

Extended local equilibrium approach to stochastic thermodynamics

Y. De Decker^{1,2}, A. Garcia Cantú Ros³, and G. Nicolis¹

¹ Center for Nonlinear Phenomena and Complex Systems (CENOLI), Université libre de Bruxelles (ULB), Campus Plaine, CP 231, 1050 Brussels, Belgium

² Nonlinear Physical Chemistry Unit, Université libre de Bruxelles (ULB), Campus Plaine, CP 231, 1050 Brussels, Belgium

³ Potsdam Institute for Climate Impact Research, 14412 Potsdam, Germany

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Abstract. A new approach to stochastic thermodynamics is developed, in which the local equilibrium hypothesis is extended to incorporate the effect of fluctuations. A fluctuating entropy in the form of a random functional of the fluctuating state variables is introduced, whose balance equation allows to identify the stochastic entropy flux and stochastic entropy production. The statistical properties of these quantities are analyzed and illustrated on representative examples.

1 Introduction

Nonequilibrium thermodynamics provides fundamental insights on key properties of wide classes of systems at a macroscopic level of description in which the entropy production, measuring the dissipation released by the irreversible processes taking place within the system, plays a central role [1].

The most familiar and far-reaching approach to nonequilibrium thermodynamics is the one based on the local equilibrium hypothesis, whereby the entropy density at a given point in space and at a given time is taken to depend on the state variables through the same relation as in the state of equilibrium [1, 2]. As it turns out this covers an extremely wide range of systems and processes, where variations of the state observables in space and time induced by the nonequilibrium constraints occur on much longer scales than those associated to molecular-level processes. The simplicity and elegance of the resulting formalism allows then one to address phenomena beyond the traditional realm of the linear range and in particular the stability of nonequilibrium states, thereby establishing unexpected links with the field of nonlinear dynamics [2].

Stochastic thermodynamics was originally introduced as an extension of classical nonequilibrium thermodynamics aiming to formulate the evolution of nonequilibrium states and their stability in a way incorporating the effect of the fluctuations of the macroscopic observables around their average values [3–6]. As such it was based on a probabilistic approach in which (i) entropy production and entropy itself are defined in terms of probabilities of states or sequences thereof, and (ii) probabilities

evolve as a result of transitions between states through a master-type equation. This allowed, among others, to gain a more fundamental view on the problem of stability where the disturbances responsible for the variability around a given steady state or for transitions between states are not taken to be of external origin as in traditional thermodynamics, but are actually of intrinsic origin, generated spontaneously from microscopic-level processes occurring within the system. Over the last two decades stochastic thermodynamics experienced important further developments following the growing interest in processes occurring in nanoscale materials and the discovery of some intriguing connections with information theory and the foundations of nonequilibrium statistical mechanics [7–11].

In the present paper a new approach to stochastic thermodynamics is developed. The basic idea is to extend the local equilibrium hypothesis to incorporate the effect of fluctuations. We start with the set of evolution equations for the state variables featured in the traditional macroscopic description, with the additional ingredient that fluctuations are accounted for through appropriate source terms assimilated to Gaussian Markov processes, in a way similar to fluctuating hydrodynamics [12]. We next introduce a fluctuating entropy in the form of a random functional, related to the fluctuating state variables by the same relations 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, such as mean values and probability densities. Explicit examples are provided dealing with transport processes and chemically reacting systems and the role of nonlinearities is assessed.

2 Formulation

Let $\{X_i(\mathbf{r}, t)\}$, with $i = 1, \dots, n$, be a set of macroscopic variables (such as the energy density, the concentration of a chemical in a solvent, etc.) describing the state of a system. These variables evolve in time as a result of two kinds of processes:

- Exchanges with the external world, modeled by a flux Φ_i through the surface surrounding the volume occupied by the system.
- Internal processes generated by the system itself, even when it is completely isolated, modeled by a rate of production per unit volume σ_i .

Consequently, the evolution laws for the above mentioned variables read [1]

$$\frac{\partial X_i}{\partial t} = -\text{div}\Phi_i + \sigma_i. \quad (1)$$

To account for the presence of fluctuations we decompose Φ_i and σ_i into a systematic part driven by the nonequilibrium constraints acting on the system (chemical potential or temperature differences, etc.), and a random force modeling the effect of microscopic level processes on the evolution of the macroscopic variables [12–14]:

$$\Phi_i = \mathbf{J}_i(\{X_j(\mathbf{r}, t)\}, \{\nabla X_j(\mathbf{r}, t)\}, \dots) + \mathbf{j}_i(\mathbf{r}, t) \quad (2)$$

$$\sigma_i = \sum_{\rho} \alpha_{i\rho} [w_{\rho}(\{X_j(\mathbf{r}, t)\}) + R_{\rho}(\mathbf{r}, t)]. \quad (3)$$

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

As discussed in the Introduction, within the framework of a local equilibrium approach, the entropy density $s(\mathbf{r}, t)$ of the system will depend on space and time

through the space and time dependencies of the observables $\{X_i\}$, $s = s(\{X_i(\mathbf{r}, t)\})$. The rate of change of entropy can thus be written as

$$\frac{\partial s}{\partial t} = \sum_i \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} \frac{\partial X_i}{\partial t} \quad (4a)$$

or, using (1)–(3),

$$\frac{\partial s}{\partial t} = \sum_i \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} \left[-\text{div}(\mathbf{J}_i + \mathbf{j}_i) + \sum_\rho \alpha_{i\rho} (w_\rho + R_\rho) \right]. \quad (4b)$$

Relation (4b) allows us to derive a balance equation for entropy of the form of Eq. (1),

$$\frac{\partial s}{\partial t} = -\text{div} \mathbf{J} + \sigma \quad (5)$$

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

$$\mathbf{J} = \sum_i (\mathbf{J}_i + \mathbf{j}_i) \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} \quad (6a)$$

$$\sigma = \sum_i (\mathbf{J}_i + \mathbf{j}_i) \cdot \nabla \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} + \sum_{i,\rho} \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} \alpha_{i\rho} (w_\rho + R_\rho). \quad (6b)$$

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

It should be kept in mind that the decomposition into the two terms of the right hand side of Eq. (5) 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 chosen, the following condition should be satisfied:

$$\sum_i \mathbf{J}_i \cdot \mathbf{F}_i + \sum_\rho \mathcal{A}_\rho w_\rho \geq 0, \quad (7a)$$

where we introduced the *thermodynamic forces*

$$\mathbf{F}_i = \nabla \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i}, \quad \mathcal{A}_\rho = \sum_i \alpha_{i\rho} \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i}. \quad (7b)$$

Processes of different spatial symmetries are expected to satisfy separately inequalities like Eq. (7a). Basically, such inequalities express that the *fluxes* \mathbf{J}_i and w_ρ should somehow be aligned to the forces. This type of dependence becomes specially transparent in the linear range of irreversible processes, where fluxes are linearly related to forces through the (positive definite) Onsager matrix of phenomenological coefficients [1].

In the presence of fluctuations it seems natural to still adopt the decomposition leading to Eqs. (5)–(6). 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 (7). On the other hand, the random parts \mathbf{j}_i and R_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 R_ρ may be led to be in “opposition” with respect to the action of an instantaneous thermodynamic force. The parts

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

will then yield negative contributions. Our goal 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 to 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 will be specially interested in the evolution around an asymptotically stable steady state, in which case $\{X_{im}\}$ are known to correspond to the maxima of the invariant probability density associated to the stochastic differential Eq. (1) [15]. Setting

$$\begin{aligned} X_i &= X_{im} + \Delta X_i \\ \mathbf{J}_i &= \mathbf{J}_{im} + \Delta \mathbf{J}_i, \quad \mathbf{F}_i = \mathbf{F}_{im} + \Delta \mathbf{F}_i \\ w_\rho &= w_{\rho m} + \Delta w_\rho, \quad \mathcal{A}_\rho = \mathcal{A}_{\rho m} + \Delta \mathcal{A}_\rho \end{aligned} \quad (8)$$

we may decompose the fluctuating entropy production σ as (cf. (6b) and (7))

$$\sigma = \sigma_m + \Delta\sigma \quad (9)$$

with

$$\begin{aligned} \sigma_m &= \sum_i \mathbf{J}_{im} \cdot \mathbf{F}_{im} + \sum_\rho \mathcal{A}_{\rho m} w_{\rho m} \\ \Delta\sigma &= \sum_i (\Delta \mathbf{J}_i \cdot \mathbf{F}_{im} + \mathbf{J}_{im} \cdot \Delta \mathbf{F}_i + \mathbf{j}_i \cdot \mathbf{F}_{im}) \\ &\quad + \sum_\rho (\Delta w_\rho \mathcal{A}_{\rho m} + w_{\rho m} \Delta \mathcal{A}_\rho + R_\rho \mathcal{A}_{\rho m}) \\ &\quad + \sum_i \Delta \mathbf{J}_i \cdot \Delta \mathbf{F}_i + \sum_\rho \Delta w_\rho \Delta \mathcal{A}_\rho \\ &\quad + \sum_i \mathbf{j}_i \cdot \Delta \mathbf{F}_i + \sum_\rho R_\rho \Delta \mathcal{A}_\rho. \end{aligned} \quad (11)$$

We will refer to $\Delta\sigma$ as the stochastic entropy production, or the entropy production of the fluctuations.

The first two sums in Eq. (11) 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 correspond to the excess entropy production familiar from classical irreversible thermodynamics as developed by Glansdorff and Prigogine [2]. A similar procedure can be carried out for the entropy flux.

Ordinarily, in the framework of a probabilistic description one decomposes the variables into the sum of their average values and the fluctuations. In the present case this would lead to

$$\begin{aligned} X_i &= \bar{X}_i + \delta X_i \\ \sigma &= \bar{\sigma} + \delta\sigma \end{aligned} \quad (12)$$

with $\bar{\sigma}$, $\delta\sigma$ given by expressions similar to those of Eqs. (10)–(11), 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 most probable values coincide, and the deviation 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 the sequel we will be interested in the statistical properties of $\Delta\sigma$ for some prototypical irreversible processes and, in particular, in mean values and probability densities. For this purpose the properties of the random forces \mathbf{j}_i and R_ρ will need to be prescribed. We will adopt the assumption of Gaussian white noise usually made in the literature, being aware that this introduces singular contributions in expressions such as Eq. (11). These singularities will be smoothed out at the level of the averages but will subsist as far as the probability densities are concerned. To cope with this difficulty we will be led to focus on the net entropy production over a time interval t ,

$$P_t = \int_0^t dt' \sigma(t'). \quad (13)$$

In all cases, and provided the system is ergodic, the mean value of the entropy derivative in Eq. (5) will be zero for asymptotically long times and thus

$$\bar{\sigma} = \text{div}\bar{\mathbf{J}}. \quad (14a)$$

An equality of this kind is known to hold true in classical irreversible thermodynamics when a system has reached a steady state [1,2]. 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,

$$\overline{\Delta\sigma} = \text{div}\overline{\Delta\mathbf{J}}. \quad (14b)$$

3 Transport processes

In this section we apply the formalism developed in Sect. 2 to two prototypical examples of irreversible processes, namely, diffusion and heat conduction. We identify the macroscopic and stochastic parts of the entropy production and entropy flux and study their general structure and their dependence on the nonequilibrium constraints.

3.1 Diffusion

We consider a non-reactive isothermal binary mixture in absence of external forces and bulk motion. For simplicity we assume that the mixture is diluted, consisting of a solute of mass fraction $c_1 \ll 1$ diffusing within a solvent of mass fraction $c_2 \approx 1$. In the framework of a local equilibrium hypothesis and as long as one is limited to the contributions due to mass transfer, the entropy of such system depends solely on the variable c_1 (thereafter denoted by c), $s = s(c)$, with $\partial s/\partial c = -\mu/T$ where T is the temperature. It follows that (cf. Eq. (4a))

$$\frac{\partial s}{\partial t} = -\frac{\mu}{T} \frac{\partial c}{\partial t} \quad (15)$$

with (see Eqs. (1) and (2))

$$\frac{\partial c}{\partial t} = -\text{div}[\mathbf{J}_d + \mathbf{j}_d(\mathbf{r}, t)] \quad (16)$$

it being understood that by virtue of mass conservation the source term in the general balance equation is absent.

The thermodynamic force associated to the process of diffusion is [1] (cf. Eq. (7b))

$$\mathbf{F}_d = -\nabla \frac{\mu(c)}{T}. \quad (17)$$

Limiting ourselves to the linear range of irreversible processes we may express the systematic part of the flux, \mathbf{J}_d , as

$$\mathbf{J}_d = -L \nabla \frac{\mu(c)}{T}$$

where L is the Onsager coefficient or, setting for a diluted mixture $\mu(c) = \mu_0 + k_B T \ln c$,

$$\mathbf{J}_d = -\frac{k_B L}{c} \nabla c = -D \nabla c. \quad (18)$$

Here D is Fick's diffusion coefficient, hereafter considered as constant (c -independent), in accordance with empirical data applicable to a wide range of concentration values.

Utilizing relation (18) reduces Eq. (16) to the linear form

$$\frac{\partial c}{\partial t} = D \nabla^2 c - \operatorname{div} \mathbf{j}_d(\mathbf{r}, t) \quad (19a)$$

where from now on \mathbf{j} will be assimilated to a Gaussian white noise in space and time,

$$\begin{aligned} \overline{j_{d,k}(\mathbf{r}, t)} &= 0 \\ \overline{j_{d,k}(\mathbf{r}, t) j_{d,k'}(\mathbf{r}', t')} &= q_{kk'}^2 \delta_{kk'}^{\mathbf{K}_r} \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \end{aligned} \quad (19b)$$

The strength $q_{kk'}^2$ of these noises, assumed to be small, scales with the inverse of the system size Ω [15]. Using eqs. (6) the local entropy production σ and entropy flux \mathbf{J} associated to diffusion may now be identified,

$$\sigma = \frac{1}{T} \nabla \mu \cdot [D \nabla c - \mathbf{j}_d(\mathbf{r}, t)] \quad (20a)$$

$$\mathbf{J} = \frac{\mu}{T} [D \nabla c - \mathbf{j}_d(\mathbf{r}, t)]. \quad (20b)$$

To get a clear picture of the essential features present let us apply these relations to a slab of length l in contact with two reservoirs of fixed chemical potentials μ_a, μ_b on $x = 0$ and $x = l$ respectively, taking the bulk outside the boundaries to be spatially uniform. Equation (20) become

$$\sigma = \frac{1}{T} \{(\mu_a - \mu) [D(c_a - c) + j_a] + (\mu_b - \mu) [D(c_b - c) - j_b]\} \quad (21a)$$

$$J = \frac{1}{T} \{\mu_a [D(c - c_a) - j_a] + \mu_b [D(c - c_b) + j_b]\} \quad (21b)$$

in which J is the global entropy flux and where the concentration c satisfies the discretized form of (19a),

$$\frac{dc}{dt} = D(c_a + c_b - 2c) + R(t) \quad (22a)$$

with

$$R(t) = j_a - j_b. \quad (22b)$$

The solution of (22a) is

$$c = c_m + \Delta c = \frac{c_a + c_b}{2} + \Delta c \quad (23)$$

where c_m is the macroscopic, mean-field value at the steady state and Δc satisfies the differential equation

$$\frac{d\Delta c}{dt} = -2D\Delta c + R(t) \quad (24)$$

defining an Ornstein-Uhlenbeck process [13]. Introducing this decomposition in Eqs. (21), we are in a position to identify the mean-field values J_m and σ_m of the entropy flux and entropy production as deduced from classical irreversible thermodynamics and the parts due to fluctuations, see Eq. (11),

$$J_m = -k_B D \frac{c_a - c_b}{2} (\mu_a - \mu_b) \quad (25a)$$

$$\sigma_m = k_B D \frac{c_a - c_b}{2} (\mu_a - \mu_b) \quad (25b)$$

$$\Delta J = \frac{1}{T} [(\mu_a + \mu_b)\Delta c - j_a \mu_a + j_b \mu_b] \quad (26a)$$

$$\begin{aligned} \Delta \sigma &= \frac{1}{T} [D(2\mu_m - \mu_a - \mu_b)\Delta c + (\mu_a - \mu_m)j_a + (\mu_m - \mu_b)j_b] \\ &\quad + \frac{1}{T} \Delta \mu [2D\Delta c - j_a + j_b]. \end{aligned} \quad (26b)$$

The following points are worth noticing.

- (i) J_m, σ_m depend entirely on chemical potential differences and vanish, as expected, in equilibrium.
- (ii) Chemical potential differences also appear throughout the expression for $\Delta \sigma$, with e.g.

$$\begin{aligned} \mu_m - \mu_a &= k_B T \ln \frac{c_m}{c_a} = k_B T \ln \frac{c_a + c_b}{2c_a} \\ \Delta \mu &= k_B T \Delta \ln c = k_B T \ln \left(1 + \frac{\Delta c}{c_m} \right) \end{aligned}$$

where we used the expression for μ in a diluted system.

- (iii) Since the diffusion equation is linear, averaging Eqs. (22a) or (24) over realizations of the process yields $\overline{\Delta c} = 0$. In other words, the most probable value c_m coincides here with the mean value \bar{c} of the concentration.
- (iv) It follows from the linear dependence of ΔJ in Eq. (26a) on Δc and on the fluctuating flux that $\overline{\Delta J} = 0$. This entails that $\overline{\Delta \sigma} = 0$ as well, on the grounds of the comments made in the end of Sect. 2. This property can also be checked directly from Eq. (26b) in conjunction with Eq. (24). Indeed, the first part in (26b) is linear in $\Delta c, j_a$ and j_b and thus gives trivially a zero average. For the second part, multiplying both sides of Eq. (24) by $\Delta \mu$ one obtains

$$\overline{\Delta \mu \frac{d\Delta c}{dt}} = -2D\overline{\Delta \mu \Delta c} + \overline{\Delta \mu (j_a - j_b)}.$$

The right hand side of this relation is just the part of $\Delta \sigma$ in question with opposite sign. Since on the other hand $\Delta \mu$ is a function of Δc , the left hand side is the average of the time derivative of $\int_0^{\Delta c} d\Delta c' \Delta \mu'(\Delta c')$, which vanishes in an ergodic system. This establishes the desired property.

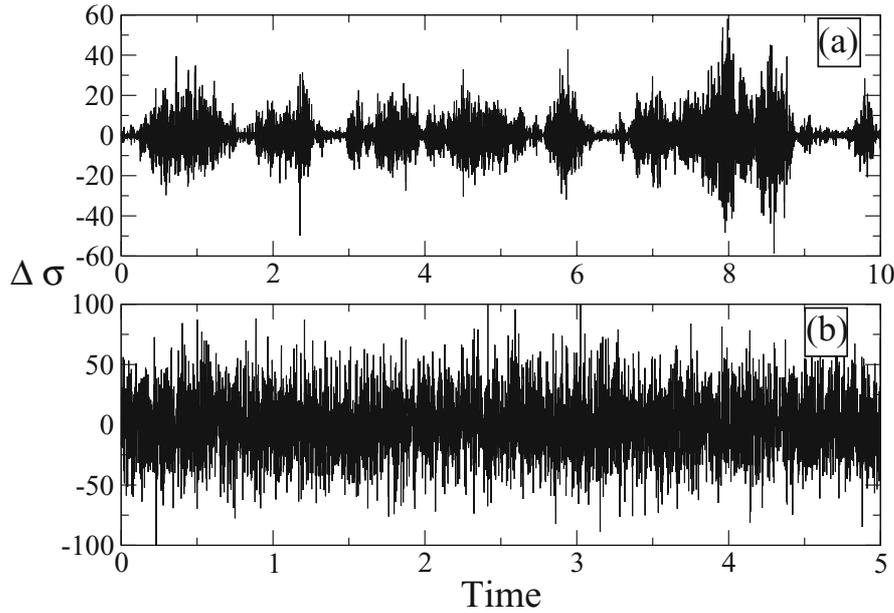


Fig. 1. Time series of the entropy production of the fluctuations, Eq. (26b), as obtained from an Euler-Maruyama integration [13] of the stochastic differential Eq. (22a) with (a) $c_a = c_b = D = 1, \Omega = 100$ and (b) $c_a = D = 1, \Omega = 100$ and $c_b = 2.0$. The Stratonovich interpretation was used, with a time step $dt = 1.0 \times 10^{-5}$. Parameters are scaled by k_B .

In short, in the process of diffusion, the average entropy production of the fluctuations $\overline{\Delta\sigma}$ vanishes. This is a direct consequence of the linearity of the process and is in accordance with early results based on the Shannon-Gibbs entropy balance as deduced from a probabilistic description based on the master equation [5]. On the other hand, $\Delta\sigma$ itself displays a complex time dependence around this zero average. Figure 1 depicts this dependence under equilibrium (Fig. 1a) and non-equilibrium (Fig. 1b) conditions. We notice a marked difference, which can be traced to the fact that by virtue of Eq. (26b) in equilibrium the contributions linear in the fluctuations vanish ($\mu_a = \mu_b = \mu_m$), entailing that the first non-trivial parts are due to quadratic terms. In both cases we observe that $\Delta\sigma$ can take negative values, as anticipated in the Introduction. These properties will be analyzed in more detail in Sect. 5.

3.2 Heat conduction

We next consider a one-component non-reactive mixture in absence of external forces and bulk motion, in contact with external heat reservoirs maintained at constant temperature. The entropy of such a system depends solely on the internal energy u (we again use our local equilibrium hypothesis), $s = s(u)$, with $\partial s/\partial u = 1/T$. It follows that

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\partial u}{\partial t} \quad (27)$$

with, using energy conservation,

$$\frac{\partial u}{\partial t} = -\text{div} [\mathbf{J}_q + \mathbf{j}_q(\mathbf{r}, t)] \quad (28)$$

The thermodynamic force associated to heat conduction is [1]

$$\mathbf{F}_q = -\frac{\nabla T}{T^2}.$$

In the linear range of irreversible processes the corresponding systematic part of the flux \mathbf{J}_q can be written as

$$\mathbf{J}_q = -L \frac{\nabla T}{T^2} = -\kappa \nabla T. \quad (29)$$

Here $\kappa = L/T^2$ is Fourier's heat conduction coefficient which hereafter will again be considered as constant (T -independent), similarly to the assumption made in the previous subsection on diffusion. On the other hand, again in the spirit of local equilibrium, under the conditions set u depends solely on T through an "equation of state" $u = u(T)$, with $du = \rho c_V dT$ (ρ being the mass density and c_V the specific heat at constant volume). Substituting into Eq. (28) we obtain the linear form

$$\frac{\partial T}{\partial t} = \lambda \nabla^2 T - \text{div } \mathbf{j}_T(\mathbf{r}, t) \quad (30)$$

where $\lambda = \kappa/\rho c_V$ is the thermal diffusivity and \mathbf{j}_T is a normalized random flux satisfying relations (19b). Using the above relations the entropy production σ and the entropy flux \mathbf{J} associated to heat conduction may be identified,

$$\sigma = \frac{1}{T^2} \left[\lambda (\nabla T)^2 - \mathbf{j}_T \cdot \nabla T \right] \quad (31a)$$

$$\mathbf{J} = \frac{1}{T} [\mathbf{j}_T - \lambda \nabla T]. \quad (31b)$$

To get explicit expressions we apply, in the spirit of the previous subsection, these expressions to a conductive slab of length l in contact with two heat reservoirs of fixed temperatures T_a and T_b , on $x = 0$ and $x = l$ respectively. Eqs (31) simplify to

$$\sigma = \left(\frac{1}{T} - \frac{1}{T_a} \right) [\lambda(T_a - T) + j_a] + \left(\frac{1}{T} - \frac{1}{T_b} \right) [\lambda(T_b - T) - j_b] \quad (32a)$$

$$J = \frac{\lambda}{T_a} (T_a - T) + \frac{j_a}{T_a} + \frac{\lambda}{T_b} (T_b - T) - \frac{j_b}{T_b}, \quad (32b)$$

where J is again the total flux of entropy and where the temperature T satisfies the discretized form of (30)

$$\frac{dT}{dt} = \lambda (T_a + T_b - 2T) + R(t) \quad (33a)$$

with

$$R(t) = j_a - j_b. \quad (33b)$$

Proceeding as before we are led to identify the macroscopic and fluctuating parts of T

$$T = T_m + \Delta T \quad (34a)$$

where

$$T_m = \frac{T_a + T_b}{2}$$

and ΔT is an Ornstein-Uhlenbeck process [13]

$$\frac{d\Delta T}{dt} = -2\lambda \Delta T + R(t). \quad (34b)$$

A similar treatment gives for σ

$$\sigma = \sigma_m + \Delta\sigma \quad (35a)$$

with

$$\sigma_m = \lambda \frac{T_a - T_b}{2} \left(\frac{1}{T_b} - \frac{1}{T_a} \right)$$

and

$$\begin{aligned} \Delta\sigma = & \left(\frac{1}{T_b} + \frac{1}{T_a} - \frac{2}{T_m} \right) \lambda \Delta T + \left[\left(\frac{1}{T_m} - \frac{1}{T_a} \right) j_a + \left(\frac{1}{T_b} - \frac{1}{T_m} \right) j_b \right] \\ & + \Delta \frac{1}{T} (j_a - j_b - 2\lambda \Delta T). \end{aligned} \quad (35b)$$

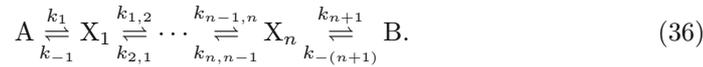
Similar expressions hold for the entropy flux. Following the same procedure as before, it is easy matter to show that $\Delta\sigma = \Delta\bar{J} = 0$. This is, again, due to the linearity of Eq. (34b) satisfied by the excess variable as a result of which the mean and the most probable values coincide, $T_m = \bar{T}$ and $\Delta\bar{T} = \delta\bar{T} = 0$.

4 Reactive systems

We now turn to processes, typical examples of which are chemical reactions, involving non-conserved variables and giving rise to source terms σ_i in the general balance Eq. (1). We consider successively a chain of first-order reactions and a prototypical nonlinear model.

4.1 First-order reactions

Let A be a reactant giving rise to a final product B through the intermediates X_i ($i = 1, \dots, n$):



The overall system is supposed to be isothermal, well-stirred, free of external forces and closed with respect to the X_i s but open with respect to A and B. Following our local equilibrium hypothesis, the entropy of the system depends on the concentrations a , b and $\{x_i\}$ of substances A, B and $\{X_i\}$, $s = s(a, x_1, \dots, x_n, b)$ with $\partial s / \partial a = -\mu_a / T$ and similarly for the other state variables. Focusing on the contributions of mass exchange and reactions to the evolution equation of s , one gets

$$\frac{ds}{dt} = -\frac{\mu_a}{T} \frac{da}{dt} - \frac{\mu_b}{T} \frac{db}{dt} - \sum_{i=1}^n \frac{\mu_i}{T} \frac{dx_i}{dt}. \quad (37)$$

The rates of change of x_i depend entirely on the chemical reactions rates in (36):

$$\begin{aligned} w_0 &= k_1 a - k_{-1} x_1, \\ w_i &= k_{i,i+1} x_i - k_{i+1,i} x_{i+1} \quad (i = 1, \dots, n-1) \\ w_n &= k_{n+1} x_n - k_{-(n+1)} b. \end{aligned} \quad (38)$$

A random force reflecting the effect of fluctuations is associated to each of these systematic processes. This leads to the rate equations (cf. Eqs. (1)–(3))

$$\begin{aligned}\frac{dx_1}{dt} &= w_0 + R_0(t) - (w_1 + R_1(t)) \\ \frac{dx_i}{dt} &= w_{i-1} + R_{i-1}(t) - (w_i + R_i(t)) \quad (i = 2, \dots, n-1) \\ \frac{dx_n}{dt} &= w_{n-1} + R_{n-1}(t) - (w_n + R_n(t)).\end{aligned}\quad (39)$$

On the other hand, the rates γ_a, γ_b at which substances A and B are injected into the reaction volume through the surface are supposed to cancel their rates of change resulting from the first and the last chemical reactions in (36), thereby maintaining the concentrations a, b fixed within the volume. This leads to

$$\begin{aligned}\frac{da}{dt} &= \gamma_a - (w_0 + R_0(t)) = 0 \\ \frac{db}{dt} &= \gamma_b + (w_n + R_n(t)) = 0.\end{aligned}\quad (40)$$

Using Eq. (6a) we may identify the entropy flux in Eq. (37) as

$$J = \frac{1}{T} (-\mu_a \gamma_a - \mu_b \gamma_b)$$

or, using (40),

$$J = \frac{1}{T} [-\mu_a (w_0 + R_0(t)) + \mu_b (w_n + R_n(t))]. \quad (41)$$

The entropy production part comprises, in addition to the “boundary” terms associates to the first and the last reactions, terms arising from the reactions 2 to $n-1$. This leads to (cf. Eq. (6b))

$$\begin{aligned}\sigma &= \frac{1}{T} \left[(\mu_a - \mu_1) (w_0 + R_0(t)) + \sum_{i=2}^n (\mu_i - \mu_{i+1}) (w_i + R_i(t)) \right. \\ &\quad \left. + (\mu_n - \mu_b) (w_n + R_n(t)) \right].\end{aligned}\quad (42)$$

We notice that the rate equations (39) are linear in the concentrations. It follows that the macroscopic (mean-field) values x_{im} are equal to the mean values \bar{x}_i , in other words in the decomposition

$$x_i = x_{im} + \Delta x_i \quad (43a)$$

the deviations Δx_i may be identified to the fluctuations around the mean: $\Delta x_i = \delta x_i$ with

$$\overline{\Delta x_i} = \overline{\delta x_i} = 0. \quad (43b)$$

Furthermore, we see from Eq. (41) that J is linear in the concentrations x_1 and x_m . It follows that in the decomposition

$$J = J_m + \Delta J$$

$\overline{\Delta J} = 0$, i.e. the mean entropy flux associated to the fluctuations vanishes. By virtue of ergodicity the mean entropy production of the fluctuations $\Delta\sigma$ in the decomposition $\sigma = \sigma_m + \Delta\sigma$ is then also vanishing, $\overline{\Delta\sigma} = 0$. These conclusions are in complete

agreement with those obtained from the balance equation of the Gibbs-Shannon entropy previously derived by using a master equation approach [5].

As an illustration, we consider the simplest realization of scheme (36), where only one intermediate X is present. The rate equation for the concentration x reads

$$\begin{aligned} \frac{dx}{dt} &= w_0 + R_0(t) - (w_1 + R_1(t)) \\ &= k_1 a - (k_{-1} + k_2)x + k_{-2}b + R(t) \end{aligned} \quad (44)$$

with $R(t) = R_0(t) - R_1(t)$. The entropy flux J is still given by Eq. (41), while the entropy production becomes

$$\sigma = \frac{1}{T} [(\mu_a - \mu)(k_1 a - k_{-1}x + R_0(t)) + (\mu - \mu_b)(k_2 x - k_{-2}b + R_1(t))]. \quad (45)$$

The decomposition in Eq. (43a) now leads to

$$x_m = \frac{k_1 a + k_{-2} b}{k_{-1} + k_2}$$

and

$$\frac{d\Delta x}{dt} = -(k_{-1} + k_2)\Delta x + R(t) \quad (46)$$

where Δx coincides with the fluctuation δx around the mean. Accordingly, decomposing σ as in eqs. (9), (25b)–(26b) and (35) yields at the steady state, using as in Sect. 3.1 the expression for the chemical potential of a diluted mixture,

$$\sigma_m = \frac{1}{T} (\mu_a - \mu_b) w_0 = k_B \left(\frac{k_1 k_2 a - k_{-1} k_{-2} b}{k_{-1} + k_2} \right) \ln \frac{k_1 k_2 a}{k_{-1} k_{-2} b} \quad (47a)$$

$$\begin{aligned} \Delta\sigma &= \frac{1}{T} \{ [k_{-1}(\mu_m - \mu_a) + k_2(\mu_m - \mu_b)] \Delta x + (\mu_a - \mu_m)R_0(t) + (\mu_m - \mu_b)R_1(t) \} \\ &\quad + \frac{1}{T} \Delta\mu [(k_2 + k_{-1})\Delta x + R_1(t) - R_0(t)]. \end{aligned} \quad (47b)$$

We note that, similarly to the case of diffusion, both σ_m and $\Delta\sigma$ depend on chemical potential differences. Furthermore, the first part in Eq. (47b) which contains contributions of first order vanishes at equilibrium. As for the property $\overline{\Delta\sigma} = 0$, it can again be checked explicitly by multiplying both sides of Eq. (46) by $\Delta\mu = k_B T \ln(1 + \Delta x/x_m)$ and averaging over the realizations of the noise. Finally, as in the case of diffusion and heat conduction, $\Delta\sigma$ itself displays a marked variability around its zero average.

4.2 Nonlinear effects

The principal effect of nonlinearities in the structure and the statistical properties of the rate laws for the concentrations, of the entropy flux and of the entropy production is to introduce deviations between the mean values and the most probable values that are featured in the macroscopic description. The origin of these deviations is the non-commutation of the averaging operation of a nonlinear function of the state variables and of the averaging of the variables themselves,

$$\overline{f(x_1, \dots, x_n)} = f(\overline{x_1}, \dots, \overline{x_n}) + \text{Corrections involving variances and higher order moments.}$$

In this subsection we analyze the consequences of this property on a prototypical model involving an autocatalytic step,



assuming as in the previous subsection that the concentrations a, b of reactant A and product B are maintained constant within the reaction volume. Equations (38)–(39) are now replaced by

$$w_0 = k_1 a x - k_{-1} x^2, \quad w_1 = k_2 x - k_{-2} b \quad (49)$$

and

$$\begin{aligned} \frac{dx}{dt} &= w_0 + R_0(t) - (w_1 + R_1(t)) \\ &= (k_1 a - k_2) x - k_{-1} x^2 + k_{-2} b + R(t) \end{aligned} \quad (50)$$

with

$$R(t) = R_0(t) - R_1(t).$$

The macroscopic value x_m satisfies the equation

$$(k_1 a - k_2) x_m - k_{-1} x_m^2 + k_{-2} b = 0. \quad (51a)$$

On the other hand, averaging Eq. (50) over the realizations of the noise yields

$$(k_1 a - k_2) \bar{x} - k_{-1} \bar{x}^2 + k_{-2} b - k_{-1} \overline{\delta x^2} = 0. \quad (51b)$$

Comparing (51a) and (51b) we conclude that x_m differs from \bar{x} . Setting

$$\bar{x} = x_m + \Delta$$

one gets to the dominant order

$$\Delta \approx \frac{k_{-1}}{k_1 a - 2k_{-1} x_m - k_2} \overline{\delta x^2}. \quad (52)$$

We notice that the denominator in this expression is the Lyapunov exponent of the noise-free part of Eq. (50). It is negative as long as $k_2 \neq 0$ but tends to zero in the limit $k_2 \rightarrow 0$, where the system undergoes a transcritical bifurcation. In this case, then, the correction Δ and the macroscopic value x_m become comparable.

Coming next to the entropy balance, one may derive straightforwardly the expressions for the entropy flux and entropy production replacing Eqs. (41) and (42):

$$J = \frac{1}{T} [-\mu_a (k_1 a x - k_{-1} x^2 + R_0(t)) + \mu_b (k_2 x - k_{-2} b + R_1(t))] \quad (53)$$

$$\sigma = \frac{1}{T} [(\mu_a - \mu) (k_1 a x - k_{-1} x^2 + R_0(t)) + (\mu - \mu_b) (k_2 x - k_{-2} b + R_1(t))]. \quad (54)$$

As in all cases previously studied, we have $\bar{\sigma} = -\bar{J}$ in the stationary state and, separately, $\sigma_m = -J_m$ and $\overline{\Delta \sigma} = -\overline{\Delta J}$. These quantities can be easily computed starting from the expression of J rather than σ

$$\sigma_m = -J_m = \frac{1}{T} (\mu_a - \mu_m) (k_1 a x_m - k_{-1} x_m^2) \quad (55)$$

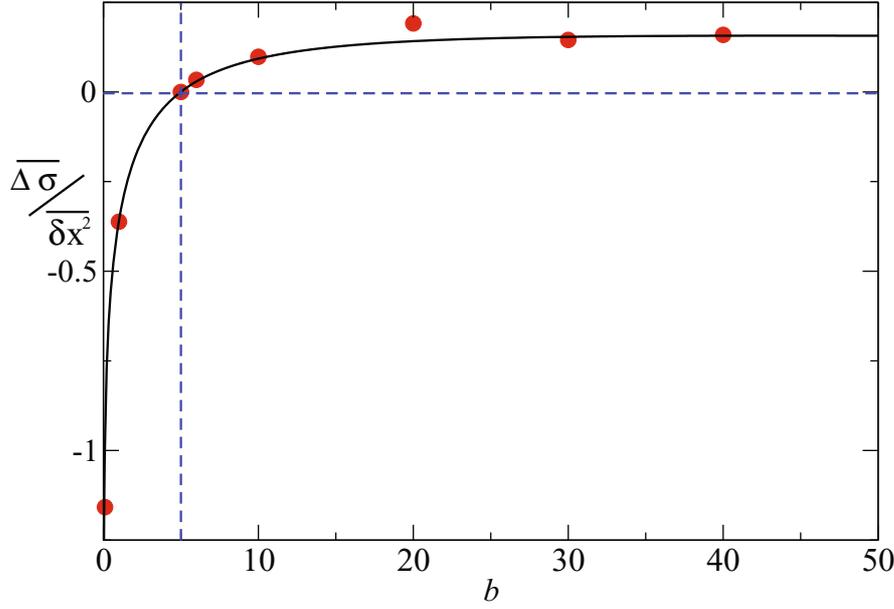


Fig. 2. Mean value of the stationary entropy production of the fluctuations normalized with the variance of x , for the model (48), as a function of concentration b . The other parameters are $k_1 a = 5, k_{-1} = k_2 = k_{-2} = 1$ and $\Omega = 100$. The dots correspond to the outcome of numerical integrations. The averaging was obtained from 10,000 realizations of the corresponding stochastic differential equations, with $dt = 1.0 \times 10^{-5}$. The plain curve is the prediction of Eq. (56), and the dashed lines indicate the state of equilibrium.

and, to the dominant order,

$$\begin{aligned} \overline{\Delta\sigma} &= -\overline{\Delta J} = \frac{1}{T} (\mu_a - \mu_b) k_2 \Delta \\ &= \frac{1}{T} (\mu_a - \mu_b) \frac{k_2 k_{-1}}{k_1 a - 2k_{-1} x_m - k_2} \overline{\delta x^2} \end{aligned} \quad (56)$$

where Eqs. (51) and (52) have been used. We conclude that the mean entropy production of the fluctuations no longer vanishes as long as the system is maintained out of thermodynamic equilibrium ($\mu_a \neq \mu_b$). Furthermore (see Fig. 2), $\overline{\Delta\sigma}$ is negative if $\mu_a > \mu_b$ and positive otherwise since the denominator in Eq. (56) is negative on the grounds of the stability of the state x_m (for $k_2 \neq 0$) [5,6]. Actually, using Eq. (54), we may also estimate the stochastic entropy production incorporating the effect of fluctuations:

$$\begin{aligned} \Delta\sigma &= \frac{1}{T} \{ (\mu_a - \mu_m) ((k_1 a - 2k_{-1} x_m) \Delta x - k_{-1} \Delta x^2 + R_0(t)) \\ &\quad + (\mu_m - \mu_b) (k_2 \Delta x + R_1(t)) \} \\ &\quad + \frac{1}{T} \Delta\mu [(k_2 + 2k_{-1} x_m) \Delta x + k_{-1} \Delta x^2 - k_1 a \Delta x + R_1(t) - R_0(t)]. \end{aligned} \quad (57)$$

Here the average value of the deviation Δx from x_m is the quantity Δ introduced in Eq. (52), with $\overline{\Delta x^2} = \overline{\delta x^2} + \Delta^2$. Δx itself satisfies the nonlinear stochastic differential equation (cf. Eq. (50))

$$\frac{d\Delta x}{dt} = (k_1 a - 2k_{-1} x_m - k_2) \Delta x - k_{-1} \Delta x^2 + R(t) \quad (58)$$

reducing to an Ornstein-Uhlenbeck process only to the dominant order. Comparing (56) and (57) we see that the dominant part of the average value $\overline{\Delta\sigma}$ comes from the first group of terms in Eq. (57). The latter can in turn be decomposed as follows.

- Terms where the thermodynamic forces (here the affinities $\mathcal{A}_0, \mathcal{A}_1$) are evaluated at their reference values in the macroscopic state x_m , and the fluxes (here the reaction rates w_0, w_1) are deviated to the first order from their reference values, $\sum_{\rho} \mathcal{A}_{\rho} \Delta w_{\rho}$.
- Terms involving explicitly the random forces, $\sum_{\rho} \mathcal{A}_{\rho} R_{\rho}(t)$.

The mean stochastic entropy production can also be calculated independently, using the balance equation for the Gibbs-Shannon entropy as derived from the master equation. Full agreement with Eq. (56) is obtained. The interest of our formulation is to give access not only to the averaged, but to the *full* stochastic entropy production and to allow us to address its statistical properties. This will be the subject of the next section.

5 Probability densities and related quantities

We start with the evaluation of the probability density associated to the entropy production of fluctuations $\Delta\sigma$ under nonequilibrium conditions and in absence of nonlinearities in the evolution equations of the state variables. The dominant part of $\Delta\sigma$ is then given by the first group of terms in Eqs. (26b), (35b) and (47b), which are linear combinations of the noises and of the deviations of the state variables from the reference state. We write this part in the generic form

$$\Delta\sigma_1 = az + F(t) \quad (59)$$

with

$$\sigma \approx \sigma_m + \Delta\sigma_1.$$

Here $F(t)$ is a white noise and z an Ornstein-Uhlenbeck process [13] which denotes, depending on the case, Δc , ΔT or Δx and satisfies an equation of the form of Eqs. (24), (34b) or (46)

$$\frac{dz}{dt} = -\alpha z + R(t). \quad (60)$$

The coefficients a and α and the variances q^2 and Q^2 of $R(t)$ and $F(t)$ can be specified by comparison with the aforementioned equations and depend, among others, on the values of the transport coefficients, rate constants and chemical potential or temperature differences.

As pointed out in the end of Sect. 2, the determination of the probability density of $\Delta\sigma$ is complicated by the presence of singularities associated to the Gaussian white noise $F(t)$. To remove them we switch from $\Delta\sigma$ to the mean entropy Σ_t produced during a time interval t ,

$$\begin{aligned} \Sigma_t &= \frac{1}{t} \int_0^t dt' \sigma(t') \\ &= \sigma_m + \frac{1}{t} \int_0^t dt' \Delta\sigma_1(t') \\ &= \sigma_m + \Delta\Sigma_t. \end{aligned} \quad (61)$$

Integrating both sides of Eq. (59) with respect to time we see that $\Delta\Sigma_t$ is the superposition of the process

$$Z_t = \frac{a}{t} \int_0^t dt' z(t') \quad (62a)$$

and of

$$V_t = \frac{1}{t} \int_0^t dt' F(t') = \frac{1}{t} (W_t - W_0) \quad (62b)$$

where z satisfies Eq. (60) and W_t is a Wiener process of variance $Q^2 t/2$.

By the central limit theorem, both Z_t and V_t are Gaussian. Their variances Δ_Z and Δ_V can be evaluated straightforwardly, yielding

$$\Delta_Z = \frac{q^2 a^2}{\alpha^2 t} + \frac{q^2 a^2}{\alpha^3 t^2} (1 - e^{-\alpha t})$$

$$\Delta_V = \frac{Q^2}{t}.$$

This determines fully the corresponding probability densities $P(Z_t)$, $P(V_t)$ and allows to evaluate $P(\Delta\Sigma_t)$ through the relation

$$P(\Delta\Sigma_t) = \int dZ_t dV_t P(Z_t) P(V_t) \delta(\Delta\Sigma_t - Z_t - V_t) \quad (63)$$

where the limits in both Z_t and V_t are set from $-\infty$ to ∞ . The integration is thus straightforward and yields again a Gaussian distribution of the form

$$P(\Delta\Sigma_t) = \sqrt{\frac{t}{2\pi\Delta_0}} \exp\left(-\frac{t\Delta\Sigma_t^2}{2\Delta_0}\right) \quad (64)$$

with (we take for simplicity time $t \gg \alpha^{-1}$)

$$\Delta_0 = Q^2 + \frac{q^2 a^2}{\alpha^2}. \quad (65)$$

From these relations, the probability of Σ_t itself can be inferred:

$$P(\Sigma_t) = \sqrt{\frac{t}{2\pi\Delta_0}} \exp\left[-\frac{t(\Sigma_t - \sigma_m)^2}{2\Delta_0}\right]. \quad (66)$$

We see that time going on, $P(\Sigma_t)$ becomes centered on σ_m with an increasingly sharp peak, entailing in particular that the probability mass associated to negative values of Σ_t becomes small. This feature can be expressed in the form of a large deviation-type property [16–18]

$$\frac{P(\Sigma_t)}{P(-\Sigma_t)} = \exp\left\{-\frac{t}{2\Delta_0} [(\Sigma_t - \sigma_m)^2 - (\Sigma_t + \sigma_m)^2]\right\}$$

$$= \exp\left(\frac{2\sigma_m}{\Delta_0} \Sigma_t t\right). \quad (67)$$

This expression is reminiscent of the ones derived, in a different context, by a number of authors. The difference is in the value of the coefficient in the exponent. In our expression, this coefficient integrates information on macroscopic-level processes through the value of σ_m , and on microscopic-level ones through the value of q^2 .

Figure 3 depicts the steady state probability distribution $P(\Delta\Sigma_t)$ for different distances from equilibrium and for different times t , in the case of mass diffusion. The distributions were obtained from the time averages of the full Eq. (26b) and a direct simulation of the stochastic differential Eq. (24). Figure 3a depicts the distribution

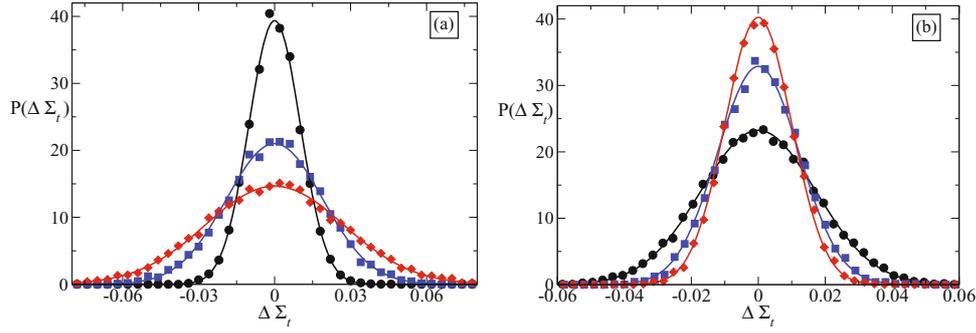


Fig. 3. Probability distribution $P(\Delta\Sigma_t)$. The marks stand for the distributions of $\Delta\Sigma_t$ obtained from 10,000 values of (26b) calculated through numerical simulations of Eq. (24) with $dt = 1.0 \times 10^{-5}$. The plain curves correspond to Eq. (64). Figure 3a was obtained with a total time $t = 20$, $c_b = D = 1$, and $c_a = 1.5$ (circles), $c_a = 2$ (squares) and $c_a = 2.5$ (diamonds). In Fig. 3b, $c_a = 1.5$ and the values of the other parameters are the same as in Fig. 3a. The three curves correspond to three different times: $t = 50$ (circles), $t = 100$ (squares) and $t = 150$ (diamonds).

of $\Delta\Sigma_t$ obtained at a fixed total time $t = 20$ for different values of the global driving force $\mu_a - \mu_b$ corresponding to different concentrations of c_a . It can be seen that the steady state probability distributions are in all cases well fitted by Gaussians of variance

$$\Delta_0 = \frac{k_B D}{\Omega} \left[(c_a + c_m) \left(\ln \frac{c_a}{c_m} \right)^2 + (c_b + c_m) \left(\ln \frac{c_b}{c_m} \right)^2 + \frac{1}{2} (c_a + c_b) \left(\ln \frac{c_a c_b}{c_m^2} \right)^2 \right], \quad (68)$$

as predicted from the form of the stochastic differential equation and of the entropy production, using the fluctuation-dissipation theorem (see also the discussion in Sect. 6). We note in particular that the variance of the distribution at a given time tends to increase with the distance from equilibrium, which can be understood from Eq. (68) as a consequence of the increase of both c_a and c_m . The role played by the averaging time t was also investigated numerically (see Fig. 3b). We observe that the distribution of the averaged entropy production gets narrower and narrower as time increases, as predicted from (64), which reproduces almost perfectly the statistics obtained from numerical simulations.

Let us rewrite (6b) as

$$\sigma = \sigma_{\text{GP}} + \sigma_{\text{Meso}}, \quad (69)$$

where the ‘‘Glandsdorff-Prigogine’’ entropy production

$$\sigma_{\text{GP}} = \sum_i \mathbf{J}_i \cdot \nabla \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} + \sum_{i,\rho} \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} \alpha_{i\rho} w_\rho \quad (70a)$$

has a structure similar to the macroscopic local equilibrium expression, but in which the X_i s are stochastic processes. We notice that despite the fluctuating character of the state variables, the terms entering σ_{GP} strictly satisfy the positivity criterion (7a). While the overall distribution of the fluctuations of Σ_t around the deterministic value σ_m is intrinsically symmetric, this contribution to the total entropy production will thus show an asymmetric behavior. In contrast, in the part containing the random

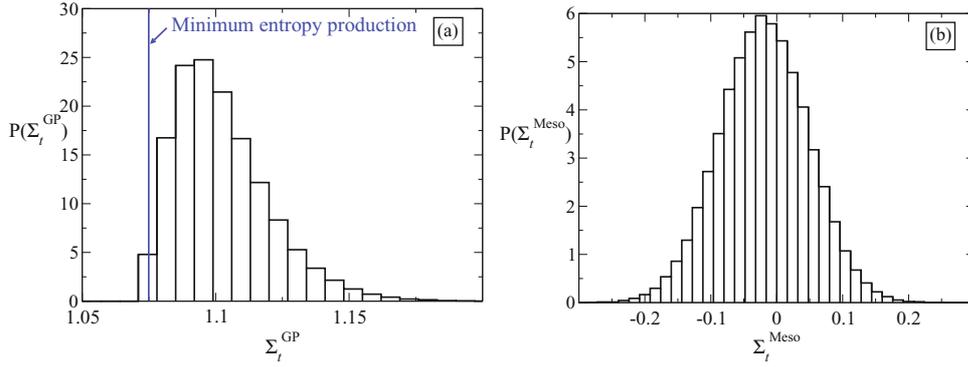


Fig. 4. Probability distribution of the time-averaged Glandsdorff-Prigogine (Fig. 4a) and mesoscopic (Fig. 4b) entropy productions for the two-compartment mass diffusion. The vertical line in Fig. 4a indicates the value of the minimum entropy production as predicted from the macroscopic expression of σ . The histograms were obtained from 10,000 realizations of the stochastic differential Eq. (24), for $c_a = 3$, $c_b = 1$, $\Omega = 100$ and a total time $t = 5$. The time step and the other parameters are identical to those of Fig. 3.

forces grouped into a “mesoscopic” entropy production term

$$\sigma_{\text{Meso}} = \sum_i \mathbf{j}_i \cdot \nabla \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} + \sum_{i,\rho} \left(\frac{\partial s}{\partial X_i} \right)_{X_j \neq i} \alpha_{i\rho} R_\rho, \quad (70b)$$

such a constraint does not apply. To illustrate this difference we consider once more the example of the two-compartment mass diffusion. We have (see Eq. (21a))

$$\sigma_{\text{GP}} = \frac{D}{T} [(\mu_a - \mu)(c_a - c) + (\mu_b - \mu)(c_b - c)]$$

and

$$\sigma_{\text{Meso}} = \frac{1}{T} [(\mu_a - \mu)j_a - (\mu_b - \mu)j_b].$$

The distributions of the corresponding time-averaged entropy productions Σ_t^{GP} and Σ_t^{Meso} are depicted in Fig. 4. The distribution of the mesoscopic contribution to the entropy production is fairly symmetric and has a slightly negative mean. The Glandsdorff-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 Glandsdorff-Prigogine entropy production, which is itself slightly larger than the deterministic value, in such a way that the sum of the mean Glandsdorff-Prigogine and mesoscopic entropy production terms is indeed equal to σ_m . Such asymmetric distributions would arise if one calculates the entropy production with the traditional macroscopic expression, based on the measurement of the fluctuating state variables only, while the full distribution (and the correct average entropy production) should be obtained when using both the fluctuating state variables and fluxes to evaluate the instantaneous value of σ .

We next consider the limiting case of equilibrium. As pointed out previously, the first non-trivial contribution to $\Delta\sigma$ comes now from nonlinear terms and can be cast in the generic form

$$\begin{aligned} \Delta\sigma_2 &= \alpha z^2 - zR(t) \\ &= -\frac{1}{2} \frac{dz^2}{dt}, \end{aligned} \quad (71)$$

up to a multiplicative factor. Introducing as before the mean entropy produced during the time interval $(0, t)$ we are led to inquire about the probability distribution density of

$$\Delta\Sigma_t = \frac{1}{2t} (z_0^2 - z_t^2) \quad (72)$$

which we express in a way similar to Eq. (63),

$$P(\Delta\Sigma_t) = \int_0^\infty dz_0^2 \int_0^\infty dz_t^2 P(z_0^2) P(z_t^2) \delta(2\Delta\Sigma_t t - z_0^2 + z_t^2)$$

or, integrating over z_0^2 ,

$$\begin{aligned} P(\Delta\Sigma_t) &= \int_0^\infty dz_t^2 P(z_t^2) \delta(2\Delta\Sigma_t t + z_t^2) \quad \text{if } \Delta\Sigma_t > 0, \text{ and} \\ &= \int_{-2\Delta\Sigma_t t}^\infty dz_t^2 P(z_t^2) \delta(2\Delta\Sigma_t t + z_t^2) \quad \text{if } \Delta\Sigma_t < 0. \end{aligned}$$

Taking the distribution of both z_0 and z_t to be the invariant distribution of the Ornstein-Uhlenbeck process and carrying out the change of variables to z_0^2 and z_t^2 , we obtain (up to a normalization factor)

$$P(\Delta\Sigma_t) \propto K_0 \left(\left| \frac{2\alpha}{q^2} \Delta\Sigma_t t \right| \right)$$

where K_0 is the modified Bessel function. Further asymptotic expansion of K_0 with respect to its argument (valid as long as q^2 is small and/or αt is large) leads to

$$\begin{aligned} P(\Delta\Sigma_t) &\propto \frac{1}{(\Delta\Sigma_t t)^{\frac{1}{2}}} \exp\left(-\frac{2\alpha}{q^2} \Delta\Sigma_t t\right) \quad \text{if } \Delta\Sigma_t > 0, \text{ and} \\ &\propto \frac{1}{|\Delta\Sigma_t t|^{\frac{1}{2}}} \exp\left(\frac{2\alpha}{q^2} \Delta\Sigma_t t\right) \quad \text{if } \Delta\Sigma_t < 0. \end{aligned} \quad (73)$$

We obtain a peculiar, non-differentiable at $\Delta\Sigma_t = 0$ structure, with longer tails in the positive and negative values of $\Delta\Sigma_t$ as compared to the Gaussian-like distribution found in the nonequilibrium case.

This property is confirmed by the numerical evaluation of $P(\Delta\Sigma_t)$, as seen in Fig. 5 which plots the distribution of the time-averaged entropy production at equilibrium for the linear reaction (36) with a single intermediate species. Note that the initial condition z_0 of the numerical integrations has to be sampled over its stationary distribution. For the chosen example, $\alpha = k_{-1} + k_2$ and $q^2 = (k_1 a + k_{-2} b + \alpha x_m)/\Omega$ [14, 15]. We observe in particular that, as predicted, the probability tends to diverge as $\Delta\Sigma_t$ tends to zero. The chance to observe a time-averaged entropy production deviating from zero is thus small, in particular for large systems and for long times, but at the same time these deviations can be relatively large in view of the long tails that $P(\Delta\Sigma_t)$ presents both in the domain of positive and negative entropy productions.

We close this section with a brief discussion on the role of nonlinearities in the structure of the probability density of the stochastic entropy production, using the model of Sect. 4.2. The steady state solution of the Fokker-Planck equation associated to the stochastic differential Eq. (50), satisfying zero flux boundary conditions is

$$\rho(x) = Z^{-1} \exp \left\{ \frac{2}{q^2} \left[(k_1 a - k_2) \frac{x^2}{2} - k_{-1} \frac{x^3}{3} + k_{-2} b x \right] \right\}$$

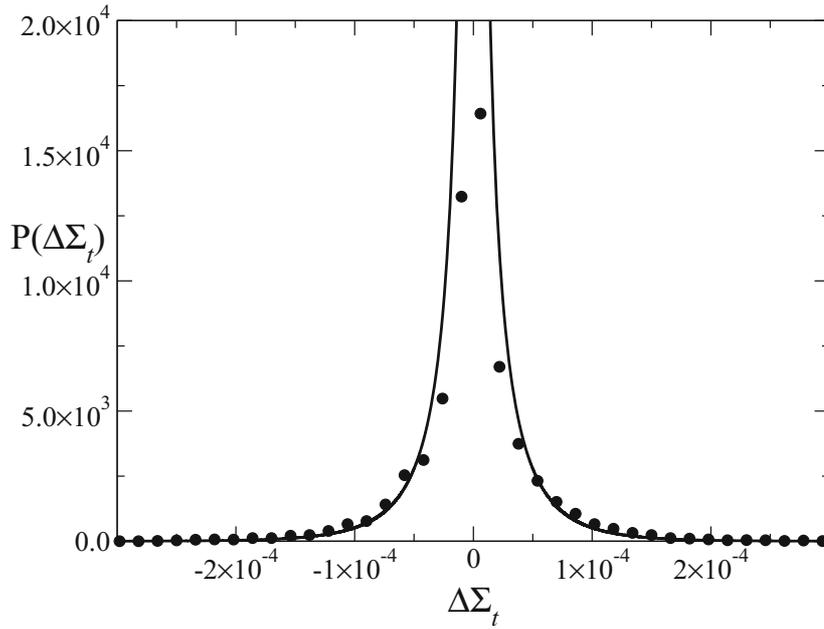


Fig. 5. Equilibrium probability distribution of the time-averaged entropy production for the linear reaction model (36) with a single intermediate species X. The histograms were obtained from 10,000 realizations of the stochastic differential Eq. (44), σ being calculated at each time step using Eq. (45). The parameters were $k_1 = k_{-1} = k_2 = k_{-2} = 1$, $a = b = 1$, $\Omega = 100$ and a total time $t = 200$, and $dt = 1.0 \times 10^{-5}$. The plain curves correspond to Eqs. (73), with a coefficient of proportionality fitted to a value of ≈ 81 .

where Z is the normalization constant. We notice, as stressed also in Sect. 4.2, that the extremum of $\rho(x)$ corresponds to the reference state x_m . Introducing the deviation Δx from x_m and expanding the part of the exponential in Δx^3 in powers keeping the first non-trivial terms, we obtain

$$\rho(\Delta x) \approx Z^{-1} \exp \left\{ -\frac{2}{q^2} |k_1 a - k_2 - 2k_{-1} x_m| \Delta x^2 \right\} \left[1 - \frac{2k_{-1}}{q^2} \frac{\Delta x^3}{3} \right]. \quad (74)$$

The point is that while the variance of this distribution is identical to the Gaussian variance, the second term introduces an asymmetry correction entailing that the mean value Δ of Δx is not zero (alternatively, the mean value \bar{x} of x is different from x_m).

Carrying on the calculation we end up with a form of Eq. (57) limited to the linear parts in δx and $R(t)$ and following the same procedure as earlier in this section, we conclude that the probability density of $\Delta \Sigma_t$ will inherit the asymmetry of $P(\Delta x)$, while still being peaked around σ_m . This is fully confirmed by the numerically evaluated probability (see Fig. 6) as obtained by direct simulation of the stochastic differential Eq. (50).

6 Conclusions

The local equilibrium hypothesis constitutes the basis of classical nonequilibrium thermodynamics. In the present work this hypothesis has been extended to incorporate the effect of the fluctuations. We developed on this basis a stochastic thermodynamics extending the classical theory, in which entropy becomes a random functional

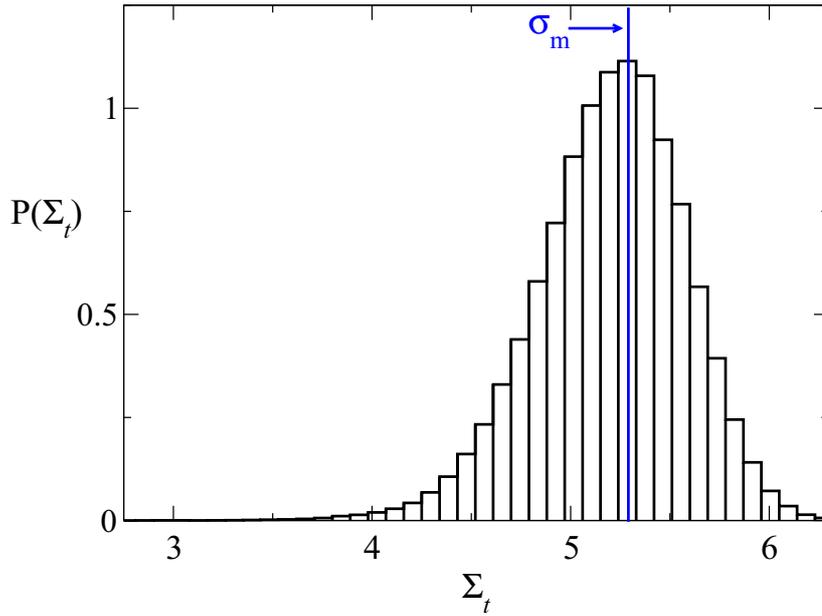


Fig. 6. Probability distribution of the time-averaged entropy production for the nonlinear model (48). The histograms were obtained from 10,000 realizations of the stochastic differential Eq. (50), with σ being computed from Eq. (54). The parameters were chosen to be $k_1 = k_{-1} = k_2 = k_{-2} = 1$, $a = 2$, $b = 0.01$, $\Omega = 100$ and a total time $t = 5$, the time step being again 1.0×10^{-5} .

related to the fluctuating state variables by the same relation as in thermodynamic equilibrium. We derived a balance equation for this quantity from which a stochastic entropy flux and a stochastic entropy production were identified. Explicit expressions for these quantities in terms of generalized fluxes and forces were obtained for systems possessing a unique stable steady state and illustrated on representative cases involving mass diffusion, heat conduction and chemical reactions.

As it turned out, in linear systems the contribution of the fluctuations in the average entropy flux and average entropy production vanishes. This is no longer so in nonlinear systems, for which fluctuation-induced corrections to classical irreversible thermodynamics become thus necessary. Finer statistical properties such as probability densities were analyzed using the mean entropy produced over a time interval t rather than the instantaneous entropy production, bringing out the important role of the distance from equilibrium. Away from equilibrium the probability densities are nearly Gaussian around their most probable values (with a slight asymmetry in the presence of nonlinear kinetics). In contrast, in the state of equilibrium the contributions to the fluctuating entropy production linear in the fluctuations vanish and the probability density becomes markedly non-Gaussian. In both cases there is a non-zero probability of having negative values of the entropy produced, owing to the fact that the part of the generalized fluxes associated to the noise sources introduced in the evolution equations to account for the fluctuations need not be aligned to the associated generalized forces. This probability satisfies, however, a large-deviation type property [16–18], becoming exponentially small as the time interval t and the system size are increased.

By construction, our approach reduces in a most natural way to classical thermodynamics in the mean-field limit, gives access to local information in space and time,

and allows one to follow the contribution of the elementary processes going on in the system on the behavior of the principal observables of interest. It also leads to generic results, such as the non-Gaussian distribution of entropy production at equilibrium, which could in principle be verified experimentally. In this respect, it constitutes an alternative to the formalism of stochastic thermodynamics developed in recent years [5–11] in which thermodynamic quantities are defined in terms of probabilities. A detailed comparison of the two approaches for both equilibrium and nonequilibrium cases would thus be desirable.

A central part of the formalism developed in this work was the introduction of random forces in the evolution equations of the state variables, whose variances were generally left unspecified except for their dependence in the inverse of the system size Ω , see Eq. (19) and reference [15]. A finer information can be obtained under conditions guaranteeing the validity of the fluctuation-dissipation theorem [13–15, 19], such as being close to equilibrium. The variances become then related to the parameters appearing in the systematic part of the evolution equations. It would be interesting to carry out such evaluations for the systems considered in this work.

Throughout our analysis systems fluctuating around a simple, stable steady state were considered. Our results show that under these conditions fluctuations do not substantially affect stability, their main role being to induce in the presence of nonlinear kinetics deviations from the mean-field values and asymmetries in the probability densities. A challenging, largely open problem would be to extend the formalism developed here to systems undergoing bifurcation to new (possibly time-dependent) states and/or systems possessing multiple steady states. The evolution of such systems becomes now fluctuation-driven and thus raises the question of possible thermodynamic signatures of the bifurcations, of the different states available and of the transitions between them.

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