Kinetic Derivation of Gauss's Law and Its Thermodynamic Significance*

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Gauss's error law for generalized jump processes in which the average value is also the most probable value is derived from the maximum likelihood path for the growth of a fluctuation. Evolution towards equilibrium and the spontaneous growth of a fluctuation from equilibrium are analyzed and compared in the continuous, diffusion limit.

1. Introduction

Both classical and quantum statistics can be derived from Gauss's principle [1]

$$P(n;\bar{n}^s)=\exp\left\{S(n)-S(\bar{n}^s)-\left(\frac{\partial S}{\partial \bar{n}^s}\right)_V(n-\bar{n}^s)\right\} \tag{1}$$

and the second law in the form

$$\left(\frac{\partial S}{\partial \bar{n}^s}\right)_V=\frac{1}{T}\left\{\left(\frac{\partial E}{\partial \bar{n}^s}\right)_V-\mu\right\}. \tag{2}$$

The entropy S is a dimensionless quantity since the temperature T has dimensions of energy so that it can be measured in energy units. The random variable n is the number of particles, and $\bar{n}^s$ denotes its average or most probable value. E is the internal energy, μ the chemical potential and V the volume. According to (1), the entropy is the thermodynamic potential that determines the error law for which the average value is also the most probable value. In order to determine the entropy, it was necessary to provide a continuous time Markov process that admits an invariant probability distribution [1]. Casting this stationary distribution in the form of (1) identifies the entropy, and subsequent application of the second law (2) gives the physical "distributions" in the physicist's sense of the meaning; that is, $\bar{n}^s$ as a function of the temperature.

For a general derivation of Gauss's error law (1) in terms of the entropy we should like to make no reference to any particular mechanism. In order to accomplish this, we must consider the full time-dependent transition probability of a completely general form of a jump process and determine under what conditions (1) holds. We shall see that such a kinetic derivation involves the optimal path for the growth of a spontaneous fluctuation from equilibrium. The transition probability becomes path independent, which implies a lack of statistical correlations between the endpoints of transition, since one of the endpoints is the equilibrium state.

If we consider the reverse evolution of the system toward equilibrium, we find that the deterministic rate equation overwhelmingly maximizes the path probability, and again we find no correlations between nonequilibrium states. In order to take into account such statistical correlations, we consider the diffusion limit of the general jump process already introduced. In the presence of thermal fluctuation, modelled as Brownian motion, there are no longer optimal paths which maximize the path probability. We shall see that only in the asymptotic time limit where the statistical correlations have had sufficient time to wear off, is the probability distribution given by Gauss's law (1). The entropy and its derivative are related to the quasipotential, which governs the evolution of the diffusion process, only in the asymptotic time limit.

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2. Optimal Paths of Jump Processes

Consider a bivariate Poisson distribution

$$P(k, l) = \Pr\{n(t+\Delta t) - n(t) = k - l\}$$
$$= \frac{(g\,\Delta t)^k}{k!}\, e^{-g\Delta t} \cdot \frac{(r\,\Delta t)^l}{l!}\, e^{-r\Delta t}, \tag{3}$$

where the intensity parameters, g and r, denote rates of generation and recombination, respectively. After each observation, we can compare the values of k and l with their expected values, respectively, $g\,\Delta t$ and $r\,\Delta t$. Certainly deviations will occur, and we wish to obtain a measure of these. A widely used method in statistical mechanics employs "conjugate" [2] distributions

$$P^{\#}(k, l; \chi) = \frac{e^{\chi(k-l)}}{Z(\chi)}\, P(k, l), \tag{4}$$

where Z is the moment generating, or "partition", function

$$Z(\chi) = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} e^{\chi(k-l)}\, P(k, l)$$
$$= \exp\{g\,\Delta t\,(e^{\chi} - 1) + r\,\Delta t\,(e^{-\chi} - 1)\}. \tag{5}$$

For finite time differences, the conjugate distribution (4) can be written in the canonical form

$$P^{\#}(n, n_0; \chi) = \int_{(n, n_0)} \exp\left\{\int_{T_0}^{T} [\chi\, \mathrm{d}n - \mathscr{H}(n, \chi)\, \mathrm{d}t]\right\} P(\mathrm{d}n), \tag{6}$$

where $\int_{(n,n_0)}$ denotes the integral over all paths connecting n_0 to n, and the function

$$\mathscr{H}(n, \chi) = g\,(e^{\chi} - 1) + r\,(e^{-\chi} - 1) \tag{7}$$

will be seen to play a role analogous to that of the Hamiltonian in mechanics. As a problem of statistical interference, the unknown parameter χ could be estimated from the observations made on the random process n [3].

Since the probability measure density $\mathrm{d}P^{\#}/\mathrm{d}P > 0$, the measure P can be expressed by integration with respect to $P^{\#}$, namely

$$P(n, n_0) \tag{8}$$
$$= \boldsymbol{E}^{\#}\left[\exp\left\{\int_{T_0}^{T} [\mathscr{H}(n, \chi)\, \mathrm{d}t - \chi\, \mathrm{d}n]\right\} \mid n_0 < n(t) < n\right].$$

Using Jensen's inequality, we have

$$P(n, n_0) \tag{9}$$
$$\geqq \exp\left\{\boldsymbol{E}^{\#}\left[\int_{T_0}^{T} \{\mathscr{H}(n, \chi)\, \mathrm{d}t - \chi\, \mathrm{d}n\} \mid n_0 < n(t) < n\right]\right\}.$$

Equating average and most probable values, we replace the conditional expectation in the exponent of (9) by the negative of

$$\left[\int_{T_0}^{T} \{-\mathscr{H}(n, \chi)\, \mathrm{d}t + \chi\, \mathrm{d}n\}\right]_{\min} \tag{10}$$

subject to the given endpoints of transition. Expression (10) is *not* any longer a functional of fluctuating paths [4]. It is a function only of the endpoints of the transition. The $n(t)$ in (10) is a continuous and, at least, twice differentiable function which makes the functional in brackets a minimum subject to the endpoint conditions. The equivalence of average and most probable values therefore yields the asymptotic equivalence

$$P(n, n_0) \quad \exp\left\{-\left[\int_{T_0}^{T} \{-\mathscr{H}(n, \chi)\, \mathrm{d}t + \chi\, \mathrm{d}n\}\right]_{\min}\right\} \tag{11}$$

between the transition probability and the minimum of the "action" [5]. For discontinuous jump processes, Friedlin and Wentzell [5] show that (11) is the dominant term as a small parameter, characterizing the intensity of the fluctuations that tends to zero. Hence, (11) is a logarithmic ($\asymp$) equivalence, and it is only in this limit that we should expect that average and most probable values coincide. In other words, the supposed equivalence of the mean and mode of the distribution implies implicitly that we are considering an asymptotic process whose realizations are statistically independent.

The most probable paths of a fluctuation can be derived from an extremum principle [6]. The equation of motion has the Hamiltonian form

$$\dot{n} = \frac{\partial \mathscr{H}}{\partial \chi} = g\, \mathrm{e}^{\chi} - r\, e^{-\chi}. \tag{12}$$

The paths of maximum likelihood are determined from the dissipation balance condition [7]

$$\mathscr{H}\left(n, \frac{\partial U}{\partial n}\right) = 0, \tag{13}$$

where it reduces, in the diffusion limit, to the equivalence of the Rayleigh-Onsager dissipation function and the generating function [c.f. (24) below]. With the general expression for the Hamiltonian given in (7), we find there are two values

$$\chi^{\dagger} = 0, \quad \chi^{\ddagger} = \ln(r/g) \tag{14}$$

of the force which satisfy (13). The first value determines the overwhelmingly most probable path since it yields the deterministic rate equation when it is substituted into (12). This tells us nothing about the magnitude of the fluctuations and can be excluded by requiring that $\partial U/\partial n \neq 0$ for $n \neq \bar{n}^s$, where $\bar{n}^s$ is a solution of the detailed balance condition

$$r(\bar{n}^s) = g(\bar{n}^s). \tag{15}$$

The second value of χ in (14) yields the mirror image solution of the deterministic rate equation when inserted into (12).

The difference

$$U(n) - U(\bar{n}^s) = \int_{\bar{n}^s}^{n} \ln\left(\frac{r}{g}\right) \mathrm{d}n \tag{16}$$

is always positive, regardless of whether $n > \bar{n}^s$ or $n < \bar{n}^s$. For this reason it has been referred to as a "quasi-potential" [5]. The monotonic increasing property of $U(n)$ is due to the concavity of the entropy [8]

$$U(n) - U(\bar{n}^s) = S(\bar{n}^s) - S(n) + \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V (n - \bar{n}^s) \geqq 0. \tag{17}$$

From (17) it follows that

$$\frac{\partial U}{\partial n} = \chi^{\ddagger} = -\left\{\frac{\partial S}{\partial n} - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V\right\}, \tag{18}$$

the negative of the thermodynamic force [9]. Just as the thermodynamic force measures the tendency of the system to *seek* equilibrium [9], so the force (18) is a measure of the system's ability to *deviate* from equilibrium. It may be noted that, in general, $U(\bar{n}^s) = -PV/T$, where P is the pressure, and this coincides with F/T, where F is the Helmholtz free energy, in the case of a vanishing chemical potential.

Another way to distinguish between the two maximum likelihood solutions, given in (14), is to set the lower limit of integration $T_0 = -\infty$ in (11), assuring that the aged system must have certainly been at equilibrium some long time ago. We then obtain

$$\begin{aligned} P(n, \bar{n}^s) &= \exp\left\{-\int_{\bar{n}^s}^{n} \chi^{\ddagger} \,\mathrm{d}n\right\} = \exp\left\{\int_{\bar{n}^s}^{n} \ln\left(\frac{g}{r}\right) \mathrm{d}n\right\} \\ &= \exp\left\{S(n) - S(\bar{n}^s) - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V (n - \bar{n}^s)\right\}, \end{aligned} \tag{19}$$

which identifies the scalar potential S in Gauss's principle (1) as the entropy.

As an illustration, consider Einstein's radiation mechanism [10] where the intensity parameters of the jump process are $r = \alpha n$ and $g = \beta n + \gamma$. The coefficients α, β, and γ are related to, but not identical with [11], Einstein's coefficients of absorption, induced emission and spontaneous emission, respectively. The detailed balance condition (15) implies that $\alpha > \beta$ since $\bar{n}^s = \gamma/(\alpha - \beta)$. In order that this conforms with Planck's law, $\alpha/\beta = \exp(E'/T)$, where the prime means differentiation with respect to $\bar{n}^s$, and $\gamma/\beta = m$, the density of states in the given energy interval. According to Boltzmann's principle, the entropy of the process is

$$S(n) = \ln\binom{m + n - 1}{n}, \tag{20}$$

so that for the second optimal value of the force in (14) we find

$$\begin{aligned} -\chi^{\ddagger} &= \ln\left(\frac{g}{r}\right) = \ln\left(\frac{m+n}{n}\right) - \frac{E'}{T} \\ &= \frac{\partial S}{\partial n} - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V, \end{aligned} \tag{21}$$

provided Stirling's approximation is valid. In the second line we have used the fact that for thermal radiation the chemical potential is zero. Integrating (21) between the limits $\bar{n}^s$ and n and introducing the result into the first line of (19) yields the second line.

3. Diffusion Processes and Non-Optimal Paths

The parameter χ is a measure of the strength of the fluctuations, and it will take on different values depending upon the intensity of the noise. In particular, let us consider the diffusion limit where χ is a small but finite quantity.

Expanding the Hamiltonian (7) to second order in χ gives

$$\mathscr{H}_{\text{diff}}(n, \chi) = b\,\chi + \frac{D}{2}\chi^2, \tag{22}$$

where the drift $b = g - r$ and the diffusion coefficient $D = r(\bar{n}^s) + g(\bar{n}^s)$ in the diffusion approximation. The equation of motion (12) reduces to

$$\dot{n} = \frac{\partial \mathscr{H}_{\text{diff}}}{\partial \chi} = b + D\,\chi. \tag{23}$$

Optimal values of the parameter are determined from the dissipation balance condition (13) obtained by setting (22) equal to zero or equivalently,

$$\mathscr{H}_{\text{diff}} = \frac{1}{2D}(\dot{n}^2 - b^2) = 0. \tag{24}$$

The designation of (24) as a dissipation balance condition comes from the fact that the first term is the Rayleigh-Onsager dissipation function and the second term is the generating function [6]. Their numerical equivalence determines the paths of maximum likelihood. This condition yields the optimal values

$$\chi^{\dagger}=0, \quad \chi^{\ddagger}=-2\,(b/D). \tag{25}$$

Again the first value corresponds to the deterministic path while the second is related to its mirror image in time. The value of $\chi^{\ddagger}$ is identical to the value given in (14) in the same approximation. That is, $\ln(r/g)$ is to be approximated by the average of its upper and lower bounds [12]

$$\chi^{\ddagger}=\ln\frac{r}{g}\approx\frac{1}{2}(r-g)\,\frac{r+g}{r\,g}\approx-2\,\frac{b}{D}, \tag{26}$$

where the second approximation arises from evaluating $(r+g)/r\,g$ at $n=\bar{n}^{s}$. Certainly this will not do for large deviations since the form of the diffusion coefficient requires the deviations from the time-independent state $\bar{n}^{s}$ to be small.

Introducing χ given in (23) into (11) gives

$$P(n,n_0)\asymp\exp\left\{-\left[\int_{T_0}^{T}\frac{(\dot{n}-b)^2}{2D}\,\mathrm{d}t\right]_{\min}\right\}, \tag{27}$$

which is the form given by Friedlin and Wentzell [5] as a direct generalization of the Onsager-Machlup function [9] of Gaussian-Markov processes. The drift need not be a linear function of n in order for (27) to be applicable. As in the case of jump processes, Friedlin and Wentzell [5] show that (27) is the dominant term as a small parameter, characterizing that the intensity of the fluctuations of a continuous diffusion process, tends to zero.

In the presence of statistical correlations between nonequilibrium states that are not well-separated in time, the parameter χ will not be given by either of its optimal values (14). In the continuous diffusion limit, the prior probability density will be given by the Wiener expression

$$p(n,n_0)=\frac{1}{\sqrt{2\pi D(T-T_0)}}\exp\left\{-\frac{(n-n_0)^2}{2D(T-T_0)}\right\} \tag{28}$$

describing the "free" diffusion process

$$\tilde{n}(T)=n_0+w(T)-w(T_0), \tag{29}$$

where w is the time integral of white noise. The process (29) is a solution to the equation $\mathrm{d}\tilde{n}(t)=\mathrm{d}w(t)$ for $t>T_0$ with the initial condition $\tilde{n}(T_0)=n_0$.

Suppose that the system is displaced from equilibrium – regardless of whether it is due to a spontaneous fluctuation or an imposed constraint – and then "released" and allowed to return. The process is now described by the stochastic equation

$$\mathrm{d}n=b\,\mathrm{d}t+\mathrm{d}w \tag{30}$$

with the same initial condition as the free diffusion process. The drift b induces a transformation of the free diffusion process into a biased diffusion process whose posterior probability density is related to the Wiener density by [13]

$$\begin{aligned}&p^{\#}(n,n_0;\chi) \\ &=\boldsymbol{E}\left[\exp\left\{\int_{T_0}^{T}[\chi\,\mathrm{d}n-\mathscr{H}_{\mathrm{diff}}\,\mathrm{d}t]\right\}\,|\,n_0<n(t)<n\right],\end{aligned} \tag{31}$$

where the Hamiltonian is given by (22). In terms of the Wiener process, we may write (31) as

$$\begin{aligned}&p^{\#}(n,n_0;\chi) \\ &=\boldsymbol{E}\left[\exp\left\{\int_{T_0}^{T}[\chi\,\mathrm{d}\tilde{n}-\frac{D}{2}\chi^2\,\mathrm{d}t]\right\}\,|\,n_0<\tilde{n}(t)<n\right].\end{aligned} \tag{32}$$

Letting

$$\frac{\partial V}{\partial n}=\chi, \tag{33}$$

we find from Itô's formula [14]

$$V(n)-V(n_0)=\int_{T_0}^{T}\left[\chi\,\mathrm{d}\tilde{n}+\frac{D}{2}\chi'\right]\mathrm{d}t, \tag{34}$$

where the prime stands for differentiation. Inserting (34) into (32) we obtain

$$p^{\#}(n,n_0;\chi)=\exp\{V(n)-V(n_0)\}\cdot\mathscr{K}(n,n_0), \tag{35}$$

where the kernel $\mathscr{K}$ is given by

$$\begin{aligned}&\mathscr{K}(n,n_0) \\ &=\boldsymbol{E}\left[\exp\left\{-\frac{D}{2}\int_{T_0}^{T}(\chi^2+\chi')\,\mathrm{d}t\right\}\,|\,n_0<\tilde{n}(t)<n\right].\end{aligned} \tag{36}$$

The evaluation of the conditional Wiener integral (36) can be reduced to solving the diffusion equation [15]

$$\frac{\partial\mathscr{K}}{\partial\tau}=\frac{D}{2}\{\mathscr{K}''-(\chi^2+\chi')\,\mathscr{K}\}, \tag{37}$$

where $\tau=T-T_0$ and the primes denote differentiation at either the final or initial state. It is well-known that the kernel can be expressed in a bilinear expansion

$$\mathscr{K}(n,n_0;\tau)=\sum_{n=0}^{\infty}\psi_j(n)\,\psi_j(n_0)\,e^{-\gamma_j\tau} \tag{38}$$

in terms of normalized eigenfunctions ψ_j and discrete eigenvalues γ_j. In time, all terms in the sum of (38) will decay, leaving only the term with eigenvalue $\gamma_0 = 0$. Since $\psi_0 \propto \exp(V)$ is the solution to

$$\psi_0'' - (\chi^2 + \chi')\,\psi_0 = 0, \tag{39}$$

we have, in the asymptotic time limit,

$$\lim_{\tau \to \infty} \mathscr{K}(n, n_0; \tau) = V(n) + V(n_0) + \text{const} \tag{40}$$

and, in the same limit, the transition probability density (35) transforms into the invariant probability density

$$\lim_{\tau \to \infty} p^{\#}(n, n_0; \tau) = p_\infty(n) = \exp\{2\,V(n) + \text{const}\}, \tag{41}$$

independently of the initial state of the system.

In order that Gauss's principle be satisfied, the asymptotic form of the quasi-potential V must be given by

$$V(n) = \frac{1}{2}\left\{S(n) - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V n\right\}. \tag{42}$$

Then, according to (33), the force which measures the tendency of the system to seek equilibrium is [13]

$$\chi = \frac{1}{2}\left\{\frac{\partial S}{\partial n} - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V\right\}. \tag{43}$$

We will discuss the factor of one-half in the next section. It thus turns out that Gauss's principle (1) is given by the ratio $p_\infty(n)/p_\infty(\bar{n}^s)$, since $p_\infty(\bar{n}^s)$ provides the proper normalization. In the discrete case, this is a consequence of the binomial theorem.

In an isolated system, the second term in (43) vanishes and we are left with

$$\frac{p_\infty(n)}{p_\infty(\bar{n}^s)} = \exp\{S(n) - S(\bar{n}^s)\}, \quad \text{(isolated)}. \tag{44}$$

Although this is the commonly cited relation between entropy and probability due to Boltzmann [16], it does not correspond to any form of physical statistics. The reason is that it implies that $(\partial S/\partial \bar{n}^s)_V \equiv 0$ and such a system can never come to equilibrium with a thermostat at temperature T. In the case of the negative binomial distribution that was used in the Einstein radiation mechanism, the invariant density (41) is

$$\begin{aligned} p_\infty(n) &= \exp\left\{S(n) - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V n\right\} \\ &= \binom{m+n-1}{n}\left(\frac{\bar{n}^s}{m+\bar{n}^s}\right)^n. \end{aligned} \tag{45}$$

The fact that

$$\begin{aligned} \sum_{n=0}^{\infty} \binom{m+n-1}{n}\left(\frac{\bar{n}^s}{m+\bar{n}^s}\right)^n &= p_\infty(\bar{n}^s) \\ &= \exp\left\{S(\bar{n}^s) - \left(\frac{\partial S}{\partial \bar{n}^s}\right)_V \bar{n}^s\right\} \end{aligned} \tag{46}$$

provided Stirling's approximation is valid, ensures that the ratio $p_\infty(n)/p_\infty(\bar{n}^s)$ is a proper fraction. Setting the invariant probability density equal to the negative binomial coefficient will never yield a normalizable ratio of the probability densities. Hence (44) is an untenable relation even on the basis of equal *a priori* probabilities.

The physical reason why the *a priori* probability argument will not work is because, as soon as the energy constraint is introduced, the "cells" among which the particles are to be distributed are no longer equiprobable [3], [17]. Consider the (classical) placement of n particles in m cells under the assumption that all m^n possible placements are equally probable. The probability of obtaining a given set of occupancy numbers $\{n_i\}$ is

$$p_\infty(\{n_i\}) = \frac{n!}{n_1!\, n_2! \ldots n_m!}\, m^{-n}. \tag{47}$$

The entropy is

$$S(\{n_i\}) = n \ln n - \sum_{i=1}^{m} n_i \ln n_i. \tag{48}$$

According to Boltzmann's formula for an *isolated* system, (44), the invariant probability density would be equal to the multinomial coefficient. Yet, by the second law we have

$$\left(\frac{\partial S}{\partial \bar{n}_i^s}\right)_V = -\ln\left(\frac{\bar{n}_i^s}{n}\right) = \frac{1}{T}\left\{\left(\frac{\partial E}{\partial \bar{n}_i^s}\right)_V - \mu\right\}, \tag{49}$$

which is precisely Boltzmann's law. Hence, the system cannot be isolated and the invariant probability density must be given by

$$\begin{aligned} p_\infty(\{n_i\}) &= \exp\left\{S(\{n_i\}) - \sum_{i=1}^{m}\left(\frac{\partial S}{\partial \bar{n}_i^s}\right)_V n_i\right\} \\ &= \frac{n!}{n_1!\, n_2! \ldots n_m!}\left(\frac{\bar{n}_1^s}{n}\right)^{n_1} \cdots \left(\frac{\bar{n}_m^s}{n}\right)^{n_m} \end{aligned} \tag{50}$$

provided Stirling's approximation is valid. Under the same approximation $p_\infty(\{\bar{n}_i^s\}) = 1$. In contrast to our original assumption of equal *a priori* probabilities in (47), the *a priori* probabilities are no longer equal in (50). What has previously been attributed to the energy constraint – the non-equivalence of the cells – is now seen to be a direct consequence of the second law (49). Hence, the invariant probability density (44), for an isolated system, is not compatible with either classical or quantum statistics.

4. Optimal Versus Non-Optimal Paths

The difference between the forces, (18) and (43), is not only the anticipated change in sign but also a factor of one-half involved. The sign change indicates a change in the direction of evolution of the system, either away from, (18), or toward, (43), equilibrium. Whatever relation we choose for the thermodynamic force, expression (31) is always equivalent to (32). The fact that the conditional expectation is taken with respect to the prior probability measure in (31), rather than the posterior measure as in (8), introduces an additional term that would not have appeared in (8). Therefore, even if the thermodynamic force is derivable from a scalar potential, its integral does not determine the transition probability density. Moreover, there is an additional term, of stochastic rather than deterministic origin, emanating from the Itô nature of this integral. The last term in (34) takes into account the indeterminancy in the final endpoint of the transition [6]. It is this term which is responsible for establishing the limiting invariant distribution [13], for without it there would be no zero eigenvalue in the expression for the kernel (38).

Hence, although $\chi^{\ddagger}$ in (14) characterizes an optimal path with respect to the measure $P^{\#}$, namely the mirror image in the time solution to the deterministic rate equation, the negative of $\chi^{\ddagger}$ does not characterize an optimal path with respect to the measure P. It is precisely, the kernel (38) that accounts for the statistical correlations between nonequilibrium states which are not widely separated in time [7]. Asymptotically, the kernel (38) tends to (40), which wipes out all information regarding the initial state of the system and contributes the missing half to form Gauss's principle. A long time elapse makes the states statistically independent and all physical systems tend to "forget" their initial states with the passage of time. Due to the presence of statistical correlations between nonequilibrium states that are not well separated in time, the thermodynamic force, measuring the tendency to seek equilibrium, should not be the negative of (18). That the thermodynamic force (43) is precisely *half* of its "optimal" value implies stationarity for, according to (23), the rate of change of the number of particles vanishes. Consequently, (42) is the asymptotic form of the quasi-potential, and likewise (43) is the asymptotic form of the thermodynamic force.

[1] B. H. Lavenda, Int. J. Theor. Phys. **27**, 1371 (1988).
[2] A. I. Khinchin, Mathematical Foundations of Statistical Mechanics, transl. by G. Gamow, Dover, New York 1949, Chapt. IV.
[3] B. H. Lavenda and C. Scherer, Riv. Nuovo Cim. **11**, no. 6 (1988).
[4] D. Falkoff, Ann. Phys., New York **4**, 325 (1958).
[5] M. I. Friedlin and A. D. Wentzell, Random Perturbations of Dynamical Systems, Springer-Verlag, New York 1984, p. 159.
[6] B. H. Lavenda, Nonequilibrium Statistical Thermodynamics (Wiley, Chichester, 1985), Chapt. 1 and 7 and references cited therein.
[7] B. H. Lavenda and E. Santamato, J. Stat. Phys. **29**, 345 (1982); B. H. Lavenda and C. Cardella, Int. J. Theor. Phys. **25**, 95–111 (1986).
[8] See, for example, N. G. Van Kampen, Stochastic Processes in Physics and Chemistry, North-Holland, Amsterdam, 1981, p. 118.
[9] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).
[10] A. Einstein, Physikalische Zeitschrift **18**, 121 (1917) [reprinted and translated in Sources in Quantum Mechanics, B. L. van der Waerden, ed., North-Holland, Amsterdam 1967, pp. 63–67].
[11] B. H. Lavenda, Int. J. Theor. Phys. **28**, 619–631 (1989).
[12] G. H. Hardy, J. E. Littlewood, and G. Pólya, Inequalities, Cambridge Univ. Press, Cambridge 1934, p. 106, th. 150.
[13] B. H. Lavenda and E. Santamato, J. Math. Phys. **22**, 2926–2933 (1981).
[14] I. I. Gihman and A. V. Skorohod, Stochastic Differential Equations, Springer-Verlag, Berlin 1972, p. 93.
[15] M. Kac, Probability and Related Topics in the Physical Sciences, Interscience, New York 1960, Chapt. 4.
[16] M. Planck, Theory of Heat, Macmillan, London 1932, Part 4, Chapt. 1.
[17] D. Costantini, Phys. Lett. A **123**, 433–436 (1987).