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On the stochastic thermodynamics of reactive systems

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HIGHLIGHTS

- We develop a framework for the stochastic thermodynamics of reactive systems.
- We derive constraints acting on the transition probabilities of reactive events.
- The constraints make the stochastic picture coherent with classical thermodynamics.
- They affect the properties of stochastic fluxes, forces and entropy production.
- We show how they can be used to derive various types of fluctuation theorems.

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ABSTRACT

We develop a theoretical framework for the stochastic thermodynamics of reactive systems. We show that the transition probabilities per unit time of reactive events must satisfy specific constraints, in order for stochastic approaches to lead to physically meaningful results in the macroscopic limit. We discuss how these constraints affect the properties of stochastic fluxes and forces, and entropy production. We also see how they can be used to derive various expressions of fluctuation theorems.

1. Introduction

The recent years have witnessed important advances in the development of non-equilibrium thermodynamics. Stochastic thermodynamics proved to be an especially fruitful and powerful way to assess the properties of small systems, since they naturally include the effect of fluctuations of energy, mass, etc. Stochastic analogues of the laws of thermodynamics have been put forward [1–6], and new relations describing the properties of fluctuating thermodynamic variables, known as fluctuation theorems, have been proposed [2,5,7–13].

Despite such impressive developments, the author's opinion is that stochastic thermodynamics has not reached full maturity yet. The plethora of high-quality contributions has led to a multitude of approaches using different conventions and definitions, which can make the interpretation and comparison of the various works difficult. This difficulty arises in particular for the connection between the stochastic approach and its traditional, macroscopic counterpart. As an example, (free) energy is sometimes introduced as a stochastic variable [2,5,6] or alternatively as the logarithm of the probability distribution [3,4]. Furthermore, in most applications to reactive systems, chemical reactions are considered to modify the internal energy of the system [2,5], while according to macroscopic thermodynamics this is not the case as long as the properties of the particles that are responsible for the interaction with external fields are conserved [14]. Examples

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include reactions in a gravitational field (because of the conservation of mass), and in electrical fields (since the charge is conserved). There are also several coexisting definitions of entropy, as stochastic thermodynamics is often treated in terms of the Shannon (informational) entropy, which is different from the thermodynamic (Gibbs) entropy. As a consequence, one can find oneself confronted with different expressions for the exchange of entropy with the environment, depending on the definition used. As a last example, we note that in some stochastic approaches the mechanical work is considered to contribute to the entropy flow [6], which is not the case in traditional thermodynamics. These examples show the apparently contradictory conclusions that can be drawn from stochastic descriptions, and illustrate the need to rationalize the different approaches and to build a coherent theoretical framework.

The goal of this work is to propose a self-consistent stochastic thermodynamics, in such a way that all the principles of macroscopic, non-equilibrium thermodynamics are respected in the appropriate limit. We use for this a theoretical framework based on the master equation. For the sake of illustration, we will consider the case of open, spatially uniform reactive systems. The corresponding macroscopic description is first outlined in Section 2. Section 3 is devoted to a general presentation of the problem. The master equation is introduced and the different stochastic thermodynamic quantities are defined. The main results are presented in Section 4. We discuss how compatibility with the laws of thermodynamics puts constraints on the transition probabilities of the different processes, including the reactions. In Section 5, we illustrate these results on a simple chemical reaction and show how they can help to clarify the ambiguities mentioned above. In Section 6, we analyze how these constraints affect the properties of fluxes, forces and entropy production. We also discuss there how they contribute to the different types of fluctuation theorems. We finally conclude and point towards possible future developments.

2. Thermodynamics of open reactive systems

We start by a short presentation of the traditional macroscopic thermodynamics of open reactive systems. We consider the case of a spatially uniform system with no bulk velocity, in contact with an environment at a temperature T and a pressure p. Here, we define the system as being a given region of space being delimited by boundaries with well-defined properties, which allows defining its volume unambiguously. The only force acting on the system is the uniform pressure exerted by the environment on its boundaries, in other words we consider systems that are not subjected to external forces acting on its bulk properties. These choices are here justified because we want to focus on the contributions of chemical reactions to the different thermodynamic quantities, which appears to be at the source of most of the contradictory statements found in the literature. The thermodynamic state of such a system is supposed to be entirely defined by a set of macroscopic variables. Here we choose to work with the internal energy E, the volume V, and the number of molecules of each of the c chemical species $\mathbf{N} = \left\{N_\gamma\right\} = (N_1, N_2 \ldots N_c)$.

The first principle of thermodynamics postulates that the total energy of a system can vary only because of exchanges with the environment. Since under the above assumptions the internal energy E is itself equal to the total energy, it changes according to

$$\frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}_e E}{\mathrm{d}t} + \frac{\mathrm{d}_i E}{\mathrm{d}t} = \frac{\mathrm{d}\Phi}{\mathrm{d}t} - p\,\frac{\mathrm{d}V}{\mathrm{d}t}; \qquad \frac{\mathrm{d}_i E}{\mathrm{d}t} = 0, \tag{1}$$

where $\mathrm{d}\Phi/\mathrm{d}t$ is a combination of energy transferred as heat, and energy transferred with mass. It is often referred to as the generalized heat [15]. The term $-p\,\mathrm{d}V/\mathrm{d}t$ accounts for the energy exchanged in the form of mechanical work. In the above equations, the subscripts e and i represent, respectively, contributions due to exchanges with the environment and contributions related to internal processes.

In the presence of chemical reactions, the number of moles of each species can vary either because matter is being exchanged with the environment, or because of the reactions themselves:

$$\frac{\mathrm{d}N_\gamma}{\mathrm{d}t} = \frac{\mathrm{d}_e N_\gamma}{\mathrm{d}t} + \frac{\mathrm{d}_i N_\gamma}{\mathrm{d}t}. \tag{2}$$

Note that the internal changes are connected to the advancement ξ_ρ of each elementary reaction ρ

$$\sum_{\gamma=1}^{c} \overrightarrow{\nu}_{\gamma\rho} M_\gamma \rightleftharpoons \sum_{\gamma=1}^{c} \overleftarrow{\nu}_{\gamma\rho} M_\gamma, \tag{3}$$

by

$$\frac{\mathrm{d}_i N_\gamma}{\mathrm{d}t} = \sum_{\rho=1}^{r} \nu_{\gamma\rho} \frac{\mathrm{d}\xi_\rho}{\mathrm{d}t} \equiv \sum_{\rho=1}^{r} \nu_{\gamma\rho} J_\rho, \tag{4}$$

in which

$$\nu_{\gamma\rho} = \overleftarrow{\nu}_{\gamma\rho} - \overrightarrow{\nu}_{\gamma\rho} \tag{5}$$

is the stoichiometric coefficient of the species M_γ in the corresponding reaction and where $\mathrm{d}\xi_\rho = \mathrm{d}N_\gamma/\nu_{\gamma\rho}$.