

**Stochastic thermodynamics based on an Einstein-Boltzmann definition of fluctuating entropy**

Yannick De Decker

*Center for Nonlinear Phenomena and Complex Systems (CENOLI), Université libre de Bruxelles (ULB),  
Campus Plaine, C.P. 231. B-1050 Brussels, Belgium*

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Stochastic thermodynamics is an extension of classical nonequilibrium thermodynamics to small systems, where fluctuations are expected to play an important role. A central difficulty met when developing such an extension is how to define a nonequilibrium fluctuating entropy. Typically, the expression used is based on Gibbs' formula for entropy at equilibrium. In this work, we show that one can construct an alternative framework for stochastic thermodynamics based on an extension of Einstein's formula connecting the probability of fluctuations and entropy around equilibrium states. We compare the two approaches and discuss, in particular, how they lead to different interpretations of what a stochastic entropy and entropy production represent.

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Stochastic thermodynamics can be seen as an extension of equilibrium statistical mechanics to systems placed under nonequilibrium constraints. Its main purpose is to quantify the extent to which fluctuations affect the laws of classical thermodynamics. Initially, stochastic thermodynamics was mainly concerned with ensemble-averaged properties of Markovian systems [1–5]. More recently, a growing attention has been paid to the properties of thermodynamic quantities along individual trajectories [6–14] and to non-Markovian systems [15,16].

An important step in the development of stochastic thermodynamics is to define thermodynamic quantities in terms of stochastic processes. This problem proves particularly delicate in the case of entropy and entropy production. Any potential definition of these quantities must be such that (i) macroscopic thermodynamics is recovered in the fluctuation-free limit and (ii) the properties of equilibrium statistical mechanics are correctly reproduced. The Gibbs-Shannon entropy, which is an extension of Gibbs' formula for entropy at equilibrium, has been widely used for this purpose. Combining this definition of entropy and the master equation ruling the time evolution of probabilities, it is possible to deduce a form of entropy production for Markovian systems which is always nonnegative and converges to the expected classical expression in the macroscopic limit [2–4]. Because it is based on Gibbs' statistical definition, this choice of entropy also leads to results that are consistent with the Gibbs ensemble approach to equilibrium statistical mechanics.

The fact that the Gibbsian approach to stochastic thermodynamics satisfies all the necessary requirements does not preclude the existence of other acceptable definitions of stochastic entropy. Different definitions will lead to different frameworks, which will give the same results in the macroscopic limit because of the requirement of compatibility with classical thermodynamics. However, these frameworks can be expected to predict different behaviors at small scale. In this context, it would be important to point out these differences

and to assess which of the fluctuation-induced effects are definition-dependent and which ones are “universal.”

As mentioned before, the Gibbs formulation has also led to the development of a corresponding pathwise stochastic thermodynamics. Fluctuation theorems for entropy production, which can be seen as extensions of the second law of thermodynamics to small systems, have been obtained in this framework and one might again wonder whether these theorems are definition-dependent. Moreover, the Gibbsian definition of pathwise entropy can lead to results that are not compatible with macroscopic thermodynamics. For example, it predicts that the entropy production of systems with linear (or linearized) evolution laws is zero in the macroscopic limit, in contradiction with classical nonequilibrium thermodynamics [12].

For all these reasons, the possibility of developing alternative frameworks for stochastic thermodynamics should be pursued. We show here that the Gibbs-Shannon definition is, indeed, not the only admissible one. Entropy can also be defined from Einstein's postulate connecting the probability of equilibrium fluctuations to thermodynamic potentials. This alternative approach is, from the outset, consistent with equilibrium statistical mechanics in the sense that it leads to Einstein's celebrated formula for fluctuations around equilibrium. It gives birth to an expression for the stochastic entropy production that differs from the one obtained with the Gibbs-Shannon approach, but which is nevertheless consistent with its macroscopic counterpart. This new formulation of stochastic thermodynamics thus represents a legitimate alternative to the previously developed approaches.

In the present work, we illustrate these ideas with the case of open and spatially uniform reactive systems, maintained at constant volume and constant temperature. The procedure we use here can however be easily applied to systems with different constraints. In Sec. II, we recall the main features of the classical approach to nonequilibrium thermodynamics. Section III is devoted to a presentation of the new approach to stochastic thermodynamics. We show how Einstein's formula for the probability of fluctuations around equilibrium can

be used to define entropy in the presence of nonequilibrium constraints. Evolution laws for thermodynamic quantities of interest are derived, based on the master equation and on the previously introduced definition of stochastic entropy. A simple example is provided to illustrate the proposed framework. In Sec. IV, we discuss the main differences between the present approach and the one based on the Gibbs-Shannon definition of entropy. We finally summarize our results in Sec. V, where we also point toward possible future developments of the present work.

## II. CLASSICAL NONEQUILIBRIUM THERMODYNAMICS

We consider a spatially uniform system with constant volume  $V$  and temperature  $T$ . This system is in contact with external reservoirs at the same temperature and containing  $c$  different types of particles whose chemical potentials  $\boldsymbol{\mu} = (\mu_1, \mu_2, \dots, \mu_c)$  are constant as well. We moreover assume that no external forces act on the system's bulk properties.

The number of particles of each species  $k$  in the system can change due to the occurrence of one of the  $r$  processes taking place. These processes correspond either to a chemical reaction or to an exchange of particles with the external reservoirs. The state of the system is defined by the number of particles of each species,

$$N = (N_1, N_2, \dots, N_c). \quad (1)$$

Each elementary process  $\rho = (1, 2, \dots, r)$  can induce a change in this state in the form of a jump,

$$N \xrightarrow{\rho} N + \mathbf{v}_\rho, \quad (2)$$

where  $\mathbf{v}_\rho = (v_{1\rho}, v_{2\rho}, \dots, v_{c\rho})$  is a vector of stoichiometric coefficients, which are integers reflecting the process-induced variation in the number of particles. Notice that there corresponds to each process  $\rho$  a backward process  $-\rho$  such that

$$N \xrightarrow{-\rho} N - \mathbf{v}_\rho. \quad (3)$$

We now turn to the evaluation of thermodynamic quantities of interest. We focus here more specifically on the time evolution of entropy and on the rate of entropy production. In classical nonequilibrium thermodynamics, the evolution equations for state functions are obtained by assuming that their dependence on the state variables under nonequilibrium conditions is the same as in equilibrium [17,18]. Consequently, the time evolution for the entropy  $S$  of a system with the above-mentioned constraints is given by

$$\begin{aligned} \frac{dS}{dt} &= \sum_k \left( \frac{\partial S}{\partial N_k} \right)_{T,V,N_{i \neq k}} \frac{dN_k}{dt} \\ &= \sum_k s_k \frac{dN_k}{dt}, \end{aligned} \quad (4)$$

where we introduced the molar entropy  $s_k$ . Evolution equations for the number of particles are needed to evaluate entropy in the course of time. For macroscopic systems, these equations are of the type

$$\frac{dN_k}{dt} = \sum_\rho v_{k\rho} w_\rho. \quad (5)$$

In the above expression,  $w_\rho$  is the rate of process  $\rho$  and  $v_{k\rho}$  are the previously introduced stoichiometric coefficients. Introducing Eq. (5) into Eq. (4) yields

$$\frac{dS}{dt} = \sum_\rho w_\rho \Delta_\rho S, \quad (6)$$

in which

$$\Delta_\rho S = \sum_k v_{k\rho} s_k \quad (7)$$

is called the entropy of process  $\rho$ .

We introduce at this stage the chemical potential of species  $k$ ,

$$\mu_k = \left( \frac{\partial F}{\partial N_k} \right)_{T,V,N_{i \neq k}}. \quad (8)$$

$F = U - TS$  is the Helmholtz free energy, where  $U$  is the internal energy of the system. Consequently, the chemical potential and the molar entropy are related by

$$s_k = \frac{u_k - \mu_k}{T}, \quad (9)$$

in which

$$u_k = \left( \frac{\partial U}{\partial N_k} \right)_{T,V,N_{i \neq k}} \quad (10)$$

is the partial internal energy of species  $k$ . Using relation (9) in Eq. (7) leads to

$$\Delta_\rho S = \frac{\Delta_\rho U - \Delta_\rho F}{T}, \quad (11)$$

where

$$\Delta_\rho U = \sum_k v_{k\rho} u_k \quad (12)$$

is the isochoric heat of the process and

$$\Delta_\rho F = \sum_k v_{k\rho} \mu_k \quad (13)$$

is the corresponding change in free energy.

Inserting Eq. (11) into Eq. (6) leads to a decomposition of the rate of change in entropy into two distinct contributions:

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt}, \quad (14)$$

where

$$\frac{d_e S}{dt} = \sum_\rho w_\rho \frac{\Delta_\rho U}{T} \quad (15)$$

is the entropy flux and

$$\frac{d_i S}{dt} = - \sum_\rho w_\rho \frac{\Delta_\rho F}{T} \quad (16)$$

is the entropy production. This entropy production term is usually expressed in terms of the affinities,

$$\mathcal{A}_\rho = -\Delta_\rho F, \quad (17)$$

which leads to

$$\frac{d_i S}{dt} = \sum_{\rho} w_{\rho} \frac{A_{\rho}}{T}. \quad (18)$$

The second law of thermodynamics stipulates that  $d_i S/dt \geq 0$  for any spontaneously occurring macroscopic process, with equality holding only at equilibrium. The rate and the affinity of a process must thus have the same sign. For elementary reactive processes, this constraint has the consequence that the affinity can be rewritten in terms of the rates as

$$A_{\rho} = k_B T \ln \frac{w_{\rho}}{w_{-\rho}}, \quad (19)$$

in which  $k_B$  is Boltzmann's constant, so that one has

$$\frac{d_i S}{dt} = \frac{k_B}{2} \sum_{\rho} [w_{\rho} - w_{-\rho}] \ln \frac{w_{\rho}}{w_{-\rho}}. \quad (20)$$

### III. STOCHASTIC THERMODYNAMICS

The extension of nonequilibrium thermodynamics to fluctuating systems is most often based on the assumption that the underlying stochastic processes are Markovian. As a consequence, the probability  $P(N, t)$  to be in state  $N$  at time  $t$  obeys a birth-and-death master equation of the form

$$\begin{aligned} \frac{dP(N, t)}{dt} = \sum_{\rho} [W_{\rho}(N - \mathbf{v}_{\rho}) P(N - \mathbf{v}_{\rho}, t) \\ - W_{-\rho}(N) P(N, t)] \equiv \sum_{\rho} J_{\rho}(N, t). \end{aligned} \quad (21)$$

In this equation, the  $W_{\rho}s$  are the transition probabilities per unit time associated with the various aforementioned processes. A major step in stochastic thermodynamics is to derive, from Eq. (21), an evolution equation for thermodynamic quantities of interest. As mentioned earlier, this requires to define entropy in terms of the state of the system.

#### A. Definition of entropy based on the Einstein formula

To define entropy, we first consider the equilibrium probability distribution. The equilibrium distribution is here defined as the stationary solution of Eq. (21) in the special case where all the probability flows  $J_{\rho}$  are zero. Since we are considering systems at constant  $T$  and  $V$ , this solution is nothing else but the grand-canonical distribution [19]

$$P(N, \text{eq}) = Z(N) \exp \beta \left[ \Phi_{\text{eq}} + \sum_k \mu_k N_k \right]. \quad (22)$$

In this equation,  $\beta = 1/k_B T$ ,  $Z(N) = Z(T, V, N)$  is the canonical partition function, and  $\Phi_{\text{eq}} = \Phi_{\text{eq}}(T, V, \mu)$  is the grand potential, here evaluated at equilibrium. This potential is related to the equilibrium values of the Helmholtz free energy ( $F_{\text{eq}}$ ) and of the Gibbs free energy ( $G_{\text{eq}}$ ) appearing in thermodynamics by the relation

$$\Phi_{\text{eq}} = F_{\text{eq}} - G_{\text{eq}} = U_{\text{eq}} - T S_{\text{eq}} - G_{\text{eq}}. \quad (23)$$

We now want to use Eq. (22) to infer a definition for the fluctuating (or statewise) entropy  $S(N)$ . Inverting Boltzmann's famous expression for the microcanonical entropy, Einstein

proposed that for an isolated system, the equilibrium probability scales like [20,21]

$$P(N, \text{eq}) \propto \exp \left( \frac{\Delta S}{k_B} \right), \quad (24)$$

where  $\Delta S = S(N) - S_{\text{eq}}$  is a measure of the deviation of the statewise entropy from its thermodynamic value. This expression shows that the probability of a fluctuation away from the equilibrium state is dictated by the associated variation of the thermodynamic potential, which in this case is entropy because an isolated system has been considered. This idea can be extended to closed and open systems [19]. In particular, for systems at constant  $T$  and  $V$  one expects to have

$$P(N, \text{eq}) \propto \exp -\beta \Delta \Phi, \quad (25)$$

with

$$\Delta \Phi = \Phi(N) - \Phi_{\text{eq}} \quad (26)$$

being the difference between the statewise value  $\Phi(N)$  taken by the grand potential and its macroscopic value at equilibrium,  $\Phi_{\text{eq}}$ .

The grand-canonical distribution (22) can indeed be cast in such a form. Introducing the statewise Gibbs free energy

$$G(N) = \sum_k \mu_k N_k \quad (27)$$

in this equation, we note that it can be rewritten as

$$P(N, \text{eq}) = \exp \beta [\Phi_{\text{eq}} + k_B T \ln Z(N) + G(N)]. \quad (28)$$

Comparing Eqs. (28) and (25), we conclude that statewise grand potential takes the form

$$\Phi(N) = A - k_B T \ln Z(N) - G(N), \quad (29)$$

where  $A = A(T, V, \mu)$  is state-independent. Now, we also have that

$$\Phi(N) = F(N) - G(N). \quad (30)$$

Combining Eqs. (29) and (30), we readily reach the conclusion that

$$F(N) = A - k_B T \ln Z(N). \quad (31)$$

This leads to the conclusion that the statewise entropy is given, at equilibrium, by

$$S(N) = \frac{U(N) - F(N)}{T} = \frac{U(N)}{T} + k_B \ln Z(N) - \frac{A}{T}. \quad (32)$$

Evaluating this quantity *a priori* requires having explicit expressions for the internal energy of the system, for the canonical partition function, and for the constant  $A$ .

To evaluate the time evolution of entropy and related quantities (such as the entropy production), the definition (32) must be extended to nonequilibrium situations. We will adopt in the present work a "local equilibrium" assumption, with which we suppose that the nonequilibrium expression for  $S(N)$  should have the same structure as in equilibrium. This is, in fact, exactly what is done in the more traditional approach to stochastic thermodynamics, in which the equilibrium Gibbsian form of entropy is used as such in nonequilibrium cases (see Sec. IV for a more detailed discussion on this topic).

With this definition, we can now turn to the evaluation of stochastic thermodynamic functions out of equilibrium.

### B. Temporal evolution of entropy and entropy production

Consider the mean entropy

$$\bar{S} = \sum_N S(N) P(N, t). \quad (33)$$

Using the master equation (21), we conclude that its time variation obeys

$$\begin{aligned} \frac{d\bar{S}}{dt} &= \sum_N S(N) \frac{dP(N, t)}{dt} \\ &= \sum_{N, \rho} S(N) [W_\rho(N - \mathbf{v}_\rho) P(N - \mathbf{v}_\rho, t) \\ &\quad - W_{-\rho}(N) P(N, t)] \\ &= \sum_{N, \rho} S(N) [W_\rho(N - \mathbf{v}_\rho) P(N - \mathbf{v}_\rho, t) \\ &\quad - W_\rho(N) P(N, t)] \\ &= \sum_{N, \rho} [W_\rho(N) \Delta_\rho S] P(N, t), \end{aligned} \quad (34)$$

in which one finds the variation of statewise entropy due to process  $\rho$ ,

$$\Delta_\rho S = S(N + \mathbf{v}_\rho) - S(N). \quad (35)$$

Notice that the structure of Eq. (34) is very similar to that of its macroscopic counterpart, Eq. (6).

A major issue in nonequilibrium thermodynamics consists in choosing a way to decompose the evolution equation (34) into an entropy flow and an entropy production terms. As we have seen in Sec. II, entropy production should be defined in such a way that it measures the total change in free energy due to the various processes taking place. We thus introduce the stochastic free energy of process  $\rho$  with

$$\Delta_\rho F = F(N + \mathbf{v}_\rho) - F(N), \quad (36)$$

where  $F$  is defined by Eq. (31). The Evolution law (34) can thus be split into a flux and a production of entropy,

$$\frac{d\bar{S}}{dt} = \frac{d_e \bar{S}}{dt} + \frac{d_i \bar{S}}{dt}, \quad (37)$$

where the entropy flux reads

$$\frac{d_e \bar{S}}{dt} = \sum_{N, \rho} \left[ W_\rho(N) \frac{\Delta_\rho U}{T} \right] P(N, t), \quad (38)$$

in which

$$\Delta_\rho U = U(N + \mathbf{v}_\rho) - U(N) \quad (39)$$

is the corresponding change in internal energy at constant  $T$  and  $V$ , while the production term is given by

$$\frac{d_i \bar{S}}{dt} = - \sum_{N, \rho} \left[ W_\rho(N) \frac{\Delta_\rho F}{T} \right] P(N, t). \quad (40)$$

In analogy with the macroscopic formulation, we can introduce the mesoscopic affinity

$$\tilde{\mathcal{A}}_\rho = -\Delta_\rho F \quad (41)$$

and express Eq. (40) as

$$\frac{d_i \bar{S}}{dt} = \sum_{N, \rho} \left[ W_\rho(N) \frac{\tilde{\mathcal{A}}_\rho}{T} \right] P(N, t). \quad (42)$$

We will focus here on the properties of entropy production. Using Eq. (31) in the definition (41) of the affinities  $\tilde{\mathcal{A}}_\rho$ , we find that

$$\tilde{\mathcal{A}}_\rho = k_B T \ln \frac{Z(N + \mathbf{v}_\rho)}{Z(N)}. \quad (43)$$

Now, the ratio of canonical distribution functions can be related to transition probabilities per unit time. Indeed, because at equilibrium all the probability currents  $J_\rho$  vanish, the transition probabilities must be such that

$$\ln \frac{W_\rho(N)}{W_{-\rho}(N + \mathbf{v}_\rho)} = \ln \frac{P(N + \mathbf{v}_\rho, \text{eq})}{P(N, \text{eq})} = \ln \frac{Z(N + \mathbf{v}_\rho)}{Z(N)}. \quad (44)$$

Note that we used Eq. (22) together with the fact that, by definition,  $\sum_k v_{kr} \mu_k = 0$  at equilibrium for each reaction. Equation (43) can thus be rewritten as

$$\tilde{\mathcal{A}}_\rho = k_B T \ln \frac{W_\rho(N)}{W_{-\rho}(N + \mathbf{v}_\rho)}. \quad (45)$$

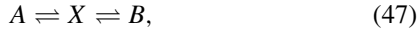
The corresponding entropy production reads

$$\begin{aligned} \frac{d_i \bar{S}}{dt} &= k_B \sum_{N, \rho} W_\rho(N) P(N, t) \left[ \ln \frac{W_\rho(N)}{W_{-\rho}(N + \mathbf{v}_\rho)} \right] \\ &= k_B \sum_{N, \rho} W_{-\rho}(N) P(N, t) \left[ \ln \frac{W_{-\rho}(N)}{W_\rho(N - \mathbf{v}_\rho)} \right] \\ &= k_B \sum_{N, \rho} W_\rho(N - \mathbf{v}_\rho) P(N - \mathbf{v}_\rho, t) \left[ \ln \frac{W_\rho(N - \mathbf{v}_\rho)}{W_{-\rho}(N)} \right] \\ &= \frac{k_B}{2} \sum_{N, \rho} J_\rho(N, t) \left[ \ln \frac{W_\rho(N - \mathbf{v}_\rho)}{W_{-\rho}(N)} \right]. \end{aligned} \quad (46)$$

This expression will obviously lead to the correct macroscopic equation (20). Indeed, in the limit of infinite size  $N - \mathbf{v}_\rho \approx N$  and the probability distribution is a Kronecker  $\delta$  function centered on the macroscopic solution  $N_m(t)$ . Equation (46) thus becomes equal to Eq. (20), provided that  $\lim_{V \rightarrow \infty} W_\rho[N_m(t)] = w_\rho$ . It is moreover based on a definition of the Helmholtz free energy that is consistent with Einstein's statistical mechanics, in the sense that Eq. (31) ensures that the Einstein formula (25) is satisfied. The two necessary constraints (agreement with equilibrium statistical mechanics and with macroscopic thermodynamics) are thus respected in this ‘‘Einstein-Boltzmann’’ approach to stochastic thermodynamics.

### C. Example

In this subsection, we discuss a simple example of nonequilibrium reaction to illustrate the proposed framework. Consider the reaction scheme



where the concentrations of  $A$  and  $B$  are fixed. The system is considered ideal and all kinetic constants are set to 1, for simplicity. The associated transition probabilities thus read

$$W_1(N) = N_A, \quad W_{-1}(N+1) = N+1, \quad (48)$$

$$W_2(N) = N, \quad W_{-2}(N-1) = N_B, \quad (49)$$

where  $N_A$ ,  $N_B$ , and  $N$  are the number of particles of species  $A$ ,  $B$ , and  $X$ , respectively. The mesoscopic affinities are given by

$$\tilde{A}_1 = k_B T \ln \frac{N_A}{N+1}, \quad \tilde{A}_{-1} = k_B T \ln \frac{N}{N_A}, \quad (50)$$

$$\tilde{A}_2 = k_B T \ln \frac{N}{N_B}, \quad \tilde{A}_{-2} = k_B T \ln \frac{N_B}{N+1}. \quad (51)$$

and the entropy production is given by

$$\begin{aligned} \frac{d_i \bar{S}}{dt} &= k_B \sum_N [N_A P(N, t) - (N+1) P(N+1, t)] \ln \frac{N_A}{N+1} \\ &+ k_B \sum_N [N_B P(N, t) - (N+1) P(N+1, t)] \ln \frac{N_B}{N+1}. \end{aligned} \quad (52)$$

Generally speaking, Eq. (52) will not be equal to the macroscopic expression, which reads here

$$\frac{d_i \bar{S}}{dt} = k_B [N_A - \bar{N}(t)] \ln \frac{N_A}{\bar{N}(t)} + k_B [N_B - \bar{N}(t)] \ln \frac{N_B}{\bar{N}(t)}, \quad (53)$$

where  $\bar{N}(t) = N_m(t)$  obeys

$$\frac{d\bar{N}(t)}{dt} = A + B - 2\bar{N}(t). \quad (54)$$

For large enough systems, however, we can expect that states for which  $N \gg 1$  are the most probable, and the stochastic entropy production reduces to

$$\frac{d_i \bar{S}}{dt} \approx k_B \sum_N \left[ (N_A - N) \ln \frac{N_A}{N} + (N_B - N) \ln \frac{N_B}{N} \right] P(N, t). \quad (55)$$

As mentioned before, in the macroscopic limit  $P(N, t)$  is a Kronecker  $\delta$  centered on the macroscopic solution for all times, provided that it is initially so. Equation (52) will thus converge to Eq. (53), as expected. It should also be noted that because of the linearity of transition probabilities in the present example,  $d_i \bar{S}/dt$  will also be equal to its macroscopic expression for all steady states, irrespective of the size of the system. Indeed, this linearity has the consequence that the steady-state solution for the probability distribution is

Poissonian:

$$P(N, \text{st}) = \frac{\bar{N}^N e^{-\bar{N}}}{N!}. \quad (56)$$

Replacing  $N+1$  with  $\bar{N} P(N, \text{st})/P(N+1, \text{st})$  in Eq. (52) leads to Eq. (53), since at steady state

$$\begin{aligned} \sum_{N, \rho} \ln \frac{P(N, t)}{P(N + \nu_\rho, t)} W_\rho(N) P(N, t) \\ = - \sum_N \ln P(N, t) \frac{dP(N, t)}{dt} = 0. \end{aligned} \quad (57)$$

The conclusion that the macroscopic solution for entropy production is recovered at steady state is intimately related to the fact that the probability distribution is Poissonian. For systems with nonlinearities, the probability will not be a Poisson distribution at steady state and deviations from the macroscopic value of entropy production should be expected for finite-size systems.

## IV. COMPARISON WITH THE GIBBS-SHANNON APPROACH

We mentioned on several occasions that stochastic thermodynamics usually rests on a different definition of entropy. More precisely, the Gibbs-Shannon expression is typically used:

$$\bar{S} = \sum_N [S^0(N) - k_B \ln P(N, t)] P(N, t). \quad (58)$$

One finds in this definition two contributions to entropy: a part  $S^0$  representing the entropy of a system with a fixed number of particles, and a logarithmic part accounting for the variability of the system by assigning to the number of particles a probability distribution. Choosing this expression amounts to defining the statewise entropy by

$$S(N) = S^0(N) - k_B \ln P(N, t). \quad (59)$$

Consequently, the statewise Helmholtz free energy reads

$$F(N) = F^0(N) + k_B T \ln P(N, t), \quad (60)$$

in which

$$F^0(N) = U(N) - T S^0(N) \quad (61)$$

can be interpreted as the free energy of a system with fixed composition. Just like our choice, these definitions can be said to be consistent with equilibrium statistical mechanics, albeit in a different sense, as we will show now.

### A. The Gibbs-Shannon approach

Consider the equilibrium value of the mean of the Helmholtz free energy:

$$\bar{F} = \sum_N F(N) P(N, \text{eq}). \quad (62)$$

We wish to define  $F^0(N)$  in Eq. (60) in such a way that the means of the statewise thermodynamic functions coincide with their macroscopic values at equilibrium:

$$\bar{F} = F_{\text{eq}}, \quad \bar{G} = G_{\text{eq}}, \quad \bar{\Phi} = \Phi_{\text{eq}}. \quad (63)$$

This leads to

$$\bar{F} = \bar{G} + \Phi_{\text{eq}}. \quad (64)$$

Such constraint can be fulfilled by choosing

$$F(N) = \sum_k \mu_k N_k + \Phi_{\text{eq}}$$

or, using Eq. (22),

$$F(N) = -k_B T \ln Z(N) + k_B T \ln P(N, \text{eq}). \quad (65)$$

Comparing Eqs. (60) and (65), one readily arrives to the conclusion that imposing  $F^0 = -k_B T \ln Z$  leads to the correct result. This result makes sense from the point of view of statistical mechanics: In the Gibbs-Shannon approach,  $F^0$  can be interpreted as the Helmholtz free energy of a system with fixed composition, and  $-k_B T \ln Z$  is the expression for this quantity in the canonical ensemble, where the number of particles are constant.

To extend this result to nonequilibrium situations, we simply need to invoke again the same form of ‘‘local equilibrium’’ hypothesis as the one we used for the Einstein-formula inspired definition of entropy. We suppose that the nonequilibrium expression for  $F$  should have the same structure as in equilibrium,

$$F(N) = -k_B T \ln Z(N) + k_B T \ln P(N, t), \quad (66)$$

the only difference with Eq. (65) being that the probability distribution does not need to be the equilibrium grand-canonical expression (22). Note that this choice also has the consequence that

$$S^0(N) = \frac{U(N)}{T} + k_B \ln Z(N) \quad (67)$$

in the Gibbs-Shannon entropy (58). These expressions allow us to estimate the rate of change in entropy and entropy production explicitly. Focusing again on entropy production, we note that the above definition of  $F$  leads to a mesoscopic affinity of the form

$$\begin{aligned} \tilde{A}_\rho &= F(N) - F(N + \mathbf{v}_\rho) = k_B T \ln \frac{Z(N + \mathbf{v}_\rho) P(N, t)}{Z(N) P(N + \mathbf{v}_\rho, t)} \\ &= k_B T \ln \frac{W(N) P(N, t)}{W(N + \mathbf{v}_\rho) P(N + \mathbf{v}_\rho, t)}. \end{aligned} \quad (68)$$

This expression leads to the most commonly used formula for entropy production [2,3],

$$\begin{aligned} \frac{d_i \bar{S}}{dt} &= k_B \sum_{N, \rho} W_\rho(N) P(N, t) \left[ \ln \frac{W_\rho(N) P(N, t)}{W_{-\rho}(N + \mathbf{v}_\rho) P(N + \mathbf{v}_\rho, t)} \right] \\ &= \frac{k_B}{2} \sum_{N, \rho} J_\rho(N, t) \left[ \ln \frac{W_\rho(N - \mathbf{v}_\rho) P(N - \mathbf{v}_\rho, t)}{W_{-\rho}(N) P(N, t)} \right], \end{aligned} \quad (69)$$

which was first proposed by Schnakenberg [22]. It should be noticed that this stochastic entropy production is always nonnegative because of the inequality  $(a - b) \ln(a/b) \geq 0$ . It is zero only when the system is at equilibrium, because of the condition of detailed balance.

Just like the expression derived earlier, Eq. (46), the entropy production (69) can be considered a satisfactory

stochastic extension of its macroscopic counterpart. It is indeed based on definitions of thermodynamic quantities that are, by construction, consistent with Gibbsian equilibrium statistical mechanics. Moreover, the stochastic affinity (68) converges to the macroscopic expression (19) in the limit of large systems, which has the consequence that the stochastic entropy production converges to its macroscopic value as well [3].

The possibility to construct two acceptable stochastic extensions of thermodynamics naturally leads to the question of what the main differences are between these two approaches, and the consequences that the different choices have in terms of interpretation of stochastic thermodynamics.

## B. The equilibrium state

The two approaches are based on different thermodynamic interpretations of the functions appearing in the equilibrium probability distribution. This means that these two approaches also differ in what they consider to be an equilibrium state.

In the Gibbsian approach, equilibrium is attained whenever the probability distribution reaches its equilibrium form, Eq. (22). It thus coincides with the detailed balance condition for the master equation, Eq. (44). In the Einstein-Boltzmann approach, we introduce a thermodynamic potential  $\Phi(N)$ . Consequently, equilibrium is there restricted to the set of values taken by  $N$  for which this potential is extremal and coincides with its equilibrium value. This has the consequence that equilibrium corresponds to the set of variables  $N_{\text{eq}}$  that maximizes the equilibrium probability distribution.

A major consequence of this difference is that the Gibbsian approach includes in the equilibrium state many configurations which, in the Einstein-Boltzmann approach, would be considered as being out of equilibrium. Consider as an illustration the simple example (47). In classical thermodynamics, the equilibrium state corresponds to  $N/N_B = N/N_A = 1$ , which can be satisfied only if  $N_A = N_B = N$ , i.e., whenever  $\mu_A = \mu_B = \mu_X$ . In the Gibbsian framework, equilibrium corresponds to the double condition

$$N_A P(N, \text{eq}) = (N + 1) P(N + 1, \text{eq}) \quad (70)$$

$$(N + 1) P(N + 1, \text{eq}) = N_B P(N, \text{eq}). \quad (71)$$

As a consequence, equilibrium is solely defined by  $N_A = N_B$  and no restriction is being put on  $N$ . All  $N$  values are considered acceptable equilibrium states as long as they have a nonzero probability in the equilibrium distribution  $P(N, \text{eq})$ . What equilibrium imposes here is the relative probability of the different possible values.

In the Einstein-Boltzmann approach, equilibrium is attained whenever the grand potential  $\Phi = F - G$  is extremal. In the present example, we have

$$\Phi(N) = -k_B T \ln Z(N) - \mu_A N_A - \mu_B N_B - \mu N. \quad (72)$$

In the above equation,  $Z$  is the canonical partition function of an ideal mixture,

$$Z(N) = \frac{\zeta_A^{N_A} \zeta_B^{N_B} \zeta^N}{N_A! N_B! N!}, \quad (73)$$

in which the  $\zeta$ s are the molecular partition functions. Differentiating  $\Phi$  with respect to  $N$  (and using Stirling's approximation  $\ln N! \approx N \ln N - N$ ) leads to the conclusion that

$$N_{eq} = \exp(\beta \mu + \ln \zeta) \quad (74)$$

must hold at equilibrium. Using standard expressions from equilibrium statistical thermodynamics one readily arrives to the conclusion that, for the Einstein-Boltzmann approach equilibrium is defined by

$$N_{eq} = K N_A = N_A, \quad (75)$$

where  $K$  is the equilibrium constant for the reaction  $A \rightleftharpoons X$ , which is here equal to 1 in view of our choice of parameters. A similar relation holds between  $N$  and  $N_B$ ,  $N_{eq} = N_B$ . The equilibrium state thus corresponds to a single, well-defined value for the number of  $X$  particles. Any value of  $N$  that does not respect  $N = N_A = N_B$  is considered to correspond to a system out of equilibrium. This includes, among others, values respecting the detailed balance condition.

To summarize, one could say that the Einstein-Boltzmann approach defines an equilibrium *state* while the Gibbsian approach defines an equilibrium *distribution of states*.

### C. Entropy

Comparing expressions (67) and (32), one reaches the conclusion that up to a constant term

$$S_{GS}(N) = S_{EB}(N) - k_B \ln P(N, t) \quad (76)$$

or, equivalently,

$$\bar{S}_{GS} = \bar{S}_{EB} - k_B \sum_N P(N, t) \ln P(N, t). \quad (77)$$

The subscripts GS and EB stand for Gibbs-Shannon and Einstein-Boltzmann interpretations, respectively. The Einstein-Boltzmann entropy can thus be seen as the part  $S^0$  of the Gibbs-Shannon entropy that accounts for the entropy of the system at fixed number of particles.

How can this result be interpreted? The Gibbs-Shannon entropy is known to represent the amount of information required to specify the state of a system. Since in this approach, a state is actually a distribution of states, this information includes a contribution related to the variability of the number of particles. In the Einstein-Boltzmann approach, a state corresponds to a precise configuration  $N$ .  $S^0$  can thus still be interpreted as a measure of information, but only the information pertaining to "hidden" degrees of freedom that are not set when fixing the number of particles. It does not, consequently, have a privileged connection with the probability distribution of the number of particles, contrary to the Gibbs-Shannon expression.

A direct consequence of all this is that the Gibbs-Shannon entropy will always be larger than the Einstein-Boltzmann entropy, since it includes information on the distribution of states. It is only in the macroscopic limit that these quantities become equal, because the logarithmic part of the Gibbs-Shannon entropy vanishes (there is no more variability in the number of particles). Differences also appear in the rate of

change of these two entropies. Indeed,

$$\left(\frac{d\bar{S}}{dt}\right)_{GS} = \left(\frac{d\bar{S}}{dt}\right)_{EB} - k_B \sum_N \ln P(N, t) \frac{dP(N, t)}{dt}. \quad (78)$$

The Gibbs-Shannon evolution equation contains, in comparison with the Einstein-Boltzmann one, an additional term accounting for the relaxation of the probability distribution toward its steady-state. Consider again the example (47) for illustration. The probability distribution  $P(N, t)$  is known to be Poissonian all along the evolution of the system as soon as it is so at  $t = 0$ . Using Eq. (56) one obtains from Eq. (78)

$$\left(\frac{d\bar{S}}{dt}\right)_{GS} = \left(\frac{d\bar{S}}{dt}\right)_{EB} - k_B \frac{d\bar{N}(t)}{dt} \sum_N \ln \frac{\bar{N}(t)}{N+1} P(N, t). \quad (79)$$

Introducing the deviation from the mean,  $\Delta N = N - \bar{N}$  and keeping the dominant terms in  $\Delta N$  in Eq. (79) yields

$$\left(\frac{d\bar{S}}{dt}\right)_{GS} \approx \left(\frac{d\bar{S}}{dt}\right)_{EB} + \frac{k_B}{2} \frac{d \ln \bar{N}(t)}{dt}. \quad (80)$$

Notice that the difference between the two rates has no definite sign, i.e., the Gibbs-Shannon entropy can vary more rapidly or more slowly than the other, depending on the initial condition used in Eq. (54). In any case, just like for entropy itself the difference between the rates vanishes in the macroscopic limit, since entropy is extensive while the correction term scales like the logarithm of  $N$ .

The presence of an additional term in the evolution law for the Gibbs-Shannon entropy raises the question of how the corresponding entropy flow and entropy production terms are each affected. We discuss this point in the following subsection.

### D. Entropy production

Because of the different definitions of statewise free energy (or, equivalently, of the affinities), the expressions for entropy production will in general not be the same in the two frameworks. Indeed, comparing the first lines in Eqs. (69) and (46) we find that

$$\begin{aligned} \left(\frac{d_i \bar{S}}{dt}\right)_{GS} &= \left(\frac{d_i \bar{S}}{dt}\right)_{EB} + k_B \sum_{N, \rho} \ln \frac{P(N, t)}{P(N + \mathbf{v}_\rho, t)} \\ &\quad \times W_\rho(N) P(N, t) \\ &= \left(\frac{d_i \bar{S}}{dt}\right)_{EB} - k_B \sum_N \ln P(N, t) \frac{dP(N, t)}{dt}. \end{aligned} \quad (81)$$

The two frameworks thus predict the same steady-state average entropy production but will otherwise differ. The reason behind this difference is that the production of the Gibbs-Shannon entropy includes a contribution representing the irreversible evolution of the probability distribution toward its asymptotic solution, which does not appear in the Einstein-Boltzmann formulation. Notice that the difference in the definition of entropy only affects entropy production, while the entropy flow is the same in both frameworks, because  $d\bar{S}/dt = d_e \bar{S}/dt + d_i \bar{S}/dt$  in Eq. (78).

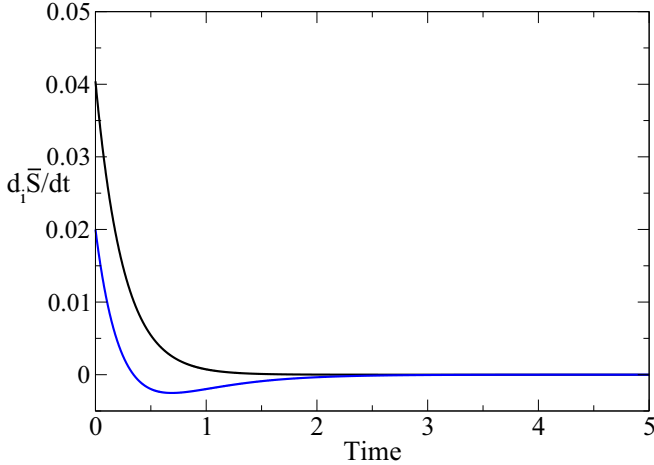


FIG. 1. Entropy production for the example (47), with  $N_A = N_B = 50$  and  $\bar{N}(0) = 49$  at  $t = 0$ , obtained by numerical integration (fourth-order Runge-Kutta,  $dt = 10^{-4}$ ). The black curve is the Gibbs-Shannon expression, Eq. (82), which is also the macroscopic solution. The blue curve is the weak-noise limit of the Einstein-Boltzmann entropy production, Eq. (80). Notice that the values of entropy production are rescaled by  $k_B$ .

As mentioned before, the Gibbs-Shannon entropy production is nonnegative by construction. Because it does not share the same structure, nothing seems to prevent *a priori* expression Eq. (46) from becoming negative. It is only in the macroscopic limit that  $(d_i S/dt)_{EB}$  can be said to be always nonnegative, since it then converges to the classical expression for entropy production. To see this, consider again the case of the linear reaction scheme (47). It is well-known that for Poisson distributions the Gibbs-Shannon entropy production is identical to its macroscopic value for all times [2]:

$$\left(\frac{d_i \bar{S}}{dt}\right)_{GS} = k_B (N_A - \bar{N}) \ln \frac{N_A}{\bar{N}} + k_B (N_B - \bar{N}) \ln \frac{N_B}{\bar{N}} \geq 0. \quad (82)$$

The Einstein-Boltzmann formulation gives

$$\begin{aligned} \left(\frac{d_i \bar{S}}{dt}\right)_{EB} &= \left(\frac{d_i \bar{S}}{dt}\right)_{GS} + k_B \frac{d\bar{N}(t)}{dt} \sum_N \ln \frac{\bar{N}(t)}{N+1} P(N, t) \\ &= \left(\frac{d_i \bar{S}}{dt}\right)_{GS} + k_B \frac{d\bar{N}(t)}{dt} [\ln \bar{N}(t) - \overline{\ln(N+1)}]. \end{aligned} \quad (83)$$

For sufficiently large systems the contribution under brackets is always positive because of Jensen's inequality ( $\overline{\ln N} \leq \ln \bar{N}(t)$  due to the concavity of logarithmic functions). However, the derivative of the mean has no predefined sign and can lead to negative contributions. This “contamination” of entropy production by stochasticity can lead to transient negative entropy productions, even in the weak-noise limit (80). An example is provided in Fig. 1 for the relaxation toward equilibrium of a system initially containing  $\approx 50$  particles of  $X$ . The plain black curve is the macroscopic entropy production, and the blue line is the Einstein-Boltzmann expression (83) [which is here indistinguishable from its weak noise limit,

Eq. (80)]. We observe that indeed,  $(d_i S/dt)_{EB}$  can become negative during the transient leading to the final state. This “antithermodynamic” behavior disappears in the macroscopic limit since the stochastic entropy production becomes then equal to its macroscopic counterpart. The physical interpretation of this result is discussed in the next section.

## V. CONCLUSIONS

In this short report, we showed that there exist at least two different ways of defining entropy and entropy production for reactive Markovian systems, which are both consistent with equilibrium statistical mechanics and classical nonequilibrium thermodynamics. One possibility consists in defining a statewise entropy in such a way that its ensemble mean corresponds to the Gibbs-Shannon formula at equilibrium. This approach leads to the most common form of stochastic thermodynamics, with entropy production obeying the expression first proposed by Schnakenberg. Another path relies on a definition of entropy that is such that fluctuations around equilibrium obey the Einstein formula, with the system being characterized by an appropriate thermodynamic potential. This approach leads to an alternative formulation of stochastic thermodynamics where both entropy and entropy production differ from those of the first approach.

The existence and the differences between the two definitions of entropy mentioned above have been identified and discussed earlier for equilibrium states [18]. The present work can be seen as an extension of these results to nonequilibrium situations. A major difference between the two approaches is that entropy production is not bound to be nonnegative in the framework based on the Einstein formula. It is only so in the macroscopic limit. To understand what this implies, let us compare the three expressions for entropy production. In the macroscopic limit, one has

$$\frac{d_i S}{dt} = \sum_{\rho} w_{\rho} \frac{A_{\rho}}{T}. \quad (84)$$

The second law of thermodynamics imposes that this quantity cannot be negative. This can be interpreted as a requirement that, at a macroscopic level, the rate of a reaction and the associated thermodynamic force must “align.” Both the Gibbs-Shannon and the Einstein-Boltzmann approaches lead to an expression of the type

$$\frac{d_i \bar{S}}{dt} = k_B \sum_{N, \rho} W_{\rho}(N) P(N, t) \frac{\tilde{A}_{\rho}}{T}, \quad (85)$$

but they differ in how the stochastic affinity  $\tilde{A}_{\rho}$  is defined. In the Schnakenberg expression (69), this affinity is a ratio of forward and reverse probability fluxes. The nonnegativity of entropy production is here thus a sign that *the probability flux and the associated stochastic force must align at all scales*, i.e., even for small systems where fluctuations are important. In the Einstein-Boltzmann approach, the affinity is a ratio of rates, not of probability fluxes. It is entirely determined by the values taken by macroscopic observables and is, in this sense, closer to the macroscopic affinity (to which it is almost equal). Entropy production in this case measures whether *the probability fluxes are aligned with macroscopic constraints*.



The fact that the corresponding entropy production can become negative for small systems means that at small scales, a system could appear to proceed “in the wrong direction” in view of the macroscopic constraints imposed. This possibility vanishes in the macroscopic limit and the second law of thermodynamics is thus respected.

Since both approaches discussed here are consistent with equilibrium statistical mechanics and nonequilibrium macroscopic thermodynamics, one could argue that choosing between them is more a matter of taste than anything else. Each framework allows probing different aspects of the nonequilibrium thermodynamics of small systems and are, in this sense, complementary. In this context, it would be particularly interesting to revisit some of the conclusions obtained with the Gibbs-Shannon framework for ensemble properties.

The problem of pathwise stochastic thermodynamics should be addressed as well. As mentioned in the Introduction, the Gibbsian definition of pathwise entropy can lead to inappropriate results even in the macroscopic limit. It is moreover incompatible with the thermodynamic theory of fluctuations around equilibrium (see Ref. [18], chap. VII, for example), since the Gibbsian entropy production is zero at equilibrium even in the presence of fluctuations. The Einstein-Boltzmann

framework is built around the equilibrium thermodynamic theory of fluctuations and is thus consistent with it from the outset. It would be interesting to analyze the properties of such a pathwise formulation of the Einstein-Boltzmann approach for nonequilibrium states as well. We are currently working on the properties of entropy production in the latter case and, more specifically, on its connection with the action functional introduced by Lebowitz and Spohn [23,24] and thus on the possibility to establish fluctuation theorems in this framework. Also in this context, the Einstein-Boltzmann approach shares many features with the “extended local equilibrium” stochastic thermodynamics developed among others by Grégoire Nicolis and the present author [11–14], and which is based on stochastic differential equations for thermodynamic quantities. It would be instructive to assess whether the extended local equilibrium formulation can be obtained as a weak-noise limit of a pathwise Einstein-Boltzmann stochastic thermodynamics.

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- [1] F. Schlögl, *Z. Phys.* **243**, 303 (1971); **248**, 446 (1971).
  - [2] L. Jiu-Li, C. Van den Broeck, and G. Nicolis, *Z. Phys. B* **56**, 165 (1984).
  - [3] C. Y. Mou, L. Jiu-li, and G. Nicolis, *J. Chem. Phys.* **84**, 7011 (1986).
  - [4] Y. De Decker, *Physica A* **428**, 178 (2015).
  - [5] T. Tomé and M. J. de Oliveira, *J. Chem. Phys.* **148**, 224104 (2018).
  - [6] U. Seifert, *Phys. Rev. Lett.* **95**, 040602 (2005).
  - [7] C. Van den Broeck, *Proc. Int. School “Enrico Fermi”* **184**, 155 (2013).
  - [8] C. Van den Broeck, and M. Esposito, *Physica A* **418**, 6 (2015).
  - [9] U. Seifert, *Rep. Prog. Phys.* **75**, 126001 (2012).
  - [10] J. M. Horowitz, *J. Chem. Phys.* **143**, 044111 (2015).
  - [11] Y. De Decker, A. García Cantú Ros, and G. Nicolis, *Eur. Phys. J. Spec. Top.* **224**, 947 (2015).
  - [12] Y. De Decker, J.-F. Derivaux, and G. Nicolis, *Phys. Rev. E* **93**, 042127 (2016).
  - [13] G. Nicolis and Y. De Decker, *Chaos* **27**, 104615 (2017).
  - [14] G. Nicolis and Y. De Decker, *Entropy* **19**, 434 (2017).
  - [15] H. P. Breuer, E.-M. Laine, and J. Piilo, *Phys. Rev. Lett.* **103**, 210401 (2009).
  - [16] A. Rivas, S. F. Huelga, and M. B. Plenio, *Rep. Prog. Phys.* **77**, 094001 (2014).
  - [17] I. Prigogine, *Etude Thermodynamique des Processus Irréversibles* (Desoer, Liège, 1947).
  - [18] S. R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (Dover Publications, New York, 2011).
  - [19] G. Nicolis and I. Prigogine, *Self-organization in Nonequilibrium Systems* (John Wiley & Sons, New York, 1977).
  - [20] A. Einstein, *Ann. Phys.* **11**, 170 (1903).
  - [21] A. Einstein, *Ann. Phys.* **33**, 1275 (1910).
  - [22] J. Schnakenberg, *Rev. Mod. Phys.* **48**, 571 (1976).
  - [23] J. L. Lebowitz and H. Spohn, *J. Stat. Phys.* **95**, 333 (1999).
  - [24] P. Gaspard, *J. Chem. Phys.* **120**, 8898 (2004).