly used to study large deviations in the sums of random variables (Feller 1971). As mentioned in § 1, the statement of the central limit theorem becomes empty for large values of the normalised sum since for large x, the actual distribution $\mathcal{F}_n(x)$ and the normal distribution $\mathcal{R}(x)$ are both close to unity. What we want to determine is how good an approximation $1 - \mathcal{R}(x)$ will be to $1 - \mathcal{F}_n(x)$ for large x and n.

It is well known that a limiting form of random walk leads to a situation similar to a central limit theorem (Feller 1968). The sum S_n respresents the particle's position at the nth step. For simplicity, if we set both the length of the individual steps and the collisional rate to unity, then S_n is the particle's displacement and n is the time interval. With this correspondence, we now estimate the relative error in approximating the actual distribution by the Onsager-Machlup distribution in the diffusion limit, based on the analogy with large deviations and the central limit theorem.

It is clear from the definition of $H(s)$ in (3.4) that it plays the role of a second characteristic function. It can be written in the form

$$H(s)=\sum_k (h_k/k!)s^k \tag{4.1}$$

where the coefficient h_k depends only on the derivative moments and is known as a cumulant or semi-invariant of order k. For instance, if we are dealing with a Poisson process with rate r and strength s then $H(s)=r(e^s-1)$. The first cumulant is the first moment per unit time, r, the second cumulant is the variance per unit time, r, and so on.

With the original distribution $\mathscr{F}$ we associate a new probability distribution $\mathscr{G}$ such that

$$\mathscr{G}(dx)=e^{-H(s)}e^{sx}\mathscr{F}(dx) \tag{4.2}$$

equipped with the norming constant $e^{-H(s)}$, and s is a parameter chosen in the interval of convergence of H. If, instead of dealing with the derivative moments, we were to deal with the moments themselves, the distributions $\mathscr{F}^*$ and $\mathscr{G}^*$ would stand in the same relationship as $\mathscr{F}$ and $\mathscr{G}$ in (4.2) except that the norming constant must be replaced by $e^{-H(s)\Delta t}$. Upon inverting the relation, we get

$$1-\mathscr{F}(x)=1-\mathscr{F}^*(x\sigma\sqrt{\Delta t})=e^{H(s)\Delta t}\int_{x\sigma\sqrt{\Delta t}}^{\infty} e^{-sy}\mathscr{G}^*(dy). \tag{4.3}$$

Motivated by the analogy with the central limit theorem, we would like to replace $\mathscr{G}^*$ by a normal distribution with density

$$[1/(2\pi H''(s)\Delta t)^{1/2}]\exp\{-[y-H'(s)\Delta t]^2/2H''(s)\Delta t\} \tag{4.4}$$

having expectation $H'(s)\Delta t$ and variance $H''(s)\Delta t$. The relative error will be small if $x\approx H'(s)\sqrt{\Delta t}/\sigma$ since then the integral will be close to unity. In this way we can derive a good approximation to the left-hand side of (4.3) for certain large values of x.

With the substitution $y=H'(s)\Delta t+z(H''(s)\Delta t)^{1/2}$, the right-hand side of (4.3) can be written as

$$\exp\{[H(s)-H'(s)s+\tfrac{1}{2}H''(s)s^2]\Delta t\}\tfrac{1}{2}\operatorname{erf}(s(H''\Delta t/2)^{1/2})=:C_s \tag{4.5}$$

provided $x\approx H'(s)\sqrt{\Delta t}/\sigma$. Expanding the Hamiltonian (2.5) in powers of s, we have

$$H(s)=\mu s+\tfrac{1}{2}\sigma^2 s^2+\tfrac{1}{6}\mu s^3+\ldots \tag{4.6}$$

where $\mu=r_l-r_u$ and $\sigma^2=r_l+r_u$. To focus our attention on the diffusion process, let us assume that $r_l\approx r_u$. Using (4.6), with $\mu\approx 0$, to evaluate the exponential in (4.5), we see that it begins with terms of $O(s^4\Delta t)$ so that

$$C_s=[1+O(s^4\Delta t)]\{1-\mathscr{R}[s(H''(s)\Delta t)^{1/2}]\}. \tag{4.7}$$

If C_s is to stand for the tail of the distribution $\mathscr{F}$ in (4.3) then the arguments of the two distributions must be of the same order, i.e. the noise strength $s=O(x/\sigma\sqrt{\Delta t})$. Using this to estimate the first factor in (4.7), we obtain

$$[1-\mathscr{F}(x)]/[1-\mathscr{R}(x)]=1+O(x^4/\Delta t). \tag{4.8}$$

Suppose that $x\sigma\sqrt{\Delta t}$ represents the maximum displacement $\Delta p_{\max}$ of the particle. It is apparent that a diffusion approximation is valid provided $s^4\Delta t\to 0$ or, what amounts to the same, if $x=o(\Delta t^{1/4})$. In terms of the maximum displacement this implies that

$\Delta p_{\max} = o(\Delta t^{3/4})$ which should certainly be satisfied by Brownian motion whose root-mean-square displacement $\Delta p_{\rm rms} = O(\sqrt{\Delta t})$. For an exponent greater than or equal to $\frac{3}{4}$, there is no asymptotic equivalence of $[1-\mathscr{F}(x)]$ and $[1-\mathscr{R}(x)]$ and, consequently, the diffusion approximation breaks down. The effect of a finite drift will be to bring this fractional power close to unity.

Parenthetically, we observe that a prediction can be made as to the minimum fractal dimension for which a diffusion approximation is valid. For ordinary Brownian motion, if we change the time interval by a factor of F^{-2}, the distance changes by a factor of F^{-1}. The index $d=2$ in F^{-d} is known as the fractal dimension (Mandelbrot 1977). The degree of crookedness is the amount by which the fractal dimension exceeds the topological dimension. For a topological dimension of 1 (a line) a Brownian motion path is infinitely crooked. In order for a diffusion approximation to apply, the fractal dimension must be greater than $\frac{4}{3}$, say for a self-avoiding random walk where $d=\frac{5}{3}$. The effect of a finite drift will be to reduce the fractal dimension and consequently lead to a more orderly path trajectory.

If an asymptotic equivalence exists, the Lagrangian can be read off the exponent in (4.4). We can write it formally as

$$L(p,\dot{p}) = (\dot{p}_{\rm u}-\mu)^2/2\sigma^2 \tag{4.9}$$

since an instantaneous velocity does not exist. The Lagrangian (4.9) can be taken as a measure of the difficulty that the process has in reaching the causal path which is a solution of the deterministic rate equation (3.9). The paths of maximum likelihood are determined by the vanishing of (4.1). In addition to the deterministic path $s^{\dagger}=0$, we also have

$$s^* = -2\mu/\sigma^2 \tag{4.10}$$

which is proportional to the ratio of the mean and variance in the diffusion limit. The relation between (4.10) and the general criterion (3.12) can be seen by employing the expansion $\ln z = 2[(z-1)/(z+1)+\ldots]$ and discarding terms of $O[(\mu/\sigma^2)^3]$.

In regard to our two-level atom model, the critical noise strength, (4.10), can be expressed in terms of the deviation of the process from its stationary state value along the anticausal path, namely

$$s^* = (p_{\rm u}^*(t)-p_{\rm u}^{\infty})/p_{\rm u}^{\infty}p_l^{\infty}. \tag{4.11}$$

The Lagrangian along the critical path is therefore

$$\begin{aligned} L[p^*(t),\dot{p}^*(t)] &= (\mathrm{d}/\mathrm{d}t)\mathscr{W}[p^*(t)] = s^*\dot{p}_{\rm u}^*(t) \\ &= (\theta_l+\theta_{\rm u})[(p_{\rm u}^*(t)-p_{\rm u}^{\infty})^2/p_{\rm u}^{\infty}p_l^{\infty}] \geqslant 0 \end{aligned} \tag{4.12}$$

which is seen to vanish only at the stationary state. We now want to compare this expression with the entropy production along the critical path in the high-temperature limit.

The entropy production comprises two terms: one due to the system's entropy production which, per atom, is

$$(\mathrm{d}/\mathrm{d}t)S_s[p(t)] = -(\mathrm{d}/\mathrm{d}t)\sum_i p_i(t)\ln p_i(t) \tag{4.13}$$

and the entropy production of the heat bath

$$(\mathrm{d}/\mathrm{d}t)S_{\rm b}[p(t)] = (E/T)\theta_{\rm b}[p_{\rm u}(t)\,\mathrm{e}^{E/T}-p_l(t)], \tag{4.14}$$

again given per atom. The entropy production of the heat bath has been defined as the energy flowing into the heat bath divided by its temperature (Klein 1958).

In order to evaluate the total entropy production along the anticausal path, we have to reverse the sign of the entropy production of the heat bath in (4.14). Then for *small deviations* from the stationary state and in the *high-temperature* limit we get

$$\begin{aligned}(\mathrm{d}/\mathrm{d}t)S[p^*(t)] &= (\mathrm{d}/\mathrm{d}t)\{S_s[p^*(t)] - S_b[p^*(t)]\} \\ &= -(p_u^*(t) - p_u^\infty)^2(\theta_u + \theta_l)^3/\theta_l\theta_u + \mathrm{O}[(E/T)^2] \\ &\leqslant 0. \end{aligned} \tag{4.15}$$

In the high-temperature limit, we can discard terms of $\mathrm{O}[(E/T)^2]$ so that the total entropy production (4.15) reduces to the negative of the Lagrangian (4.12). Therefore, only in the case of small deviations from the stationary state will the persistency of irreversible processes be governed by a minimum relative entropy principle (Lavenda 1985b).

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