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Equality governing nonequilibrium fluctuations and its information theory and thermodynamic interpretations

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The master equation is cast in the form of an equality involving the variation, in the course of a transformation, of a quantity playing the role of a generalized potential, weighted with the probability of allowable transformations emanating from different initial states. In the most general case this equality cannot be formulated entirely in terms of thermodynamic variables and state functions. Some conditions under which such a reduction becomes possible are identified and a comparison with fluctuation and work type relationships previously reported in the literature is carried out.

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I. INTRODUCTION

Recently, some relationships concerning the probabilistic properties of key thermodynamic quantities such as the work performed on a system or the entropy produced during an irreversible process have been derived [1–6]. They provide interesting links between macroscopic behavior on the one side and microscopic or mesoscopic level dynamics on the other and, contrary to the majority of earlier studies, they account for the effect of large fluctuations and strong nonequilibrium constraints. This makes them suitable for applications in a variety of problems involving nanoscale systems, from materials science to biology.

On the other hand, the converse of this problem, namely, the possibility to cast the salient features of the evolution of a system exhibiting complex behavior far away from equilibrium in terms of the key quantities featured in phenomenological thermodynamics remains open and in its most general version is, in fact, likely to have a negative answer [7,8]. In the present work we address this question from an alternative standpoint for a class of systems obeying Markovian dynamics as described by the master equation. We show in Secs. II and III that a quantity playing the role of a generalized potential exists, which satisfies an equality governing the nonequilibrium fluctuations underlying a transformation joining two states whose structure is reminiscent of the relations derived in Refs. [1,2], but which, in general, is not expressible in thermodynamic terms. Some conditions under which such a reduction becomes possible are subsequently identified (Secs. IV and V). The large system size limit of the master equation is considered in Sec. VI and the main conclusions are summarized in Sec. VII.

II. STEADY-STATE EQUALITY

Consider a system described by the master equation [9,10]

$$\frac{dP(X,t)}{dt} = \sum_{X' \neq X} [w_{XX'}P(X',t) - w_{X'X}P(X,t)], \tag{1}$$

where X is an extensive variable, $P(X,t)$ its probability distribution, and $w_{XX'}$ the probability per unit time for performing the transition from state X' to state X.

We express P in the form

$$P(X,t) = \exp[-\Psi(X,t)], \tag{2}$$

where the generalized potential Ψ (also referred to as “stochastic” potential) [9,11] is an extensive quantity in typical situations of physical relevance. Substituting Eq. (2) into eq. (1) yields

$$-\frac{d\Psi}{dt} = \sum_{X' \neq X} \{w_{XX'} \exp[-\Psi_t(X,X')] - w_{X'X}\}, \tag{3a}$$

where we have set

$$\Psi_t(X,X') = \Psi(X',t) - \Psi(X,t). \tag{3b}$$

In the steady state $d\Psi/dt=0$, we write Eq. (3a) as

$$\sum_{X' \neq X} w_{XX'} \exp[-\Psi_s(X,X')] = \sum_{X' \neq X} w_{X'X} = -w_{XX}. \tag{4}$$

Multiplying this relation by the time step Δt and using the well-known relationships between transition probabilities per unit time $w_{XX'}$ and transition probabilities $P_{\Delta t}(X|X')$,

$$w_{XX'}\Delta t = P_{\Delta t}(X|X') \quad (X' \neq X),$$

$$w_{XX}\Delta t = P_{\Delta t}(X|X) - 1 \tag{5}$$

we obtain

$$\sum_{X'} P_{\Delta t}(X|X')\exp[-\Psi_s(X,X')] = \langle \exp[-\Psi_s(X,X')]\rangle = 1, \tag{6}$$

where the average is over the one-step conditional probability and concerns the “initial” states X'.

The procedure can be easily extended to multi-step transitions. We use for this the Markov property [12]

$$P_n(X_n|X_0) = \sum_{X_1 \cdots X_{n-1}} P_{\Delta t}(X_1|X_0) \cdots P_{\Delta t}(X_n|X_{n-1}) \tag{7}$$

with

$$\sum_{X_j} P_{\Delta t}(X_j|X_{j-1}) = 1$$

as well as the identity

$$\begin{aligned} -\Psi_s(X_n,X_0) &\equiv \Psi_s(X_n) - \Psi_s(X_0) \\ &= \Psi_s(X_1) - \Psi_s(X_0) + \Psi_s(X_2) - \Psi_s(X_1) + \cdots \\ &\quad + \Psi_s(X_n) - \Psi_s(X_{n-1}) \\ &= -\Psi_s(X_1,X_0) - \cdots - \Psi_s(X_n,X_{n-1}). \end{aligned} \tag{8}$$

We obtain in this way,

$$\begin{aligned} &\sum_{X_0} P_n(X_n|X_0)\exp[-\Psi_s(X_n,X_0)] \\ &\quad = \sum_{X_0} P_{\Delta t}(X_1|X_0)\exp[-\Psi_s(X_1,X_0)]\cdots \\ &\quad \times \sum_{X_{n-1}} P_{\Delta t}(X_n|X_{n-1})\exp[-\Psi_s(X_n,X_{n-1})] \end{aligned}$$

or, using Eq. (6),

$$\sum_{X_0} P_n(X_n|X_0)\exp[-\Psi_s(X_n,X_0)] = \langle \exp[-\Psi_s(X_n,X_0)]\rangle = 1. \tag{9}$$

Equation (9) can be reexpressed in a form involving the transition from X_0 to X_n via intermediate states $X_1 \cdots X_{n-1}$, using the identity [see Eq. (8)]

$$-\Psi_s(X_n,X_0) = -\sum_{j=1}^{n} \Psi_s(X_j,X_{j-1})$$

along with the definition of marginal (reduced) probability distribution

$$P(X_n|X_0) = \sum_{X_1 \cdots X_{n-1}} P(X_1 \cdots X_n|X_0).$$

We obtain in this way

$$\sum_{X_0 \cdots X_{n-1}} P(X_1 \cdots X_n|X_0)\exp\left[-\sum_{j=1}^{n} \Psi_s(X_j,X_{j-1})\right] = 1. \tag{10}$$

Equations (9) and (10) constitute our first main result. We notice that they are formulated entirely in terms of the direct (forward in time) process as described by the master equation in its usual form of Eq. (1). Furthermore, the initial states and the transformations towards the final state are weighted by the stationary measure of the process. An extension to nonstationary states is beyond the scope of the present work. It would require the inclusion of the time derivative of the generalized potential [left-hand side of Eq. (3a)] and this would, in turn, mix one-state quantities such as $\Psi_t(X)$ to multistep ones, $\Psi_t(X_0,X_n)$.

III. CONNECTION WITH THE REVERSE MARKOV PROCESS

It is useful to write the exponential in Eq. (9) as

$$\exp[-\Psi_s(X_n,X_0)] = \exp[\Psi_s(X_n) - \Psi_s(X_0)] = \frac{P_s(X_0)}{P_s(X_n)}, \tag{11a}$$

where $P_s(X)$ stands for the invariant probability. The function summed over X_0 in Eq. (9) is thus

$$P_n(X_n|X_0)\exp[-\Psi_s(X_n,X_0)] = P_n(X_n|X_0)\frac{P_s(X_0)}{P_s(X_n)}. \tag{11b}$$

Now, for any stationary Markov process possessing a strictly positive invariant measure u_i and a conditional probability $P_{ij}^{(n)} = \mathrm{P}[X(n)=i|X(0)=j]$, the chain with conditional probabilities [12,13].

$$Q_{ji}^{(n)} = \mathrm{P}[X(0) = j|X(n) = i]$$

governs the past development of the original process, where Q_{ji} is given by a relation analogous to Eq. (11b),

$$Q_{ji}^{(n)} = \frac{P_{ij}^{(n)} u_j}{u_i}. \tag{12}$$

Furthermore $Q_{ji}^{(n)}$ is a stochastic matrix such as the sum over its "final" states j (which are the "initial" states of the original system) equals 1,

$$\sum_j Q_{ji}^{(n)} = 1. \tag{13}$$

Comparing Eqs. (11a), (11b), and (13) we see that this last relation expresses essentially the equality in Eq. (9). This connection is at first sight unexpected since, as pointed out in Sec. II, contrary to the relations derived in the context of fluctuation type theorems [1], the reverse process was not used in deriving Eq. (9). Notice that no conditions of detailed balance type need to be invoked at this stage. Detailed balance is actually recovered in the limit of a reversible chain for which $Q_{ij}^{(n)} = P_{ij}^{(n)}$, i.e., $\mathrm{P}[X(0)=i|X(n)=j] = \mathrm{P}[X(n)=i|X(0)=j]$ and Eq. (13) takes (for $n=1$) the familiar form $P_{ji}u_i = P_{ij}u_j$ expressing that the probability of i followed by j equals the probability of j followed by i.

A connection with the reverse Markov process can also be established at the level of Eq. (10). Indeed, the function summed over $X_0 \cdots X_{n-1}$ in this equation is now $P(X_1 \cdots X_n|X_0)P_s(X_0)/P_s(X_n)$. Using Bayes' rule

$$P(X_0 \cdots X_n) = P(X_0)P(X_1 \cdots X_n|X_0) = P(X_n)P(X_0 \cdots X_{n-1}|X_n), \tag{14}$$

this fuction reduces to the conditional probability $P(X_0 \cdots X_{n-1}|X_n)$ of a pathway $X_0 \cdots X_{n-1}$ given the final state X_n. This quantity, which is descriptive of the reverse process, is normalized to unity when summed over X_0 to X_{n-1}.

It is instructive to reexpress the foregoing relations in the form

$$\begin{aligned} r \equiv \exp\{-\Psi_s[X(n)=i,X(0)=j]\} &= \frac{P_s(j)}{P_s(i)} \\ &= \frac{\mathrm{P}[X(0)=j|X(n)=i]}{\mathrm{P}[X(n)=i|X(0)=j]} \end{aligned} \tag{15}$$

with

$$\begin{aligned} r_{\mathrm{eq}} \equiv \exp\{-\Psi_{\mathrm{eq}}[X(n)=i,X(0)=j]\} &= \frac{P_{\mathrm{eq}}(j)}{P_{\mathrm{eq}}(i)} \\ &= \frac{\mathrm{P}[X(n)=j|X(0)=i]}{\mathrm{P}[X(n)=i|X(0)=j]}, \end{aligned} \tag{16}$$

where the last part of equality (16) has now incorporated the detailed balance condition. Notice that r or r_{eq} are different from unity, unless P_s is state independent. This happens in the limit of an isolated system described by the microcanonical distribution.

One way to read Eqs. (15) and (16) is that if the transition from j to i leads to more probable (in the sense of the stationary measure) states (and is in this respect "thermodynamically" admissible) then r is exponentially small and Ψ_s is positive in the vast majority of realizations of this process. Furthermore, running the process backward in time is far less probable (though by no means impossible) compared to the direct evolution. These statements are reminiscent of the content of fluctuation type theorems [1], the equalities (9) and (10) themselves having a structure similar to Jarzynski's equality [2]. To implement such connections further one needs to establish a link between Ψ_s and thermodynamics, a question to which we turn shortly. But in as much as the generalized potential Ψ can be defined for arbitrary nonequilibrium states independent of any reference to phenomenological thermodynamics it seems legitimate to assert that relations such as Eqs. (9) and (10) are in fact valid in a wider range than the aforementioned relationships, embodying situations in which a thermodynamic formulation would prove impracticable.

IV. INFORMATION THEORETIC INTERPRETATION

Let us write the exponent in Eq. (9) as

$$\Psi_s(X_n,X_0) = \ln \frac{P(X_n)}{P(X_0)}. \tag{17}$$

In information theory one encounters situations where an observer disposing initially of a distribution $P_0(X)$ of a certain process is led to consider a new distribution $P(X)$ following, for instance, the availability of new data. The information gain associated with the passage from P_0 to P is then usually defined as [14]

$$\Delta I_P = \ln \frac{P(X)}{P_0(X)}. \tag{18}$$

Building on this idea, we may now regard Eq. (17) as the information gain associated with an evolution leading from X_0 to X_n, where "information" is here associated with the change of structure of P when moving from the environment of X_0 to that of X_n. Actually in the limit of X_n close to X_0 this procedure leads to the Fisher information, an established concept in statistics and information theory, defined as the mean of [15]

$$\Delta I_{x,\Delta x} = \ln \frac{P(x)}{P(x+\Delta x)}$$

over $P(x)$ in the limit $\Delta x \to 0$, where we have switched to the intensive variable x associated to X. We have

$$\Delta I_{x,\Delta x} = -\left[\Delta x \frac{dP/dx}{P} + \frac{\Delta x^2}{2}\left(\frac{dP/dx}{P}\right)^2 + \cdots\right]$$

and

$$I_F = -\lim_{\Delta x \to 0} \frac{1}{\Delta x^2}\langle \Delta I_{x,\Delta x}\rangle = \frac{1}{2}\int dx \frac{1}{P(x)}\left(\frac{dP(x)}{dx}\right)^2. \tag{19}$$

In statistics, the Fisher information provides a measure of the sensitivity of a probability distribution towards x (or, more generally, towards a set of parameters). It also shows up when considering the information entropy balance $-\frac{d}{dt}\int dx P(x) \ln P(x)$, where $P(x)$ satisfies the Fokker-Planck equation, in which it plays the role of "information entropy production" and is equal to the negative sum of the system's Lyapunov exponents [16].

In view of the foregoing one may write Eq. (9) as

$$\langle \exp[-\Delta I_{X_0,X_n}]\rangle = 1, \tag{20}$$

where the averaging is taken over the initial states X_0 and the exponent can be viewed as a "finite time" (fluctuating) generalized Fisher information. This quantity remains meaningful under both equilibrium and nonequilibrium conditions.

V. CONNECTIONS WITH THERMODYNAMICS

A. Brownian particle in an external electric field

Assuming linear friction law, the equation of motion has the form [17]

$$m\frac{dv}{dt} = -\zeta v + qE + F(t), \tag{21}$$

where v is the velocity; m, ζ, q, and E are the mass, friction coefficient, charge, and electric field, respectively; and $F(t)$ the random force, assumed to define a Gaussian white noise. The Fokker-Planck equation associated to Eq. (21), to which the master equation reduces for processes with continuous realizations reads [9,10]

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial v}\left(-\frac{\zeta}{m}v + \frac{qE}{m}\right)P + \frac{D}{m}\frac{\partial^2 P}{\partial v^2} \tag{22a}$$

and reduces further in the steady state to

$$D\frac{dP_s}{dv} = (-\zeta v + qE)P_s, \tag{22b}$$

where D is the noise strength and the boundary condition $P_s(\pm\infty)=0$ has been used. The exact solution of this equation satisfying the normalization condition is

$$P_s(v) = e^{-q^2E^2/2\zeta D}\sqrt{\frac{\zeta}{2\pi D}}\exp\left[-\frac{\zeta v^2}{2D} + \frac{q}{D}Ev\right]. \quad (23)$$

The exponent in Eqs. (9), (17), and (20) becomes

$$\Psi_s(0 \to n) = \Delta I_s(0 \to n) = \ln\frac{P_s(v_n)}{P_s(v_0)}$$
$$= \underbrace{-\frac{\zeta}{2D}(v_n^2 - v_0^2)}_{\text{equilibrium part}} + \underbrace{\frac{qE}{D}(v_n - v_0)}_{\text{nonequilibrium contribution}}. \quad (24)$$

Let us set

$$v = \bar{v} + \delta v, \quad (25a)$$

where the reference velocity $\bar{v}$ multiplied by the charge gives the macroscopic electric current switched on by the field

$$\bar{v} = \frac{qE}{\zeta}. \quad (25b)$$

Equation (24) becomes

$$\Psi_s(0 \to n) = \Delta I_s(0 \to n) = \frac{1}{kT}\frac{m}{2}(\delta v_0^2 - \delta v_n^2), \quad (26)$$

where we used the fluctuation-dissipation theorem $\zeta/D = m/(kT)$ [2,11].

We recognize in the factor multiplying $1/(kT)$, the excess kinetic energy of the particle (evaluated around the reference state $\bar{v}$) needed to bring the relative velocity to a value δv_n starting from δv_0. Notice that nonequilibrium enters at this level only through the reference state. On the other hand, expressing Eq. (21) in terms of δv, multiplying both sides by δv and integrating between the values $\delta v_n \equiv \delta v(t_n)$ and $\delta v_0 \equiv \delta v(t_0)$ yields

$$\frac{m}{2}(\delta v_n^2 - \delta v_0^2) = \int_{t_0}^{t_n} dt\, \delta v F_{\text{tot}} = -\delta W(0 \to n). \quad (27)$$

Here δW represents the excess work done on the system during the process by the total force (viscous plus electric plus random) acting on it—a quantity of direct relevance in thermodynamics—the excess being with respect to a reference situation in which the velocity of displacement would be equal to $\bar{v}$ throughout. Connections between the logarithm of the steady-state probability distribution and dissipated work have been reported in the context of kinetic theory studies of transport phenomena [17,18]. It is interesting to see that they can also be derived from the present study, where they are viewed as manifestations of a general relationship governing nonequilibrium fluctuations. Putting relations (24), (26), and (27) together we may write Eqs. (9) and (17), or (20) in the form

$$\left\langle \exp\left[\frac{-1}{kT}\delta W\right]\right\rangle = 1, \quad (28)$$

which has a structure similar to Jarzynski's equality [2].

B. Ideal, one variable systems undergoing first order reactions

The steady state measure describing this class of systems in the Poissonian [9]

$$P_s(X) = \frac{e^{-\bar{X}}\bar{X}^X}{X!}, \quad (29)$$

where X is an extensive variable representing the number of particles of a reactant and depending on the case, the reference state $\bar{X}$ is the state of equilibrium or a nonequilibrium steady state. Substituting into Eq. (11a) one obtains

$$-\Psi_s(X_n, X_0) = \ln\frac{\bar{X}^{X_0}X_n!}{\bar{X}^{X_n}X_0!}$$

or, using Stirling's formula $\ln X! \approx X\ln X - X$,

$$-\Psi_s(X_n, X_0) = -\left(X_n \ln\frac{\bar{X}}{X_n} - X_0\ln\frac{\bar{X}}{X_0} + X_n - X_0\right). \quad (30)$$

On the other hand, in an ideal system the entropy difference associated to a transformation from state X_0 to state X_n is [9,19]

$$\frac{1}{k}\Delta S = -\frac{1}{kT}(\mu_n X_n - \mu_0 X_0) + X_n - X_0, \quad (31a)$$

where

$$\mu(X) = \mu_X^* + kT\ln X. \quad (31b)$$

Let us rewrite the above expression by introducing the excess of μ_n, μ_0 over a value $\mu_{\bar{X}}$ associated to the reference state. We obtain

$$\frac{1}{k}\Delta S = X_n \ln\frac{\bar{X}}{X_n} - X_0\ln\frac{\bar{X}}{X_0} + X_n - X_0 - \frac{\mu_{\bar{X}}}{kT}(X_n - X_0)$$
$$= \Psi_s(X_n, X_0) - \frac{\mu_{\bar{X}}}{kT}(X_n - X_0), \quad (32)$$

where we used Eq. (30). Introducing the fluctuations around the reference state

$$\delta X = X - \bar{X} \quad (33)$$

one sees immediately that the last term in Eq. (32) accounts for the first order contributions to ΔS, whereas the remaining terms (which constitute Ψ_s) contain exclusively second and higher order terms in the fluctuations. Now at the level of the entropy balance equation [9,17]

$$\frac{dS}{dt} = \sigma + J_S, \quad (34)$$

second order terms in fluctuations are associated exclusively with the entropy production σ, whereas the entropy flux J_S is of the first order. Summarizing, then, $\Psi_s(X_n, X_0)$ represents the entropy cost $\Delta_i S$ for creating a fluctuating pathway between an initial and a final state or, alternatively, the excess in total dissipation (or "irreversible work")

$$\Sigma = \int_{t_0}^{t_n} dt\sigma \tag{35}$$

(beyond first order terms in the fluctuations) released as the system evolves along this pathway,

$$\Psi_s(X_n,X_0) = \frac{1}{k}\Delta_i S = \frac{1}{k}\Delta\Sigma. \tag{36}$$

Putting the above relations together we may write Eq. (9) in a form similar to Jarzynski's equality [2]

$$\left\langle \exp\left[-\frac{1}{k}\Delta\Sigma\right]\right\rangle = \left\langle \exp\left[-\frac{1}{k}\Delta_i S\right]\right\rangle = 1. \tag{37}$$

These relations should not be confused with the Einstein relation linking the probability of a fluctuation to the entropy change: the latter refers to fluctuations around a given state, whereas the former concern a transformation joining two different states.

C. Gaussian limit

In the limit of small fluctuations around $\bar{X}$, Eq. (32) reduces to a relation similar to Eq. (26),

$$\frac{1}{k}\delta^{(2)}S = \frac{1}{2\bar{X}}(\delta X_0^2 - \delta X_n^2) = \frac{1}{2k}\delta^{(2)}\Sigma, \tag{38}$$

where $\delta^{(2)}$ denotes the second order excess. As well known, in the same limit the stationary measure governing fluctuations around a reference state is given by a Gaussian as long as the system is far from criticality

$$P_s(X) \approx \exp\left[-\frac{(X-\bar{X})^2}{2s}\right], \tag{39}$$

where in equilibrium or in the continuous limit of the Poissonian the variance s reduces to $\bar{X}$, but remains otherwise different from $\bar{X}$. The quantity $\Psi_s(X_n,X_0)$ now becomes

$$\Psi_s(X_n,X_0) = \frac{1}{2s}[(X_0-\bar{X})^2 - (X_n-\bar{X})^2]. \tag{40}$$

It differs from $\frac{1}{2k}\delta^{(2)}S$ in Eq. (38) by a factor $\frac{\bar{X}}{s}$, which constitutes a signature of deviation from equilibrium or from Poisson statistics. The equality in Eq. (9) is no longer expressible entirely in terms of thermodynamic quantities, taking the form

$$\left\langle \exp\left[-\frac{\bar{X}}{s}\frac{\delta^{(2)}S}{2k}\right]\right\rangle = \left\langle \exp\left[-\frac{\bar{X}}{s}\frac{\delta^{(2)}\Sigma}{2k}\right]\right\rangle = 1. \tag{41}$$

D. Sign and order of magnitude of Ψ_s

(a) *Poisson statistics, approach to the asymptotic state* $\bar{X}$ *starting with initial states* X_0 *distributed around some* $\bar{X}_0 \neq \bar{X}$. Equation (30) becomes

$$\Psi_s(\bar{X},X_0) = \frac{1}{k}\Delta\Sigma_\infty = X_0 \ln\frac{X_0}{\bar{X}} + \bar{X} - X_0. \tag{42}$$

This quantity is positive definite. This property along with the extensive character of Ψ_s entails that $\exp[-\Psi(\bar{X},X_0)]$ featured in Eq. (9) or, alternatively, the ratio r in Eq. (15) are exponentially small. This reflects the fact that the probability to reach state $\bar{X}$ starting from a macroscopically different state X_0 through the direct process is overwhelmingly larger than the probability of a path corresponding to the reverse process.

(b) *Gaussian statistics*. According to Eq. (40),

$$\begin{aligned}\Psi(X_n,X_0) &> 0 \text{ for } |X_0-\bar{X}| > |X_n-\bar{X}|\\ &< 0 \text{ for } |X_0-\bar{X}| < |X_n-\bar{X}|\end{aligned} \tag{43}$$

with $\exp[-\Psi(X_n,X_0)]$ decreasing or increasing exponentially, respectively. The first alternative corresponds to a "thermodynamic" evolution where the system evolves towards states surrounding $\bar{X}$, the opposite being true for the second alternative. As both X_0 and X_n fluctuate Ψ will actually take negative values with some probability. This will be counteracted by the relative probabilities of the direct and the reverse process, so that the overall equality (9) will remain secured.

VI. LARGE SYSTEM SIZE (WKB) LIMIT

In this section we consider in some detail the case where the transition probabilities per unit time in the master equation (1) are extensive quantities proportional to the size N of the system, taken to be large. This is what happens in birth and death processes in general and chemical reactions in particular, as long as the units constituting the system interact via short-range forces. Writing $X' = X - r$, where X and r are integers, and introducing the intensive variable $x = X/N$ associated to X, we reexpress $w_{XX'} = Nw(\frac{X-r}{N}, r)$ and seek again for solutions of Eq. (1) of the form (2), where Ψ is now required to be extensive

$$\Psi(X,t) = N\phi(x,t) = \frac{1}{\epsilon}\phi(x,t) \ (\epsilon \ll 1). \tag{44}$$

Substituting into Eq. (1) and keeping the leading terms in ϵ one arrives in the steady state at the following equation for the generalized potential per unit size $\phi_s(x)$:

$$\sum_r w(x,r)(e^{r(\partial\phi_s/\partial x)} - 1) = 0. \tag{45}$$

This relation can be regarded as a Hamilton-Jacobi equation at zero "energy" of a system described by coordinates x and momenta $p = \partial\phi_s/\partial x$, whose "Hamiltonian" H reads [20,21]

$$H = \sum_r w(x,r)(e^{rp} - 1). \tag{46}$$

The following properties can then be established in all generality: ϕ satisfies an extremum principle expressed in terms of a path integral of the "Lagrangian" associated to H; ϕ possesses a local extremum along the solutions of the deterministic (mean field) limit of the master equation

$$\frac{d\bar{x}}{dt}=\sum_r rw(\bar{x},r)=0. \tag{47}$$

These properties subsist in the Fokker Planck limit and, on these grounds, it has been suggested by Jona-Lasinio *et al.* [22] that ϕ may be viewed as a generalized entropylike function. The question we address here is, rather, whether $\Psi_s(X_n,X_0)=\frac{1}{\epsilon}[\phi_s(x_0)-\phi_s(x_n)]$ bears any connection with the type of observables of phenomenological thermodynamics considered in the preceding section and, in particular, the entropy variation along a trajectory joining states X_0 and X_n. A glance at Eq. (45) suggests that the answer to this question should be in the negative in the most general case since, for one thing, ϕ_s appears to depend explicitly on the kinetics of the ongoing processes contrary to the entropy variation. Still, one can check straightforwardly that for the type of system considered in Sec. V B the connection sought holds true. To gain a closer insight on what may happen beyond the linear case we consider the following one-variable system involving chemical reactions of the autocatalytic type [23]

$$A+2X\underset{k_2}{\overset{k_1}{\rightleftharpoons}}3X, \quad X\underset{k_4}{\overset{k_3}{\rightleftharpoons}}B, \tag{48}$$

where X denotes the intermediate and the concentrations a and b of the initial and final products A and B are supposed to be controlled externally. The balance equation for the concentration $\bar{x}$ of X in the mean field limit is (we again limit ourselves to an ideal mixture)

$$\frac{d\bar{x}}{dt}=-k_2\bar{x}^3+k_1a\bar{x}^2-k_3\bar{x}+k_4b. \tag{49}$$

Introducing two parameters λ and μ (which are sufficient to fully unfold this cubic equation) through

$$k_3=3-\mu, \quad \frac{b}{a}=1-\lambda$$

fixing all others to the values

$$k_2=\frac{1}{a^2}, \quad k_1=\frac{3}{a^2}, \quad k_4=1$$

and performing the additional transformation $\bar{x}=a(1+z)$ one obtains in the steady state

$$z^3-\mu z+\lambda-\mu=0.$$

This equation gives rise to a pitchfork bifurcation at $\mu=0$ as long as $\lambda=\mu$, and to hysteretic behavior otherwise.

The Hamilton-Jacobi equation (45) associated to this system takes the form

$$(e^{\partial\phi_s/\partial x}-1)\left\{3\left(\frac{x}{a}\right)^2+1-\lambda-\frac{x}{a}\left[\left(\frac{x}{a}\right)^2+3-\mu\right]e^{-\partial\phi_s/\partial x}\right\}=0$$

and admits the (nontrivial) solution [24,25]

$$\frac{d\phi_s}{dx}=\ln\frac{x}{a}+\ln\frac{\left(\frac{x}{a}\right)^2+3-\mu}{3\left(\frac{x}{a}\right)^2+1-\lambda}. \tag{50}$$

Integrating over a transformation joining states $x_0=X_0/N$ and $x_n=X_n/N$ we obtain

$$\begin{aligned}-\Psi_s(X_n,X_0)&=\frac{1}{\epsilon}[\phi_s(x_n)-\phi_s(x_0)]\\&=-X_n\ln\frac{A}{X_n}+X_0\ln\frac{A}{X_0}+X_0-X_n\\&\quad+A\int_{X_0/A}^{X_n/A}d\left(\frac{X}{A}\right)\ln\frac{\left(\frac{X}{A}\right)^2+3-\mu}{3\left(\frac{X}{A}\right)^2+1-\lambda},\end{aligned} \tag{51}$$

where $A=aN$ denotes the number of particles of A. The part of the right-hand side of this relation preceding the integral over X/A has the same structure as in Eq. (30), where A plays the role of the reference state $\bar{X}$ [actually $\bar{X}=A$ is an exact steady state solution of the mean field equation (49) at the bifurcation point $\lambda=\mu=0$, but one may switch to any other reference solution up to terms linear in X_0-X_n]. If only this part were present the conclusions of Sec. V B would go through since the entropy difference along a path is still given here by Eq. (32) and the connection with thermodynamics would be secured. The presence of the last term compromizes this connection. On the other hand, ϕ_s in Eq. (50) may be interpreted as the thermodynamic potential in a hypothetical equilibrium system in which the first part of the right-hand side would correspond to the chemical potential of an ideal system while the second part would correspond to an activity coefficient accounting for the effects of nonideality. Under this mapping, then, of an ideal system undergoing nonlinear kinetics under nonequilibrium conditions into a nonideal system operating under equilibrium conditions a connection, albeit a formal one, between Eq. (9) and thermodynamics can be established.

So far our analysis accounts for arbitrarily large deviations. In the limit of small fluctuations and as long as the system remains far from the bifurcation point $\lambda=\mu=0$, Eq. (51) reduces to a quadratic form similar to Eq. (40). To determine the coefficient $1/s$ in front of the quadratic term we evaluate the second derivative of ϕ_s at a solution $\bar{x}$ of the mean-field equation (49) which, as pointed out earlier, corresponds to an extremum of the generalized potential. One finds in this way

$$\frac{1}{s}=\epsilon\frac{3\left(\frac{\bar{x}}{a}\right)^2+3-\mu-6\left(\frac{\bar{x}}{a}\right)}{\bar{x}\left[\left(\frac{\bar{x}}{a}\right)^2+3-\mu\right]}. \tag{52}$$

This expression reduces to $\epsilon/\bar{x}=1/\bar{X}$ in the equilibrium limit $k_1a=k_2\bar{x}_{\mathrm{eq}}$ or $\bar{x}_{\mathrm{eq}}=3a$. It remains otherwise different from

$1/\bar{X}$ entailing, again, that Eq. (9) is no longer expressible entirely in terms of thermodynamic quantities. As the system approaches the bifurcation point $\lambda=\mu=0$ the expansion becomes inadequate and at the bifurcation point itself the dominant contribution becomes quartic in $X-\bar{X}$, signaling the breakdown of the Gaussian approximation.

VII. CONCLUSIONS

In this work we addressed the statistical properties of transformations between states in systems obeying Markovian dynamics. We have shown that under steady-state conditions the master equation can be cast in the form of an equality involving the variation in the course of the transformation of a quantity playing the role of a generalized potential, weighted with the probability of allowable transformations emanating from different initial states. This equality is formulated entirely in terms of the direct (forward in time) process and, in the most general case, cannot be cast in terms of quantities featured in phenomenological thermodynamics. On these grounds it constitutes a generalization of fluctuation and work type relationships derived previously [1,2] in the literature. Some conditions under which the generalized potential can be expressed in information theoretic terms or in terms of thermodynamic variables and state functions have been identified. The results derived hold for arbitrarily large fluctuations and also allow one to derive straightforwardly the Gaussian limit of small fluctuations. In particular, fluctuations associated with "non-thermodynamic" transformations, reflected by a negative sign of the variation of the generalized potential are fully accounted for. The approach can accommodate evolution under both equilibrium and strongly nonequilibrium conditions.

Our approach brings out quite naturally the role of the reverse Markov process, even though this process does not enter explicitly in the formulation of equalities (9) and (10) contrary to what happens in the formulation of fluctuation theorem type relationships. In particular, from Eq. (15) one has

$$\Psi_s[X(n)=i,X(0)=j]=\ln\frac{P[X(n)=i|X(0)=j]}{P[X(0)=j|X(n)=i]}. \quad (53)$$

The quantity on the right-hand side of this equation plays an important role in the work of Lebowitz and Spohn [3], Maes [4], Gaspard [6], as well as Jiang *et al.* [5], Kawai *et al.* [26], and Porporato *et al.* [27], where it is viewed as a "deficit" of the equiprobability of the direct and reverse transformations. As stated already in the Introduction, contrary to the aforementioned works and the work of Refs. [1,2], the problem addressed here has to do with some general properties satisfied by the steady-state solution of the master equation along a transformation joining far-from-equilibrium states rather than with the statistical properties of certain observables of classical thermodynamics such as work and entropy production.

Having shown (see especially Sec. VI) that in the most general case transformations joining far-from-equilibrium states cannot be characterized solely by the standard thermodynamic quantities deriving from energy and entropy balance, the question arises as to whether one can hint at some meaningful alternatives. We have identified two such possible alternatives: information gain (Sec. IV) and, in the large system size limit (Sec. VI), the generalized potential $\frac{1}{\epsilon}\phi$. This latter quantity enjoys the variational properties of a Lyapunov function and is in this respect reminiscent of the thermodynamic potentials of classical theory, as also suggested by Jona-Lasinio *et al.* [22]. In a different vein a fluctuating "trajectory dependent" entropy has recently been introduced by Seifert [28] as the logarithm of the inverse of the probability distribution, and its time evolution has been connected to fluctuation-type theorems. Although analogous to our generalized potentials Ψ and ϕ [Eqs. (2) and (44)], as seen in Sec. IV this quantity per se is related more closely to the information rather than to the thermodynamic entropy. In particular, it was shown in Ref [16] that its balance as obtained from the forward time evolution leads to a positive definite source term involving some intrinsic properties of the dynamics such as the sum of the Lyapunov exponents. It is only when the contributions due to the nonequilibrium constraints are displayed explicitly that a connection with thermodynamic dissipation can be established. But if in the spirit of fluctuation theorems, the behavior of the weight of a trajectory under time reversal is also considered some general equalities involving the change of this fluctuating entropy along a transformation can indeed be derived [28]. This is different in scope from our formulation, in which the general equality established is expressed entirely in terms of the properties of the forward process.

The understanding of the thermodynamic status of the solutions of the master equation under far-from-equilibrium conditions remains incomplete. More work is necessary in order to disentangle the relative roles of the intrinsic dynamics (particularly of nonlinearity) and the way the system communicates with the external world through appropriate thermostats. A further interesting extension would be to consider nonstationary processes in connection, in particular, with the presence of time-dependent parameters or boundary conditions modulating the system's evolution.

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