Stochastic approach to irreversible thermodynamics

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An extension of classical irreversible thermodynamics pioneered by Ilya Prigogine is developed, in which fluctuations of macroscopic observables accounting for microscopic-scale processes are incorporated. The contribution of the fluctuations to the entropy production is derived from a generalized entropy balance equation and expressed in terms of the fluctuating variables, via an extended local equilibrium Ansatz and in terms of the probability distributions of these variables. The approach is illustrated on reactive systems involving linear and nonlinear steps, and the role of the distance from equilibrium and of the nonlinearities is assessed. *Published by AIP Publishing.*
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One of the principal attributes of thermodynamics is to provide a unified description of natural systems which is largely independent of their internal structure and of the details of the ongoing processes. At the basis of this description are appropriately chosen state functionals depending on a limited number of observables, whose properties reflect in one way or the other the nature of the states attained by the system when the conditions to which it is submitted are varied. Thermodynamics attains its highest power and universality in the state of thermodynamic equilibrium as expressed by the extremal properties of the thermodynamic potentials, such as maximum entropy (in an isolated system) or minimum free energy (in systems at constant temperature). As a corollary, the state of thermodynamic equilibrium is unique and possesses strong stability properties. Ilya Prigogine's historical achievement has been to develop a thermodynamic approach applicable to states out of equilibrium. In doing so, he revealed new facets of thermodynamics in relation to self-organization, evolution, and the foundations of irreversibility.

I. INTRODUCTION

Let $\{x_i\}\ i = 1\ldots n$ be the set of observables determining the state of a system as a whole—for instance, total energy E, volume V, and particle numbers N_j of the system's components. At equilibrium, the state functionals are fully determined by these variables. In particular, entropy is linked to E, V, and N_j through the Gibbs relation

$$S_{eq} = S(E, V, \{N_j\}). \tag{1}$$

A decisive step toward the development of nonequilibrium thermodynamics has been to apply Gibbs type relations locally, within each volume element surrounding an arbitrary point $\mathbf{r}$, being understood that the state variables may now depend on space and evolve in time[1–3]

$$s = s\big(e(\mathbf{r}, t), v(\mathbf{r}, t), \{c_j(\mathbf{r}, t)\}\big), \tag{2}$$

where the quantities featured are now entropy and energy densities, specific volume, and concentrations, or more generally

$$s = s\big(\{x_i(\mathbf{r}, t)\}\big). \tag{3}$$

The range of validity of this local equilibrium approach to nonequilibrium thermodynamics has been analyzed extensively in the literature[2,4–6] and shown to include all phenomena described by the laws of macroscopic physics and chemical kinetics, as long as the constraints acting on the system vary in space and/or time on scales that are much longer than the scales of microscopic-level processes.

On the other hand, the quantities in the right hand sides of Eqs. (2)–(3) satisfy classical balance equations expressing their rates of change in time as the sum of a flux term accounting for the exchanges between a volume element and its environment and a source term accounting for processes occurring spontaneously within the volume element. The decisive step accomplished by Eqs. (2)–(3) is that one is now in the position to deduce from the balance equations of the state variables a balance equation of local entropy in the form

$$\frac{\partial s}{\partial t} = -\mathrm{div}\,\mathbf{J}_s + \sigma. \tag{4}$$

Here, $\mathbf{J}_s$ and σ are the entropy flux and entropy production, respectively, and σ takes the celebrated bilinear form

$$\sigma = \sum_k J_k X_k, \tag{5}$$

where J_k are the fluxes of different processes present and X_k the associated thermodynamic forces expressing the presence of nonequilibrium constraints. The second law of thermodynamics imposes that σ is a non-negative quantity whose value is zero at equilibrium and strictly positive out of equilibrium whatever the values of the fluxes and forces might be, a property that constitutes the thermodynamic signature of irreversibility. An important point is that X_k can be expressed entirely in terms of the state variables and their spatial gradients, whereas J_ks constitute a new set of variables to be added, *a priori*, to the set of classical state variables. Stated differently, in their most general form, the balance equations for the variables $\{x_i\}$ are not closed and do not allow one to predict the time evolution of the underlying system. To achieve closure, one needs thus to express the fluxes in terms of the thermodynamic forces subject to the condition that the entropy production should remain non-negative. Furthermore, in the state of thermodynamic equilibrium, J_k and X_k should vanish simultaneously.

The balance equations for $\{x_i\}$ take now the form

$$\frac{\partial x_i}{\partial t} = f_i(\{x_j\}, \lambda), \tag{6}$$

where the evolution laws $\{f_i\}$ are, typically, nonlinear in the state variables and λ is a set of control parameters accounting for the constraints acting on the system. We will be referring to the description afforded by Eq. (6), in which macroscopic observables are fully decoupled from the microscopic degrees of freedom, as the mean-field description. In the sequel, we will be focusing on systems undergoing purely dissipative processes such as diffusion, heat conduction, and chemical reactions, leaving out systems possessing inertial elements such as electric circuits or deformable solids.

On the basis of the foregoing, one may define the linear range of nonequilibrium thermodynamics as the range of phenomena where the constraints X_k are weak and the fluxes are related linearly to the constraints

$$J_k = \sum_l L_{kl} X_l. \tag{7}$$

The coefficients L_{kl} featured in this relation are intrinsic to the system, independent of the nonequilibrium constraints. They depend, in principle, on the state variables $\{x_i\}$ and satisfy the Onsager reciprocity relations $L_{kl} = L_{lk}$ for suitable choices of fluxes and forces. The entropy production [Eq. (5)] becomes now a quadratic function of Xs, and the positivity condition dictated by the second law imposes that the eigenvalues of the matrix formed by L_{kl} should be non-negative. Under the additional restrictions of time-independent constraints and of strict linearity in the sense that L_{kl} can be treated as constants, one can then show that the total entropy production

$$P = \int d\mathbf{r}\, \sigma(\mathbf{r}, t) > 0 \tag{8a}$$

satisfies the inequality

$$\frac{dP}{dt} \leq 0. \tag{8b}$$

Relations (8a) and (8b) express celebrated Prigogine's minimum entropy production theorem,[1–3] a variational principle, implying that in the linear range of irreversible processes, a system will evolve in a way to attain a unique nonequilibrium steady state in which the entropy production—which plays here the role of a Lyapunov function—attains its minimum value. As a corollary, such states are universal attractors, in the sense that the solutions of the dynamical system defined by the mean-field equation (6) corresponding to them are stable against perturbations. We witness here the appearance of a new thermodynamic potential extending those familiar from equilibrium thermodynamics, governing wide classes of phenomena occurring in the linear range of irreversible processes.

The possibility of extending relations such as (8a) and (8b) beyond the linear range has attracted considerable attention. Now, this is precisely the range where, beyond some critical nonequilibrium threshold, the nonlinearities in the evolution laws [Eq. (6)] become effective, giving rise to dissipative structures and other spectacular self-organization phenomena in the form of multiple steady states, sustained oscillations in time, or spatial patterns.[3,7] This has led Prigogine and his colleague Paul Glansdorff to realize that under these conditions, a universal variational principle could not be expected to exist since the uniqueness and stability of nonequilibrium states are now *a priori* compromised. However, despite this basic limitation, they were able to establish a link between thermodynamics as expressed by the local equilibrium hypothesis [Eq. (3)] and nonlinear dynamics as expressed by the mean-field equation (6). Their starting point is that within the realm of the local equilibrium assumption, the second order excess entropy around a nonequilibrium state is bound to be negative as long as the equilibrium state is stable

$$\delta^{(2)} s \leq 0. \tag{9a}$$

Now, the time derivative of $\delta^{(2)} s$ can be shown to reduce to the excess entropy production, $d\,\delta^{(2)} s/dt = \sum_k \delta J_k\, \delta X_k$, where δJ_k, δX_k stand for the excess fluxes and forces associated with process k, respectively, resulting from small perturbations of reference states on the thermodynamic branch, the branch of states extrapolating states close to equilibrium. Combining with (9a), one arrives then at a thermodynamic linear stability criterion of nonequilibrium states featuring the excess entropy production[3,8]

$$\sum_k \delta J_k\, \delta X_k > 0. \tag{9b}$$

The point is that while in the linear range this inequality holds unconditionally on the grounds of the minimum entropy production theorem, far from equilibrium, it may be compromised. The system will then evolve toward states that will be qualitatively different from those on the thermodynamic branch. Inequalities (9) highlight therefore the role of nonequilibrium as a source of self-organization and complexity. They mark the limits of how far one can go in the study of far from equilibrium phenomena within the frame of a thermodynamic description.

In this paper, an extension of thermodynamics in a form where the limitations inherent in a purely macroscopic approach are overcome is outlined. The basic idea we shall follow is to explore the properties of nonequilibrium nonlinear systems by means of an enlarged description in which $\{x_i\}$, which remain the sole state variables, satisfy now evolution laws complementing the mean-field equations (6) by information pertaining to the fluctuations, the spontaneous deviations from the values provided by the phenomenological laws of evolution arising from microscopic-scale processes. Fluctuations are universal phenomena occurring in all natural systems, but typically their effect on macroscopic sized many particle systems operating in a unique stable state is very small. The situation changes radically in nanoscale systems or in systems of restricted geometry, which are attracting increasing attention in connection with, among others, molecular and cellular biology and materials science and whose study highlights the need to address the role of microscopic-level processes on the evolution of macroscopic observables. Furthermore, even in macroscopic size systems, in the presence of instabilities arising beyond some critical distance from equilibrium, the evolution becomes at some stage fluctuation driven since, fundamentally, fluctuations are the only intrinsic source of variability (as opposed to external perturbations) enabling a system to perform transitions between states.[7]

The natural approach to fluctuations is the probabilistic approach. Looking at the system through an appropriate space and time window, one may argue that there is memory loss of the past history, owing to the large number of microscopic-scale events that drove the system in a state where all variables with the exception of the macroscopic ones are in a regime of local equilibrium. In this coarse-grained description, the dynamics of fluctuations of the observables $\{x_i\}$ reduces to a Markov process. In Sec. II, starting with the set of evolution equations for the state variables featured in the traditional macroscopic description, we account for the presence of fluctuations through appropriate flux and source terms assimilated to uncorrelated random processes. We next extend Prigogine's Ansatz [Eq. (3)] and introduce a fluctuating entropy in the form of a random functional related to the fluctuating state variables by the same relation as in thermodynamic equilibrium. We derive a balance equation from which we identify the fluctuating entropy flux and fluctuating entropy production and analyze their principal statistical properties. A complementary approach based on a master equation for the probability to be in state $\{x_i\}$ at time t is developed in Sec. III. The main properties of the solutions of this equation are summarized and are shown to lead, under quite general conditions, to generalized potential-like functions characterizing the complexity of nonequilibrium states and possessing universal variational properties applicable to the fully nonlinear range of irreversible processes. The analysis is subsequently brought in a form close to a thermodynamic formalism by deriving a balance equation for the entropy of the underlying Markov process, from which the probabilistic analog of entropy production is identified and compared to the entropy production of irreversible thermodynamics. In Sec. IV, explicit examples are analyzed, the role of nonlinearities is assessed, and the predictions of the formalisms developed in Secs. II and III are compared. The main conclusions are summarized in Sec. V.

II. STOCHASTIC THERMODYNAMICS: EXTENDED LOCAL EQUILIBRIUM APPROACH

A major challenge arising in extending thermodynamics is to dispose of an adequate definition of entropy and entropy production accounting for the effect of the fluctuations and reducing to Prigogine's formalism of classical irreversible thermodynamics in the mean-field limit. In this section, we develop an extension in which this correspondence is secured automatically.

Let us write the balance equations for the variables $\{x_i\}$ in a form to which we alluded already in Introduction

$$\frac{\partial x_i}{\partial t} = -\mathrm{div}\, \mathbf{\Phi}_i + \sigma_i, \tag{10}$$

where $\mathbf{\Phi}_i$ is the flux of x_i resulting from exchanges between a volume element surrounding point $\mathbf{r}$ and its environment and σ_i is a source term resulting from internal processes generated by the system itself. To account for the presence of fluctuations, we decompose $\mathbf{\Phi}_i$ and σ_i into a systematic part related to the nonequilibrium constraints acting on the system by appropriate closure relations as discussed in Introduction and a random force modeling the effect of microscopic level processes on the evolution of the macroscopic variables[9]

$$\mathbf{\Phi}_i = \mathbf{J}_i\big(\{x_j(\mathbf{r},t)\}, \{\nabla x_j(\mathbf{r},t)\}, \ldots\big) + \mathbf{j}_i(\mathbf{r},t), \tag{11}$$

$$\sigma_i = \sum_\rho \alpha_{i\rho}\big[W_\rho(\{x_j(\mathbf{r},t)\}) + w_\rho(\mathbf{r},t)\big]. \tag{12}$$

In these expressions, W_ρ are the rates of different internal processes $\rho = 1 \ldots r$, and $\alpha_{i\rho}$ are the process-dependent numerical coefficients.

The basic Ansatz of our extended local equilibrium approach[10,11] is that the entropy density $s(\mathbf{r},t)$ of the system will depend on space and time through the space and time dependencies of the fluctuating observables $\{x_i\}$

$$s = s(\{x_i(\mathbf{r},t)\}). \tag{13}$$

The rate of change of entropy can thus be written as

$$\frac{\partial s}{\partial t} = \sum_i \left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}} \frac{\partial x_i}{\partial t} \tag{14a}$$

or, using (10)–(12),

$$\frac{\partial s}{\partial t} = \sum_i \left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}} \left[-\mathrm{div}\,(\mathbf{J}_i + \mathbf{j}_i) + \sum_\rho \alpha_{i\rho}(W_\rho + w_\rho)\right]. \tag{14b}$$

Relation (14b) allows us to derive a balance equation for entropy extending Eq. (4)

$$\frac{\partial s}{\partial t} = -\mathrm{div}\,\mathbf{J} + \sigma, \tag{15}$$

where the entropy flux $\mathbf{J}$ and the entropy production σ are given by

$$\mathbf{J} = \sum_i (\mathbf{J}_i + \mathbf{j}_i)\left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}}, \tag{16a}$$

$$\sigma = \sum_i (\mathbf{J}_i + \mathbf{j}_i)\cdot\nabla\left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}} + \sum_{i,\rho}\left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}} \alpha_{i\rho}(W_\rho + w_\rho). \tag{16b}$$

These relations highlight the fact that s and its rate of change are to be viewed as stochastic fields incorporating the variability associated with the presence of fluctuations.

It should be kept in mind that the decomposition into the two terms of the right hand side of Eq. (15) is not unique. In the absence of fluctuations, the non-negativity of entropy production as required by the second law of thermodynamics imposes that whatever the decomposition is chosen, the following condition should be satisfied [cf. also Eq. (5)]

$$\sum_i \mathbf{J}_i \cdot \mathbf{F}_i + \sum_\rho \mathcal{A}_\rho W_\rho \geq 0, \tag{17a}$$

expressing, basically, that the fluxes $\mathbf{J}_i$ and W_ρ should somehow be aligned to the thermodynamic forces

$$\mathbf{F}_i = \nabla \left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}}, \quad \mathcal{A}_\rho = \sum_i \alpha_{i\rho} \left(\frac{\partial s}{\partial x_i}\right)_{x_{j\neq i}}. \tag{17b}$$

In the presence of fluctuations, it seems natural to still adopt the decomposition leading to Eqs. (15) and (16). The systematic parts $\mathbf{J}_i$ and W_ρ of the fluxes become now stochastic variables *via* their dependence on $\{x_i(\mathbf{r},t)\}$ but are still expected to satisfy relations (17). On the other hand, the random parts $\mathbf{j}_i$ and w_ρ need not be aligned to the thermodynamic forces, even if the latter incorporate the effects of fluctuations. This reflects the fact that with some probability, as a result of microscopic-level processes, $\mathbf{j}_i$ and w_ρ may be led to be in opposition with respect to the action of an instantaneous thermodynamic force. Then, the parts

$$\sum_i \mathbf{j}_i \cdot \mathbf{F}_i, \quad \sum_\rho \mathcal{A}_\rho w_\rho$$

will yield negative contributions. One of our goals is to analyze the extent to which these contributions may "contaminate" σ as a whole and bring it, with some probability, to negative values.

In the light of the foregoing, stochastic thermodynamics has to do with the properties of the fluctuation-generated deviations of s, $\partial s/\partial t$, $\mathbf{J}$, and σ from reference values associated with the macroscopic values $\{x_{im}\}$ taken by the observables at the level of a mean-field description in which such fluctuations are not incorporated. We are especially interested in the evolution around an asymptotically stable steady state. Setting

$$\begin{aligned} x_i &= x_{im} + \Delta x_i \\ \mathbf{J}_i &= \mathbf{J}_{im} + \Delta \mathbf{J}_i, \quad \mathbf{F}_i = \mathbf{F}_{im} + \Delta \mathbf{F}_i \\ W_\rho &= W_{\rho m} + \Delta W_\rho, \quad \mathcal{A}_\rho = \mathcal{A}_{\rho m} + \Delta \mathcal{A}_\rho \end{aligned} \tag{18}$$

we may decompose the fluctuating entropy production σ as [cf. (16b) and (17)]

$$\sigma = \sigma_m + \Delta\sigma \tag{19}$$

with

$$\sigma_m = \sum_i \mathbf{J}_{im} \cdot \mathbf{F}_{im} + \sum_\rho \mathcal{A}_{\rho m} W_{\rho m}, \tag{20}$$

$$\begin{aligned} \Delta\sigma = &\sum_i (\Delta\mathbf{J}_i \cdot \mathbf{F}_{im} + \mathbf{J}_{im} \cdot \Delta\mathbf{F}_i + \mathbf{j}_i \cdot \mathbf{F}_{im}) \\ &+ \sum_\rho (\Delta W_\rho \mathcal{A}_{\rho m} + W_{\rho m} \Delta\mathcal{A}_\rho + w_\rho \mathcal{A}_{\rho m}) \\ &+ \sum_i \Delta\mathbf{J}_i \cdot \Delta\mathbf{F}_i + \sum_\rho \Delta W_\rho \Delta\mathcal{A}_\rho \\ &+ \sum_i \mathbf{j}_i \cdot \Delta\mathbf{F}_i + \sum_\rho w_\rho \Delta\mathcal{A}_\rho. \end{aligned} \tag{21}$$

We notice that σ_m is identical to the entropy production of macroscopic thermodynamics [Eq. (5)]. The point is that, in addition to this part, we now have a contribution $\Delta\sigma$ arising from the fluctuations. We will refer to this new part as the stochastic entropy production or the entropy production of the fluctuations. The first two sums in Eq. (21) include all the first-order contributions with respect to the deviations Δx_i, while the remaining four sums start with second-order contributions. Of these, the first two have a structure similar to the excess entropy production as developed by Glansdorff and Prigogine [see Eq. (9b)]. A similar procedure can be carried out for the entropy flux.

Ordinarily, in the framework of a stochastic description, one decomposes the variables into the sum of their values averaged over different realizations of the random forces and of a term representing the fluctuations. In the present case, this would lead to

$$\begin{aligned} x_i &= \bar{x}_i + \delta x_i \\ \sigma &= \bar{\sigma} + \delta\sigma \end{aligned} \tag{22}$$

with $\bar{\sigma}$, $\delta\sigma$ given by expressions similar to those of Eqs. (20) and (21), the difference being that the subscript "m" is replaced by averaging and the deviations $\Delta\mathbf{J}_i$, etc., are replaced by the fluctuations $\delta\mathbf{J}_i$ around the averages. In a linear system, the mean and the macroscopic mean-field values coincide, and the deviations from the macroscopic state can be identified to the fluctuations around the mean. The situation is different in nonlinear systems, where the macroscopic (mean-field) values differ from the mean values by quantities related to the strength of the fluctuations. In all cases, and provided that the system is ergodic, the mean value of the entropy derivative in Eq. (15) will be zero for asymptotically long times and thus

$$\bar{\sigma} = \text{div}\,\bar{\mathbf{J}}. \tag{23a}$$

An equality of this kind is known to hold true in classical irreversible thermodynamics when a system has reached a steady state. It follows therefore that the mean total entropy production of the fluctuations is bound to be equal to the associated mean entropy flux exchanged through the boundaries

$$\overline{\Delta\sigma} = \text{div}\,\overline{\Delta\mathbf{J}}. \tag{23b}$$

The interest of the approach outlined in this section is that, in addition to the mean values, one is in the position to obtain information on the probability densities of $\Delta\sigma$ and related quantities. For this purpose, the properties of the random forces $\mathbf{j}_i$ and w_ρ will need to be prescribed. We will adopt the assumption of Gaussian white noise usually made in the literature, based once again on the time scale separation argument used in Introduction. More specifically, we stipulate that [cf. Eqs. (11) and (12)]

$$\overline{w_\rho} = 0, \quad \overline{w_\rho(\mathbf{r}, t)\, w_{\rho'}(\mathbf{r}', t)} = q_\rho^2\, \delta^{Kr}_{\rho,\rho'}\, \delta(\mathbf{r} - \mathbf{r}')\, \delta(t - t')$$
$$\bar{\mathbf{j}}_i = 0, \quad \overline{\mathbf{j}_i(\mathbf{r}, t)\, \mathbf{j}_k(\mathbf{r}', t)} = Q_i^2\, \delta^{Kr}_{i,k}\, \delta(\mathbf{r} - \mathbf{r}')\, \delta(t - t'), \tag{24}$$

where q_ρ^2, Q_i^2 are the spectral intensities of the associated noises. At this stage, they are regarded as additional parameters, but in actual fact, as will be seen in Sec. IV, their values can be related to intrinsic properties through fluctuation-dissipation type relationships. Furthermore, they are inversely proportional to the system size, a property guaranteeing that in macroscopic size systems, the contribution of the entropy production of fluctuations will be small compared to the mean-field part.[12,13]

The presence of delta functions in Eq. (24) introduces singular contributions in expressions such as Eq. (21). To cope with this difficulty, we will be led to focus on the time-averaged fluctuating entropy production over a time interval t

$$\Sigma_t = \frac{1}{t}\int_0^t dt' \sigma(t'). \tag{25}$$

Some qualitative features can already be anticipated at this stage. First, on the grounds of the central limit theorem, the probability distribution of Σ_t is expected to be Gaussian.[14] On the other hand, owing to the presence of contributions containing explicitly the random forces, the existence of a non-zero probability mass in the region of negative Σ_t values cannot be excluded. Now, the central limit theorem does not provide much information on tail effects associated with such drastic deviations from the mean. The large deviation theory provides the missing information by showing that the probability of, e.g., Σ_t being larger than some threshold values y decays exponentially with time[15,16]

$$P(\Sigma_t > y) \approx \exp(-t\, I(y)), \tag{26}$$

where the rate function $I(y)$ is threshold and system dependent. Explicit expressions of probability distributions for representative systems will be derived in Sec. IV.

III. STOCHASTIC THERMODYNAMICS: MASTER EQUATION APPROACH

In this section, we outline an alternative approach to stochastic thermodynamics based on the evolution laws of the probability distributions of the state variables. Let $P_k(t)$ be the probability to be in a state k associated with a particular set of values of those variables. This probability evolves in time as a result of transitions between k and the other available states l. We begin by adopting a discrete time picture and choose a time window Δt such that the system can undergo at most one transition. We denote by $W_{\Delta t}(k|l)$ the conditional probability to perform a transition to k starting from state l during this interval. The Markovian assumption formulated in Introduction then leads us to write the following *master equation* for $P_k(t)$ (Refs. 7, 12, and 13)

$$P_k(t + \Delta t) = \sum_l W_{\Delta t}(k|l)\, P_l(t) \tag{27a}$$

subject to positivity and normalization conditions

$$W_{\Delta t}(k|l) \geq 0, \quad \sum_k W_{\Delta t}(k|l) = 1. \tag{27b}$$

To establish the connection with macroscopic thermodynamics and with the formulation of Sec. II, we will be especially interested in the continuous time limit of Eq. (27) and in cases where the state variables are extensive quantities changing by discrete jumps r_i. To avoid confusion, we will hereafter denote these extensive variables by $\{X_i\}$.

Taking the limit $\Delta t \to 0$ in Eq. (27a) yields

$$\frac{dP_k(t)}{dt} = \sum_{l \neq k} [w(k|l)\, P_l(t) - w(l|k)\, P_k(t)], \tag{28a}$$

where the transition probabilities per unit time are related to the quantities $W_{\Delta t}$ in Eq. (27a) by

$$w(k|l) = \frac{W_{\Delta t}(k|l) - \delta^{Kr}_{k,l}}{\Delta t}. \tag{28b}$$

Arguing in terms of states leads typically to a view in which the contributions of individual processes are lumped. For instance, different processes leading to the change in a particular extensive variable from a value X to a value $X - r$ will be part of a single transition between the same initial and final states, and the associated transition rates will be added to yield the overall probability per unit time for the transition between these states. Now, in many instances, it will be essential to identify the contribution of individual variables and processes to the evolution. This will amount to setting $\{X_i\}$ for state k, $\{X_i - r_{i\rho}\}$ for state l and write the master equation for the probability $P(\{X_i\}, t)$ in the following form:[7]

$$\frac{dP(\{X_i\}, t)}{dt} = \sum_\rho \big[w_\rho(\{X_i\}|\{X_i - r_{i\rho}\})\, P(\{X_i - r_{i\rho}\}, t) - w_{-\rho}(\{X_i - r_{i\rho}\}|\{X_i\})\, P(\{X_i\}, t)\big]. \tag{29a}$$

Here, ρ runs over all elementary processes occurring within the system and $-\rho$ for the reverse processes whose presence is a consequence of the property of detailed balance at the state of equilibrium. For systems governed by short-range interactions, the conditional probabilities are extensive, i.e., equal to a parameter N measuring the size of the system multiplied by a function of the same form, in which $\{X_i - r_{i\rho}\}$ are replaced by their intensive counterparts

$$w_\rho(\{X_i\}|\{X_i - r_{i\rho}\}) = N\, \tilde{w}_\rho(\{x_i\}, \{r_{i\rho}\}), \quad \{x_i\} = \left\{\frac{X_i}{N}\right\}. \tag{29b}$$

The explicit form of the conditional probability per unit time integrates information on the physics underlying different elementary processes. Inasmuch as the mean-field rate functions f_i in Eq. (6) are also constructed on the basis of this information, a compatibility condition is needed, expressing that in the large N limit, the weighted sum of the rates of transitions involving variable i summed over all processes should reduce to the rate function f_i

$$\sum_\rho r_{i\rho}\,\tilde{w}_\rho\big(\{x_i\},\{r_{i\rho}\}\big) = f_i. \tag{30}$$

This property guarantees in turn that the equation for the average value $\langle X_i\rangle$ generated by Eq. (29a) expressed in terms of intensive variables will display the average value $\langle f_i\rangle$ of the rate function f_i. In a linear system $\langle f_i(\{x_j\})\rangle = f_i(\{\langle x_j\rangle\})$, i.e., the mean-field description is recovered as an exact consequence of the master equation. The situation is different in nonlinear systems: the equation for $\langle x_i\rangle$ then contains, in addition to the mean-field part, contributions involving higher moments (e.g., variances) of the fluctuations.

A major feature of the description adopted in this section is that Eqs. (27)–(29) are linear with respect to the probability distribution P. This is in contrast to the nonlinearity inherent to the mean-field description. A second important property is that as long as the stochastic process associated with the evolution of $\{X_i\}$ is ergodic, these equations display strong stability properties in the sense that they possess a unique stationary state distribution, which is reached irreversibly in the course of time starting from a sufficiently regular initial distribution. The conjunction of these two properties of linearity and stability allows one to overcome some of the limitations of the mean-field based formulation of irreversible thermodynamics and provides new ways of characterizing the complexity of nonequilibrium states.

Another important property of the master equation is that expanding in terms of the inverse of the size parameter N and provided that the system possesses a single stable state yields in the limit of large N an equation of the form[7,12,13]

$$\frac{\partial\rho(\{x_i\},t)}{\partial t} = -\sum_i \frac{\partial}{\partial x_i} f_i\big(\{x_j\},\lambda\big)\,\rho + \sum_{i,j} D_{ij}\,\frac{\partial^2\rho}{\partial x_i\partial x_j}. \tag{31}$$

Here, $\{x_i\}$ are the continuous intensive variables associated with $\{X_i\}$ and ρ is their probability density. The coefficients D_{ij} define a matrix possessing non-negative eigenvalues and are uniquely determined by w_ρ s and $r_{i\rho}$s. Furthermore, the extensivity condition (29b) entails that they are inversely proportional to the system size N. Now, an equation such as (31), known as the Fokker-Planck equation, defines a diffusion process in state space. This corresponds in turn to a random process in which the variables x_i evolve according to a stochastic differential equation of the form

$$\frac{\partial x_i}{\partial t} = f_i\big(\{x_j\},\lambda\big) + R_i(t), \tag{32}$$

where R_i are Gaussian white noise processes. Eq. (32) is precisely the sort of evolution equations we have been dealing with in Sec. II [see Eqs. (10)–(12)]. This establishes a connection between the master equation and the extended local equilibrium approaches and provides a justification of the assertion that the spectral intensities q_ρ^2 and Q_i^2 in Eq. (24) are inversely proportional to the system size.

A. Stochastic potentials and variational properties

In view of the presence of the N factor in Eq. (29b), we seek for steady-state solutions of the master equation in the form[7,17,18]

$$P(\{X_i\}) = \exp\left[-N\,U(\{x_i\})\right] \tag{33a}$$

with $x_i = X_i/N$ and in which $U(\{x_i\})$ is further expanded in $1/N$ as

$$U(\{x_i\}) = U_0(\{x_i\}) + \frac{1}{N}\,U_1(\{x_i\}) + \cdots. \tag{33b}$$

Limiting the expansion to the dominant part U_0 and substituting (33) into (29a), one obtains, up to terms of $\mathcal{O}(1/N)$, the following equation for U_0

$$\sum_\rho \tilde{w}_\rho\big(\{x_i\},\{r_{i\rho}\}\big)\left\{\exp\left[\sum_i r_{i\rho}\,\frac{\partial U_0}{\partial x_i}\right] - 1\right\} = 0. \tag{34}$$

This relation can be regarded as a Hamilton-Jacobi equation of zero "energy" of a system described by coordinates x_i and momenta $p_i = \partial U_0/\partial x_i$.

We now consider the time variation of U_0 along a solution of the deterministic (mean-field) Eq. (6)

$$\frac{d\,U_0(\{x_i\})}{dt} = \sum_i \frac{\partial U_0}{\partial x_i}\frac{dx_i}{dt} = \sum_i \frac{\partial U_0}{\partial x_i} f_i$$

or, with Eq. (30)

$$\frac{d\,U_0(\{x_i\})}{dt} = \sum_\rho \tilde{w}_\rho \sum_i r_{i\rho}\,\frac{\partial U_0}{\partial x_i}.$$

Using the convexity property of the exponential along with Eq. (34), one can further write[19]

$$\frac{d\,U_0}{dt} \le \sum_\rho \tilde{w}_\rho\left\{\exp\left[\sum_i r_{i\rho}\,\frac{\partial U_0}{\partial x_i}\right] - 1\right\} = 0. \tag{35}$$

In other words, U_0 is a strictly decreasing quantity along mean-field trajectories until it reaches a local minimum corresponding to one of the attractors of the macroscopic evolution equations, which in view of (33) corresponds to a maximum of ρ, i.e., to the most probable state of the system. This extremal property is reminiscent of the extremal properties of the thermodynamic potentials in the state of equilibrium, but its range of validity is now considerably wider. For this reason, we shall refer to U_0 as the generalized or stochastic potential. In general, there will be several extrema of the stochastic potential. Owing to the exponential penalization of the probability by the size parameter N [Eq. (33)], only those extrema corresponding to equal values of U_0 will be of relevance as far as the observable properties are concerned. Notice that the often prevailing idea that the macroscopic description corresponds to the mean value is in general false, except in the particular case of one-humped distributions peaked sharply on a unique attractor corresponding to a steady state.

Summarizing, we have recovered, at the level of the stochastic description, a global variational property and a new state functional—the stochastic potential—providing a way to characterize the complexity of nonequilibrium states. In general, the solutions of Eq. (34) are complicated, non-analytic functions of the state variables. However, if the system possesses a single attractor, U_0 can be expanded in a convergent power series of the distance from this reference state. This expansion remains valid even if the system operates near a bifurcation point provided that the bifurcation occurs at a simple eigenvalue of the Jacobian matrix associated with the mean-field evolution laws $\{f_i\}$. For instance, in a pitchfork bifurcation marking the transition from a unique stable state to two simultaneous stable states, the potential can be expressed as a sum of a dominant "critical" part that is quartic with respect to a suitable combination of x_is, the *order parameter*, and a non-critical part which plays no role in the qualitative properties of the system.

B. Generalized entropies: Stability revisited

The existence of a closed-form description in terms of the probability distributions of the variables $\{x_i\}$—essentially the macroscopic observables of thermodynamics—independent of the microscopic degrees of freedom such as individual particle velocities can be viewed as yet another version of an extended local equilibrium hypothesis. In order to establish a connection with irreversible thermodynamics *per se*, we now need to define a quantity that plays in this formulation a role similar to that of entropy in the formulations of Secs. I and II.

We seek for a quantity which depends entirely on P_k, provides a measure of the unpredictability in specifying the state of the system arising from the ongoing transitions between the available states, shares with the thermodynamic entropy the property of additivity, and remains unchanged if the state space is enlarged by an event of zero probability. A classic result of the theory of stochastic processes is that these requirements are satisfied by the quantity[20,21]

$$S_I(t) = -\sum_k P_k(t) \ln P_k(t) \tag{36}$$

which we will be referring to as the information or Shannon entropy on the grounds of its importance in information and communication theories. Actually, to recover the value of thermodynamic entropy (at least in the equilibrium limit), one needs to add to (36) a contribution $S_{0,k}$ equal to the entropy of degrees of freedom other than those included in the states k of the Markovian description, averaged over P_k. In the sequel, we will be mainly interested in the part S_I, which reflects the different ways of distributing the probability masses P_k among different states.

A second set of quantities of interest are relative entropies, or Kullback distances,[21,22] between two different probability distributions such as $P_k(t)$ and its value at the stationary state P_{sk} associated with the time-independent solution of Eqs. (27a) or (28a) assumed to exist and to be unique, a property that can be established rigorously provided that the states belong to an ergodic set

$$K(\{P_k\}, t) = \sum_k P_k(t) \ln \frac{P_k(t)}{P_{sk}}. \tag{37}$$

Using this quantity, one can show that once the probabilities P_k evolve according to a Markov process, irreversibility follows as a natural consequence. We first observe that K is bounded from below and vanishes at $P_k = P_{sk}$. Its time variation can be computed from (27a) or (28a). Using the convexity property of the logarithm, one then obtains that $K(t + \Delta t) \leq K(t)$ or, in the continuous time limit,

$$\frac{dK}{dt} \leq 0 \tag{38}$$

showing that the system attains irreversibly its steady state starting from an arbitrary initial distribution, K being a Lyapunov function governing this evolution. This is yet another expression of the property pointed out in the preceding subsection, namely, that the probabilistic description reveals the existence of strong stability properties. These properties are here expressed in terms of generalized entropy-like quantities and allow us to overcome the limitation of the macroscopic thermodynamic description to linear stability with respect to small perturbations, as pointed out in Introduction. Comparing Eqs. (37) and (36), one sees that K and dK/dt are just the parts of S_I and dS_I/dt that are nonlinear with respect to the deviations δP_k of P_k from the invariant distribution P_{sk} (Ref. 22)

$$K = \delta_{NL}(-S_I) \geq 0\,, \quad \frac{dK}{dt} = \frac{d}{dt}\,\delta_{NL}(-S_I) \leq 0. \tag{39}$$

Limited to their second order terms, these relations are reminiscent of the Glansdorff-Prigogine thermodynamic stability criterion [Eqs. (9a) and (9b)].

It should be pointed out that although randomness is present implicitly in Eqs. (36) and (37) through the probability distributions, the time dependence of both S_I and K is deterministic, in the sense that the probabilities evolve in time according to the master equation that drives the system irreversibly towards a unique steady-state solution. In particular, there can be no question of probability distributions of entropy and related quantities. In contrast, the entropy introduced in Sec. II through our extended local equilibrium Ansatz is a random function of fluctuating state variables characterized by an invariant probability density. The connection between these two set of quantities and indeed the very legitimacy of (36) as a definition of thermodynamic entropy needs therefore further considerations. We postpone a closer comparison to Secs. III C and IV.

On the other hand, randomness makes naturally its appearance at the level of probability of sequences of states rather than of a single state. To be specific, let the system evolve during a time interval $T = n\,\Delta t$. During this evolution, the states will succeed each other in many possible ways, corresponding to different realizations of a random process. We denote by $P_n(k_1,\ldots k_n)$ the probability of a particular path $k_1,\ldots k_n$. We can then extend Eq. (36) by defining higher order "dynamical" entropies[21]

$$S_n(t) = -\sum_{k_1,\ldots k_n} P_n(k_1,\ldots k_n)\ln P_n(k_1,\ldots k_n), \tag{40}$$

where the sum runs over all sequences compatible with the structure of the conditional probabilities. Using the Markov property in the discrete time form

$$P_n(k_1,\ldots k_n) = P_{k_1} W(k_2|k_1)\ldots W(k_n|k_{n-1}) \tag{41}$$

one can reduce (40) into an expression involving only pairs of consecutive states. Specifically,

$$S_n = S_I + (n-1)\,h, \tag{42a}$$

where

$$h = -\sum_{i,j} P_i\, W(j|i)\ln W(j|i) \tag{42b}$$

is the Kolmogorov-Sinai entropy of the Markov process, expressing the increase in dynamical entropy when the process advances by one step.[21,23] Here, it is understood that P_i is the invariant probability of the process, i.e., the steady-state solution of Eq. (27a).

We may also introduce Kullback distances between different path probability distributions. Of special interest for our purposes is the distance between the distributions of the direct and reverse paths, which for a Markov process is limited to the probability of two consecutive states i and j

$$K_2 = \sum_{i,j} P(i,j)\ln\frac{P(i,j)}{\tilde{P}(j,i)}$$

or using the normalization property of $W(i|j)$ and the property that the invariant probability distributions of both the direct and reverse process are identical

$$K_2 = \sum_{i,j} P_i\, W(j|i)\ln\frac{W(j|i)}{W(i|j)} = h^R - h, \tag{43}$$

where h^R stands for the Kolmogorov-Sinai entropy of the reverse process[23]

$$h^R = -\sum_{i,j} P_i\, W(j|i)\ln W(i|j). \tag{44}$$

To take the continuous time limit of expressions (42), we appeal to Eqs. (28a) and (28b). Expanding (42) in Δt and keeping dominant terms, we obtain

$$S_n = S_I + T\,h, \tag{45a}$$

where

$$h = (1-\ln\Delta t)\sum_{j\neq i} P_i\, w(j|i) - \sum_{j\neq i} P_i\, w(j|i)\ln w(j|i). \tag{45b}$$

We notice the presence of a logarithmic singularity as $\Delta t \to 0$. Expanding (43) in Δt and keeping dominant terms, one can easily show that this singularity disappears at the level of the Kullback distances between the direct and the reverse processes.[23,24]

C. Information entropy balance: Entropy production of the fluctuations revisited

In order to complete the connection between the formulation adopted in this Section and thermodynamics, now we need to derive a balance equation for S_I from which a probabilistic analog of entropy production can be identified. Consider first the case of discrete state and continuous time processes. Differentiating Eq. (36) in time and using the master equation in the form (29a), one arrives at[23,25]

$$\frac{dS_I}{dt} = J_I + \sigma_I, \tag{46}$$

where the information entropy flux J_I and information entropy production σ_I are given by

$$J_I = -\frac{1}{2}\sum_{\{X_i\},\rho} J_\rho \ln\frac{w_\rho\big(\{X_i\}|\{X_i - r_{i\rho}\}\big)}{w_{-\rho}\big(\{X_i - r_{i\rho}\}|\{X_i\}\big)}, \tag{47a}$$

$$\sigma_I = \frac{1}{2}\sum_{\{X_i\},\rho} J_\rho(\{X_i\},t)\, X_\rho(\{X_i\},t) \geq 0 \tag{47b}$$

with

$$J_\rho(\{X_i\},t) = w_\rho\big(\{X_i\}|\{X_i - r_{i\rho}\}\big)\,P(\{X_i - r_{i\rho}\},t) - w_{-\rho}\big(\{X_i - r_{i\rho}\}|\{X_i\}\big)\,P(\{X_i\},t), \tag{48a}$$

$$X_\rho(\{X_i\},t) = \ln\frac{w_\rho\big(\{X_i\}|\{X_i - r_{i\rho}\}\big)\,P(\{X_i - r_{i\rho}\},t)}{w_{-\rho}\big(\{X_i - r_{i\rho}\}|\{X_i\}\big)\,P(\{X_i\},t)}. \tag{48b}$$

As in Secs. I and II, the particular decomposition of the time derivative of entropy into these two terms adopted is motivated by the requirement of non-negativity of the information entropy production. Remarkably, one recovers, for free, a bilinear expression of entropy production much like in Eq. (5). In the stationary state, the probabilities—and thus also S_I—are time-independent, entailing that J_I and σ_I cancel each other. On the other hand, we observe that expressions (47 b) or (48) display the probabilities of transitions leading, e.g., from state $\{X_i - r_{i\rho}\}$ to state $\{X_i\}$ and of their reverses. If these two probabilities are equal, then the probability fluxes J_ρ and σ_I and J_I themselves vanish. We therefore recover in our probabilistic description the property of detailed balance, one of the signatures of thermodynamic equilibrium. The non-negativity of σ_I implies then that information entropy is continuously produced as long as the system is not in a state of detailed balance. This is analogous to the second law of thermodynamics.

Comparing expressions (47) with (43)–(45), one sees straightforwardly that in the steady state, σ_I is just the Kullback distance between direct and reverse paths or, equivalently, the difference between the continuous time limit of the corresponding Kolmogorov-Sinai entropies

$$\sigma_I = -\sum_i P_i\, w(j|i) \ln \frac{w(j|i)}{w(i|j)} = h^R - h, \tag{49}$$

where, as anticipated in the previous subsection, the logarithmic singularity Δt has been cancelled out. Irreversibility as expressed by σ_I is thus seen to be intimately connected to time asymmetry as expressed by the difference of Kolmogorov-Sinai entropies between the direct and the reverse paths.[23] Irreversibility as time symmetry breaking has been a central theme in Prigogine's work over the years.[26]

To evaluate σ_I and related quantities explicitly, one needs to compute the steady-state solution of the master equation. In large size systems, using the formalism of Subsection III A and keeping in mind the comments in connection with Eq. (30), one expects to recover in the large N limit the mean-field expression of entropy production plus a small correction representing the entropy production of the fluctuations. These quantities play a role analogous to expressions (20) and (21) derived in our extended local equilibrium approach. There is, however, an important difference in that they are not random variables. Their explicit forms and their relation to averages of (21) over the different realizations of the random forces introduced in the latter approach will be analyzed in Sec. IV on selected examples.

Owing to the Markov property in the formulation outlined in the present subsection, only two-state probabilities needed to be considered. On the other hand, as alluded in Subsection III B, one may consider quantities generalizing the logarithmic terms in Eqs. (43) or (48b) to paths of length n (Ref. 23)

$$Z(t) = \ln \frac{W_{\rho_1}(X_1|X_0)\ldots W_{\rho_n}(X_n|X_{n-1})}{W_{-\rho_1}(X_0|X_1)\ldots W_{-\rho_n}(X_{n-1}|X_n)}, \tag{50}$$

where $t = n\,\Delta t$. These quantities are random variables expressing statistical deviations from the regime of detailed balance associated with different paths. It can be shown that they are distributed according to a large deviation-type probability[23] similar to the form of Eq. (26), with an average value equal to σ_I.

Finally, to the extent that, as pointed out in the beginning of this Section, the Fokker-Planck equation (31) can be deduced from an asymptotic expansion of the master equation, one can expect that most of the results of Subsections III A–III C should carry through. Specific aspects of the passage from discrete to continuous state space which deserve special attention will be addressed in Sec. IV.

IV. ILLUSTRATIONS

In this section, we illustrate the formulations of stochastic thermodynamics developed in Secs. II and III on selected examples and compare the predictions of the two approaches. We will analyze a first order reaction system involving a single intermediate and a nonlinear kinetic model giving rise to multiple steady states. This will give us the opportunity to assess the role of nonlinearities in the properties of the stochastic entropy production.

Model 1:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{B}. \tag{51}$$

In this scheme, A and B are pool species whose concentrations a and b are kept constant and X is the variable intermediate. The mean-field rate equation for its concentration is

$$\frac{dx}{dt} = k_1\, a + k_{-2}\, b - (k_{-1} + k_2)\, x. \tag{52a}$$

The entropy production associated with this scheme reads

$$\frac{\sigma_m}{k_B} = (k_1\, a - k_{-1}\, x) \ln \frac{k_1\, a}{k_{-1}\, x} + (k_2\, x - k_{-2}\, b) \ln \frac{k_2\, x}{k_{-2}\, b}. \tag{52b}$$

Here, the logarithmic terms are proportional to the generalized forces (affinities)

$$\mathcal{A}_1 = \frac{\mu_\mathrm{A} - \mu_\mathrm{X}}{T}, \quad \mathcal{A}_2 = \frac{\mu_\mathrm{X} - \mu_\mathrm{B}}{T},$$

where k_B is the Boltzmann constant and μ denotes the chemical potential, and the factors multiplying them are the corresponding fluxes. As expected, σ_m vanishes when the two fluxes vanish separately, which occurs under the zero overall affinity (equilibrium) condition $k_1\, k_2\, a = k_{-1}\, k_{-2}\, b$.

Model 2 (Schlögl's model):

$$\mathrm{A} + 2\,\mathrm{X} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3\,\mathrm{X}; \quad \mathrm{X} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{B} \tag{53}$$

with

$$\frac{dx}{dt} = k_1\, a\, x^2 + k_{-2}\, b - (k_{-1}\, x^3 + k_2\, x). \tag{54a}$$

and

$$\frac{\sigma_m}{k_B} = \left(k_1\, a\, x^2 - k_{-1}\, x^3\right) \ln \frac{k_1\, a}{k_{-1}\, x} + (k_2\, x - k_{-2}\, b) \ln \frac{k_2\, x}{k_{-2}\, b}, \tag{54b}$$

where the different terms have the same interpretation as for model1. The equilibrium (zero overall affinity) condition here is again $k_1\, k_2\, a = k_{-1}\, k_{-2}\, b$.

A. Extended local equilibrium approach

We first consider the linear model (51). Introducing the random forces w_i associated with the internal processes [Eq. (12)] leads to a stochastic differential equation for x

$$\frac{dx}{dt} = k_1\, a + k_{-2}\, b - (k_{-1} + k_2)\, x + w_1 + w_{-2} - w_{-1} - w_2. \tag{55}$$

In the spirit of our local equilibrium approach, the intensity of the noise related to each processes will be determined by the fluctuation-dissipation relation

$$\overline{w_\rho(t)\, w_{\rho'}(t')} = \frac{W^m_\rho}{N}\, \delta^{Kr}_{\rho,\rho'}\, \delta(t - t'), \tag{56}$$

where N is the extensivity parameter and the superscript m indicates that the rate function takes its mean-field (deterministic) value $W_\rho(x_m)$, in which x_m is the solution of Eq. (52a). Due to the presence of noise, the fluctuating entropy production reads

$$\frac{\sigma}{k_B} = (k_1\, a - k_{-1}\, x + w_1 - w_{-1}) \ln \frac{k_1\, a}{k_{-1}\, x} + (k_2\, x - k_{-2}\, b + w_2 - w_{-2}) \ln \frac{k_2\, x}{k_{-2}\, b}$$

or

$$\sigma = (k_1\, a - k_{-1}\, x + w_1 - w_{-1})\, \mathcal{A}_1 + (k_2\, x - k_{-2}\, b + w_2 - w_{-2})\, \mathcal{A}_2, \tag{57}$$

where for compactness, we have reintroduced the affinities $\mathcal{A}_i$.

To evaluate how fluctuations affect entropy production, we decompose Eq. (57) into the mean-field contribution and the entropy of fluctuations, $\sigma = \sigma_m + \Delta\sigma$, in which σ_m is evaluated by using Eq. (52b) at x_m and

$$\Delta\sigma = (k_1\, a - k_{-1}\, x_m)\, \Delta\mathcal{A}_1 + (k_2\, x_m - k_{-2}\, b)\Delta\mathcal{A}_2 + (k_2\, \mathcal{A}_2 - k_{-1}\, \mathcal{A}_1)\, \Delta x + (w_1 - w_{-1})\, \mathcal{A}_1 + (w_2 - w_{-2})\, \mathcal{A}_2, \tag{58}$$

where the Δs denote deviations from the mean-field values. Averaging Eq. (55) over the noise and taking into account that the long-time average of the time derivative of a stationary process is zero give the stationary mean $\bar{x}_s$, which coincides with the solution of Eq. (52a) since by definition $\overline{w_\rho} = 0$ for each reaction

$$\bar{x}_s = x_m = \frac{k_1\, a + k_{-2}\, b}{k_{-1} + k_2}. \tag{59}$$

Using this result, the mean-field entropy production (52b) becomes

$$\sigma_m = k_B \ln \frac{k_1\, k_2\, a}{k_{-1}\, k_{-2}\, b}\, (k_2\, x_m - k_{-2}\, b). \tag{60}$$

Moreover, since

$$\mathcal{A}_2 = k_B \ln \frac{k_1\, k_2\, a}{k_{-1}\, k_{-2}\, b} - \mathcal{A}_1, \quad \Delta\mathcal{A}_2 = k_B \ln \frac{x}{x_m} = -\Delta\mathcal{A}_1 \tag{61}$$

the entropy production of fluctuations can be rewritten as

$$\Delta\sigma = \mathcal{A}_1\, [-(k_2 + k_{-1})\, \Delta x + w_1 + w_{-2} - w_{-1} - w_{-2}] + k_B \ln \frac{k_1\, k_2\, a}{k_{-1}\, k_{-2}\, b}\, [k_2\, \Delta x + w_2 - w_{-2}]. \tag{62}$$

The first line corresponds to $\mathcal{A}_1$ multiplied by the time derivative of Δx. One thus readily arrives to the conclusion that since $\overline{\Delta x} = \overline{w_2} = \overline{w_{-2}} = 0$

$$\overline{\Delta\sigma} = 0$$

at the steady state. This is a direct consequence of the linearity of Eq. (52a), which imposes that the macroscopic and the mean values of x coincide. We conclude that the mean-field formulation of irreversible thermodynamics for this system is an exact consequence of the master equation.

On the other hand, in the extended local equilibrium assumption, entropy production is a stochastic variable. We can thus go one step further and derive the probability distribution of entropy production around its stationary mean, $\bar{\sigma} = \sigma_m$. These deviations can be estimated by expanding in powers of $\delta x = x - \bar{x}_s$:

$$\delta\sigma = \sigma - \bar{\sigma} = \sigma'_m(\bar{x}_s)\, \delta x + \frac{\sigma''_m(\bar{x}_s)}{2}\, \delta x^2 + \sum_\rho \mathcal{A}_\rho(\bar{x}_s)\, w_\rho + \sum_\rho \mathcal{A}'_\rho(\bar{x}_s)\, w_\rho\, \delta x + \cdots, \tag{63}$$

where the primes stand for derivation with respect to x. In the weak noise limit, we expect that an appropriate expression for the probability distribution of $\delta\sigma$ can be obtained by considering only the dominant contributions of the development in (63), which typically would amount to keeping the first and the third terms of the sum. Notice that this assumption fails at equilibrium, for which both σ' and $\mathcal{A}_\rho$ vanish and higher order terms must be retained. We will actually be interested in the statistical properties of the time-averaged entropy production Σ_t in order to remove singular contributions due to the white noise [see Eq. (25)]. For non-equilibrium steady states, $\delta\Sigma_t$ is given to the dominant order by

$$\delta\Sigma_t = \frac{\sigma'_m(\bar{x}_s)}{t} \int_0^t \delta x(t')\, dt' + \sum_\rho \frac{\mathcal{A}_\rho(\bar{x}_s)}{t} \int_0^t w_\rho(t')\, dt' \equiv Z_t + V_t. \tag{64}$$

The mean $\overline{Z_t}$ of the process Z_t is zero since by definition $\overline{\delta x} = 0$, while its variance reads

$$\overline{\delta Z_t^2} = \frac{Q_Z^2\, \sigma'_m(\bar{x}_s)^2}{N\, \lambda^2\, t}, \tag{65}$$

where Q_Z^2 is the total intensity of the random forces

$$Q_Z^2 = \sum \nu_\rho^2\, W_\rho^m \tag{66}$$

and $\lambda = k_{-1} + k_2$. Moreover, since on the grounds of (55) Z_t is the time integral of an Ornstein- Uhlenbeck process, it is expected to be distributed in a Gaussian way in view of the central limit theorem. As for process V_t, it is a Wiener process of zero mean and of variance $Q_V^2/(N\, t)$ with

$$Q_V^2 = \sum_\rho \mathcal{A}_\rho^2(\bar{x}_s)\, W_\rho^m. \tag{67}$$

The distribution of $\delta\Sigma_t$ thus takes the form (see also Ref. 10)

$$P(\delta\Sigma_t) \approx \sqrt{\frac{N\, t}{2\, \pi\, \Delta_0}}\, \exp\left(-\frac{N\, t}{2\, \Delta_0}\, \delta\Sigma_t^2\right), \tag{68}$$

where

$$\Delta_0 = \frac{Q_Z^2\, \sigma'_m(\bar{x}_s)^2}{\lambda^2} + Q_V^2. \tag{69}$$

We observe that this distribution is Gaussian and includes process-specific contributions. Numerical integrations of the complete expression for entropy production show that the Gaussian solution is typically an excellent approximation of $P(\delta\Sigma_t)$, with small deviations observed only in the tails of the distribution. This means that in the extended local equilibrium approach, entropy production can be negative with some probability. Integrating (68) from $\Sigma_t = -\infty$ to $\Sigma_t = 0$ yields

$$P(\Sigma_t < 0) = \frac{1}{2} - \frac{1}{2}\,\mathrm{erf}\left[\sqrt{\frac{N\,t}{2\,\Delta_0}}\,\overline{\Sigma_t}\right], \tag{70}$$

which in the limit of large $N\,t$ reduces to

$$P(\Sigma_t < 0) \approx \sqrt{\frac{\Delta_0}{2\,\pi\,N\,t\,\sigma_m^2}}\exp\left(-\frac{N\,t}{2\,\Delta_0}\,\sigma_m^2\right), \tag{71}$$

where we have used the fact that $\overline{\Sigma_t} \to \sigma_m$ for long times and large systems. We notice that the probability of having negative entropy production is exponentially penalized by t and N, in a way similar to large deviation-type expressions such as (26).

It is instructive to analyze the stochastic properties of the different parts of entropy production as introduced in Sec. II. Let us rewrite (57) as

$$\sigma = \sigma_{\mathrm{GP}} + \sigma_{\mathrm{M}}, \tag{72}$$

where the "Glansdorff-Prigogine" entropy production

$$\sigma_{\mathrm{GP}} = (k_1\,a - k_{-1}\,x)\,\mathcal{A}_1 + (k_2\,x - k_{-2}\,b)\,\mathcal{A}_2 \tag{73a}$$

has a structure similar to the macroscopic local equilibrium expression, in which the x is a stochastic process. We notice that despite the fluctuating character of the state variable, σ_{GP} is always positive. More precisely, it is bounded from below by the minimum of entropy production. In contrast, in the part containing the random forces grouped into a "mesoscopic" entropy production term

$$\sigma_{\mathrm{M}} = (w_1 - w_{-1})\,\mathcal{A}_1 + (w_2 - w_{-2})\,\mathcal{A}_2 \tag{73b}$$

such a constraint does not apply. The distributions of the corresponding time-averaged entropy productions Σ_t^{GP} and Σ_t^{M} are depicted in Fig. 1. The distribution of the mesoscopic contribution to the entropy production is fairly symmetric and has a slightly negative mean. The Glansdorff-Prigogine part is markedly asymmetric because it is bounded from below by the minimum entropy production of the system. As a consequence, the maximum of probability does not coincide with the mean Glansdorff-Prigogine entropy production, which is itself slightly larger than the deterministic value, in such a way that the sum of the mean Glansdorff-Prigogine and mesoscopic entropy production terms is indeed equal to σ_m.

We now turn to the nonlinear Schlögl model (53). The stochastic evolution law for x now reads

$$\frac{dx}{dt} = k_1\,a\,x^2 + k_{-2}\,b - (k_{-1}\,x^3 + k_2\,x) + w_1 + w_{-2} - w_{-1} - w_2, \tag{74}$$

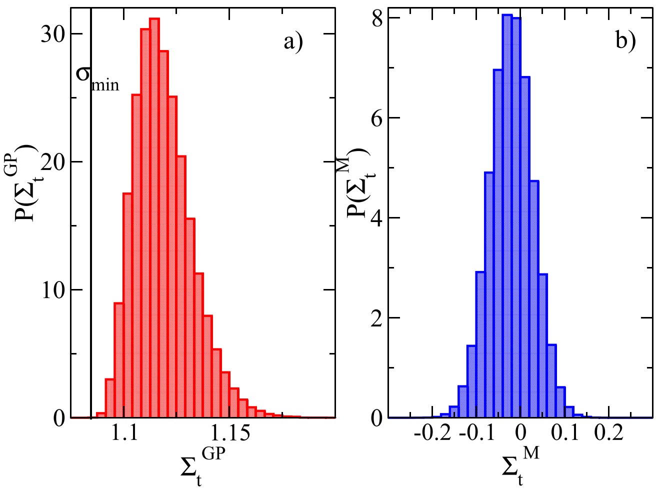

FIG. 1. Probability distribution of the time-averaged Glansdorff-Prigogine (a) and mesoscopic (b) entropy productions for the linear model 1. The vertical line in (a) indicates the value of the minimum entropy production as predicted from Eq. (73a). The histograms were obtained from 50 000 realizations of the stochastic differential Eq. (55) (Euler-Maruyama algorithm with Stratonovich interpretation), for $a = 3$, $b = 1$, $k_i = 1$, $N = 100$, and a total time $t = 10$ with $dt = 1 \times 10^{-5}$.

where the intensity of the random forces obeys again fluctuation-dissipation relations of the type (56). The corresponding stochastic entropy production is given by

$$\sigma = \left(k_1\,a\,x^2 - k_{-1}\,x^3 + w_1 - w_{-1}\right)\mathcal{A}_1 + (k_2\,x - k_{-2}\,b + w_2 - w_{-2})\,\mathcal{A}_2. \tag{75}$$

Since the connection between the affinities [Eq. (61)] remains valid for this model, σ can be rewritten as

$$\sigma = \left[k_1\,a x^2 + k_{-2}\,b - (k_{-1}\,x^3 + k_2\,x) + w_1 + w_{-2} - w_{-1} - w_2\right] \times \mathcal{A}_1 + k_B \ln\frac{k_1\,k_2\,a}{k_{-1}\,k_{-2}\,b}\,(k_2\,x - k_{-2}\,b + w_2 - w_{-2}). \tag{76}$$

Focusing again on the steady state, we first note that since the average of the derivative (54a) vanishes, the mean-field entropy production takes the same form as for the linear example [see Eq. (60)]. We thus obtain for the entropy production of fluctuations

$$\Delta\sigma = \left[k_1\,a x^2 + k_{-2}\,b - (k_{-1}\,x^3 + k_2\,x) + w_1 + w_{-2} - w_{-1} - w_2\right] \times \mathcal{A}_1 + k_B \ln\frac{k_1\,k_2\,a}{k_{-1}\,k_{-2}\,b}(k_2\,\Delta x - k_{-2}\,b + w_2 - w_{-2}). \tag{77}$$

The first term in (77) is equal to $\mathcal{A}_1\,dx/dt$, and its average vanishes again for long times. The mean of the entropy production due to fluctuations is thus given by

$$\overline{\Delta\sigma} = k_2\,\overline{\Delta x}\,k_B \ln\frac{k_1\,k_2\,a}{k_{-1}\,k_{-2}\,b}. \tag{78}$$

Here, contrary to the case of model 1, $\overline{\Delta x} \neq 0$ in the most general case since the evolution law (53) is nonlinear. The deviation from the mean-field value can be estimated by averaging Eq. (74) over the noise, which at the steady state leads to

$$k_1\, a\, \overline{x^2}_s - k_{-1}\, \overline{x^3}_s - k_2\, \overline{x_s} + k_{-2}\, b = 0. \tag{79}$$

Expanding the moments of x in powers of $\delta x = x - \bar{x}_s$ in the above equation and subsequently developing $\bar{x}$ around x_m give the leading order

$$\overline{\Delta x} = -\left[\frac{3\, k_{-1}\, x_m - k_1\, a}{2\, k_1\, a\, x_m - 3\, k_{-1}\, (x_m)^2 - k_2}\right] \overline{\delta x^2}_s. \tag{80}$$

The value taken by $\overline{\Delta\sigma}$ at the steady state thus depends on the kinetic details of the reactions through the value taken by Δx and also on the overall affinity of the reaction since

$$k_B \ln \frac{k_1\, k_2\, a}{k_{-1}\, k_{-2}\, b} = \mathcal{A}_1 + \mathcal{A}_2. \tag{81}$$

This connection with the global affinity $\mathcal{A}_1 + \mathcal{A}_2$ ensures that $\overline{\Delta\sigma} = 0$ at equilibrium as expected. We observe however that it can also be zero out of equilibrium, whenever $x_m = k_1\, a/(3\, k_{-1})$. For other values of the control parameter, the mean entropy production can be either larger or smaller than the mean-field value: contrary to what intuition might suggest, fluctuations do not always lead to more dissipation in the sense of more entropy production. Figure 2 plots $\overline{\Delta\sigma^*} = \overline{\Delta\sigma}/(k_B\, \overline{\delta x^2}_s)$ as a function of the concentration b for a specific choice of parameters. The dots in this figure stand for an evaluation of the entropy of fluctuations from numerical integrations of the full Eq. (74). The agreement with the analytic estimate is excellent. The distribution of entropy production around this mean can be evaluated like before with a series of the type (63) in the small noise limit. Moreover, since in the same limit the stochastic evolution law (74) can be considered to define an Ornstein-Uhlenbeck process, Z_t, V_t, and Σ_t are again expected to obey a Gaussian probability distribution. For small systems where the weak-noise limit is expected to fail, the steady-state distribution of the probability density $\rho(x)$ will however present asymmetries that will be inherited by the entropy production (see Ref. 10 for an example).

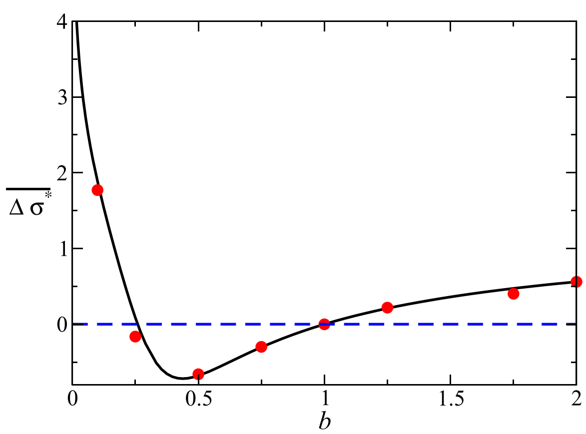

FIG. 2. Mean entropy production of fluctuations $\overline{\Delta\sigma^*}$ (see text) for the model (53), as a function of the control parameter b. The other kinetic parameters are all set to 1 and $N = 1000$. The dots correspond to the outcome of numerical integrations of (74) (Euler-Maruyama, total time = 10, and the Stratonovich interpretation was used) averaged over 10 000 realizations of the corresponding stochastic differential equation, with $dt = 1 \times 10^{-5}$. The plain curve is the analytical prediction (78) combined with (80). The dashed line is used to highlight the states of zero entropy production of fluctuations.

B. Master equation approach

We start with the linear model [Eq. (51)]. The conditional probabilities per unit time in the master Eq. (29a) for the four reaction steps and their reverse are

$$\begin{aligned}
&w_1(X|X-1) = k_1\, A, && w_{-1}(X-1|X) = k_{-1}\, X\\
&w_2(X|X+1) = k_{-1}\, (X+1), && w_{-2}(X+1|X) = k_1\, A\\
&w_3(X|X-1) = k_{-2}\, B, && w_{-3}(X-1|X) = k_2\, X\\
&w_4(X|X+1) = k_2\, (X+1), && w_{-4}(X+1|X) = k_{-2}\, B,
\end{aligned} \tag{82}$$

where we denote by capital letters the number of particles of the corresponding species. The steady-state solution of Eq. (29a) is then the Poisson distribution

$$P_s = e^{-X_m} \frac{X_m^X}{X!}, \tag{83}$$

where X_m is the steady-state solution of the mean-field rate equation (52a) in which the concentrations a and b are replaced by their extensive counterparts A and B.

The full stochastic entropy production reads [Eqs. (47b) and (48)]

$$\begin{aligned}
\sigma_I = \frac{1}{2}\sum_X \Big\{ &[k_1 A P(X-1) - k_{-1} X P(X)] \ln \frac{k_1 A P(X-1)}{k_{-1} X P(X)}\\
&+ [k_{-1}(X+1) P(X+1) - k_1 A P(X)] \ln \frac{k_{-1}(X+1) P(X+1)}{k_1 A P(X)}\\
&+ [k_2 (X+1) P(X+1) - k_{-2} B P(X)] \ln \frac{k_2 (X+1) P(X+1)}{k_{-2} B P(X)}\\
&+ [k_{-2} B P(X-1) - k_2 X P(X)] \ln \frac{k_{-2} B P(X-1)}{k_2 X P(X)} \Big\}.
\end{aligned} \tag{84}$$

Factoring out $P(X)$ in the sum over X and noticing that

$$\frac{P_s(X-1)}{P_s(X)} = \frac{X}{X_m}, \quad \frac{P_s(X+1)}{P_s(X)} = \frac{X_m}{X+1}, \quad \langle X \rangle = X_m$$

on the grounds of Eq. (83), one sees straightforwardly that the first two and the last two terms in (84) are equal. Expression (84) reduces then in the steady state to

$$\begin{aligned}
\sigma_I &= (k_1\, A - k_{-1}\, X_m) \ln \frac{k_1\, A}{k_{-1}\, X_m} + (k_2\, X_m - k_{-2}\, B) \ln \frac{k_2\, X_m}{k_{-2}\, B}\\
&= \frac{N}{k_B}\, \sigma_m,
\end{aligned} \tag{85a}$$

where N is the size parameter and σ_m is the mean-field value of the entropy production of classical irreversible thermodynamics [Eq. (52b)]. It follows that the entropy production of the fluctuations vanishes identically in this system

$$\Delta\sigma = 0. \tag{85b}$$

This conclusion actually applies to all linear systems for which, therefore, classical irreversible thermodynamics follows as an exact consequence of the master equation description.

We next consider the Schlögl model [Eq. (53)]. The conditional probabilities per unit time compatible with the extensivity condition (29b) are

$$\begin{aligned} w_1(X|X-1) &= k_1\,A\,(X-1)\,(X-2)/N^2, \\ w_{-1}(X-1|X) &= k_{-1}\,X\,(X-1)\,(X-2)/N^2 \\ w_2(X|X+1) &= k_{-1}\,(X+1)\,X\,(X-1)/N^2, \\ w_{-2}(X+1|X) &= k_1\,A\,X\,(X-1)/N^2 \\ w_3(X|X-1) &= k_{-2}\,B, \\ w_{-3}(X-1|X) &= k_2\,X \\ w_4(X|X+1) &= k_2\,(X+1), \\ w_{-4}(X+1|X) &= k_{-2}\,B. \end{aligned} \tag{86}$$

The steady-state solution of the master equation (29a) corresponding to (86) satisfies the zero overall probability flux condition, also referred to as the generalized detailed balance condition

$$\begin{aligned} &\left[\frac{k_1}{N^2}A\,(X-1)\,(X-2)+k_{-2}\,B\right]P_s(X-1) \\ &= \left[\frac{k_{-1}}{N^2}X\,(X-1)\,(X-2)+k_2\,X\right]P_s(X). \end{aligned} \tag{87}$$

The entropy production [Eqs. (47b) and (48)] reads

$$\begin{aligned} \sigma_I = &\frac{1}{2}\sum_X\Bigg\{\left[\frac{k_1}{N^2}A\,(X-1)\,(X-2)\,P(X-1)\right. \\ &\left.-\frac{k_{-1}}{N^2}X\,(X-1)\,(X-2)\,P(X)\right]\times\ln\frac{k_1\,A\,P(X-1)}{k_{-1}\,X\,P(X)} \\ &+\left[\frac{k_{-1}}{N^2}(X+1)\,X\,(X-1)\,P(X+1)-\frac{k_1}{N^2}A\,X\,(X-1)\,P(X)\right] \\ &\times\ln\frac{k_{-1}\,(X+1)\,P(X+1)}{k_1\,A\,P(X)}+[k_2\,(X+1)\,P(X+1) \\ &-k_{-2}\,B\,P(X)]\ln\frac{k_2\,(X+1)\,P(X+1)}{k_{-2}\,B\,P(X)}+[k_{-2}\,B\,P(X-1) \\ &-k_2\,X\,P(X)]\ln\frac{k_{-2}\,B\,P(X-1)}{k_2\,X\,P(X)}\Bigg\}. \end{aligned} \tag{88}$$

Limiting ourselves to the steady state, using the zero probability flux property (87) and combining the first and fourth and the second and third terms in Eq. (88), we can further reduce this expression to the simpler form

$$\begin{aligned} \sigma_I = &\frac{1}{2}\sum_X\{[k_{-2}\,B\,P(X-1)-k_2\,X\,P(X)]+[k_{-2}\,B\,P(X) \\ &-k_2\,(X+1)\,P(X+1)]\}\times\ln\frac{k_{-1}\,k_{-2}\,B}{k_1\,k_2\,A} \end{aligned} \tag{89}$$

or, using the normalization of P and the definition of the first moment

$$\sigma_I = \ln\frac{k_{-1}\,k_{-2}\,B}{k_1\,k_2\,A}\,(k_{-2}\,B - k_2\,\langle X\rangle). \tag{90}$$

On the other hand, the mean-field entropy production can be written in the form [cf. Eq. (54)]

$$\sigma_m = k_B\ln\frac{k_1\,k_2\,a}{k_{-1}\,k_{-2}\,b}\,(k_2\,x_m - k_{-2}\,b). \tag{91}$$

Comparing with (90) and setting

$$\langle X\rangle = N\,(x_m + \Delta x) \tag{92}$$

we obtain

$$\sigma_I = \frac{N}{k_B}\,(\sigma_m + \Delta\sigma) \tag{93a}$$

with

$$\Delta\sigma = k_2\,\Delta x\ln\frac{k_1\,k_2\,A}{k_{-1}\,k_{-2}\,B}. \tag{93b}$$

We conclude that the entropy production of the fluctuations $\Delta\sigma$ arises from the fact that, due to the nonlinearity, averages and mean-field values differ by an amount Δx. This is in accordance with the conclusion reached using the extended local equilibrium approach of Sec. IV A. We recall that in the master equation approach, $\Delta\sigma$ is not a random variable but corresponds rather to the mean value of the entropy production of the fluctuations obtained in the extended local equilibrium approach.

It should be pointed out that in evaluating σ_I, it is essential to use the fluxes and forces associated with different elementary processes present. Using instead global forward and backward fluxes as they appear in the two sides of Eq. (87) along with the associated forces would lead to the trivial result where the steady-state entropy production vanishes identically. A similar result arises at the level of a Fokker-Planck description.

V. CONCLUSIONS

There is currently a revival of irreversible thermodynamics, driven by the search of a unifying description applicable to large classes of complex systems that may operate under conditions beyond the realm of traditional thermodynamics.[27–29] In this work, we outlined an approach toward an extension of irreversible thermodynamics incorporating the fluctuations of the macroscopic observables arising from microscopic-scale processes. We proposed two complementary definitions of entropy, one as a random field depending on the fluctuating state variables and one in terms of probability distributions. We subsequently derived entropy balance equations from which a generalized entropy flux and entropy production could be identified. We showed that in the absence of fluctuations, these quantities reduce to those of classical irreversible thermodynamics pioneered by Prigogine and analyzed their principal properties in the presence of fluctuations. We derived global stability and variational properties extending those of the macroscopic theory and highlighted the role of time asymmetry as expressed by the breakdown of detailed balance between different elementary processes present and their reverses. We assessed the role of nonlinearities in the entropy production of the fluctuations and determined its statistical properties beyond the mean values by deriving its probability density function. This quantity possesses a positive mean value, a property that can be regarded as the expression of the second law of thermodynamics. However, owing to the presence of fluctuations, it also displays a tail in the region of negative values, reflecting that with some probability, different fluxes present may not be aligned to the corresponding forces. The probability of such events is however exponentially penalized with the system size and the time.

A crucial point stressed throughout this work is the need to define the different quantities of interest and entropy production, in particular, in terms of individual processes contributing to the evolution of the observables and of their probability distributions. Failure to account for this leads to false conclusions as, for example, that the generalized entropy production vanishes identically at the steady state for one-variable Markov processes. Special care should be devoted in this respect to the Fokker-Planck equation description where, contrary to the master equation description, all processes are lumped into the rate functions f_i featured in the mean-field description (6) or in the associated Langevin equations (32).[11,29]

Stochastic thermodynamics is still in its infancy. Its formulation and its applications are based on the assumption that the dynamics of fluctuations is described by a Markov process. It would be undoubtedly desirable to extend the current setting to stochastic processes with memory or to deterministic processes giving rise to complex chaotic signals, as could be expected to be the case in systems with few degrees of freedom. The connection with information theoretic concepts highlighted throughout Sec. III is also worth developing further. The Shannon and dynamical entropies are of special interest in this respect. They are connected with the underlying dynamics through the Kolmogorov-Sinai entropy, and at the same time, when appropriate limits are taken, they reduce to quantities playing a central role in classical irreversible thermodynamics such as the entropy production. Such relations are instrumental in addressing problems at the interface between the computation theory and the foundations of irreversibility.[30–32] They should be analyzed further and extended to other complexity measures such as Renyi entropies or non-extensive entropies[33,34] suitable for modelling multifractal structures and processes. All in all, thanks to its remarkable flexibility and its ability of self-renewal, today irreversible thermodynamics is ready to fulfill in a profoundly transformed form its unique role in science as foreseen 70 years ago by its founding father, Ilya Prigogine.

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