



Ensemble and trajectory thermodynamics: A brief introduction

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HIGHLIGHTS

- We review stochastic thermodynamics at the ensemble level.
- We formulate first and second laws at the trajectory level.
- The stochastic entropy production is the log-ratio of trajectory probabilities.
- We establish the relation between the stochastic grand potential, work and entropy production.
- We derive detailed and integral fluctuation theorems.

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ABSTRACT

We revisit stochastic thermodynamics for a system with discrete energy states in contact with a heat and particle reservoir.

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1. Introduction

Over the last few years, it has become clear that one can extend thermodynamics, which is traditionally confined to the description of equilibrium states of macroscopic systems or to the transition between such states, to cover the nonequilibrium dynamics of small scale systems. This extension has been carried out at several levels of description including systems described by discrete and continuous Markovian and non-Markovian stochastic dynamics, by classical Hamiltonian and quantum Hamiltonian dynamics and by thermostatted systems. These developments can be seen, on one side, as extending the work of Onsager and Prigogine [1–4] by including microscopic dynamical properties into the far from equilibrium irreversible realm. On the other side, they have led to the reassessment of the cornerstone of thermodynamics, namely the second law of thermodynamics, which is replaced by a much deeper symmetry relation, embodied in the integral and detailed fluctuation theorems. On the more practical side, the new formulation allows to address new questions, either related to nonequilibrium properties, such as efficiency at maximum power or information to work conversion, or relating to the thermodynamic description of small systems, e.g., the discussion of Brownian motors and refrigerators or the efficiency of quantum dots and other small scale devices. In this paper, we present a brief introduction to stochastic thermodynamics. We refer to the literature for more advanced reviews [5–13].

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2. Ensemble thermodynamics

We consider a system, with discrete non-degenerate states, in contact with a single (ideal, non-dissipative) heat and particle reservoir at temperature T ($\beta = 1/(k_B T)$) and chemical potential μ . The states are identified by an index m , with corresponding energy ϵ_m and particle number n_m . For simplicity we consider a single type of particle. We assume that the system can also exchange work with an (ideal, non-dissipative) work source which controls its energy levels $\epsilon(\lambda)$ via a time-dependent control parameter $\lambda = \lambda(t)$. The particle number in a given state is however supposed to be fixed.

In the ensemble picture, the state of the system is described by a probability distribution P_m to be in the state m , with $\sum_m P_m = 1$. Note that this distribution does not have to be of the equilibrium form, so that “traditional equilibrium concepts”, such as temperature and chemical potential need not exist for the system. They are however well defined for the ideal reservoir, and when appearing in the formulas below, T and μ refer to this reservoir. The time evolution of the state is described by a Markovian master equation:

$$d_t P_m = \sum_{m'} W_{m,m'} P_{m'}. \quad (1)$$

Here $W_{m,m'}$ is the probability per unit time to make a transition from state m' to m . We use the shorthand notation with diagonal elements defined as $W_{m,m} = -\sum_{m' \neq m} W_{m',m}$. Alternatively:

$$\sum_m W_{m,m'} = 0, \quad (2)$$

a property that guarantees the conservation of normalization. The transition rates have to satisfy an additional property. In the steady state, the system is at equilibrium with the reservoir. Statistical physics prescribes that the steady state distribution is given by the grand canonical equilibrium distribution P_m^{eq} [14]:

$$P_m^{eq} = \exp\{-\beta(\epsilon_m - \mu n_m - \Omega^{eq})\}. \quad (3)$$

The (equilibrium) grand potential Ω^{eq} follows from the normalization of P^{eq} :

$$\exp\{-\beta\Omega^{eq}\} = \sum_m \exp\{-\beta(\epsilon_m - \mu n_m)\}. \quad (4)$$

The crucial property that is required from the rates is the so-called condition of detailed balance, i.e., at equilibrium every transition, say from m to m' , and its inverse, from m' to m , have to be equally likely:

$$W_{m,m'} P_{m'}^{eq} = W_{m',m} P_m^{eq}. \quad (5)$$

Combined with the explicit expression of the equilibrium distribution, this gives:

$$k_B \ln \frac{W_{m',m}}{W_{m,m'}} = \frac{\epsilon_m - \epsilon_{m'} - \mu(n_m - n_{m'})}{T} = \frac{q_{m,m'}}{T}. \quad (6)$$

$q_{m,m'}$ is the “elementary” heat absorbed by the system to make the transition from m' to m . We stress that in the presence of driving, which is shifting the energy levels in time, this relation is supposed to hold at each moment in time, hence the rates also become time-dependent. This condition will be crucial to obtain the correct formulation of the second law.

We next introduce the basic state functions – quantities that depend on probability distribution P_m of the system, but not on the way this distribution was achieved – namely the ensemble-averaged and in general nonequilibrium values of energy, particle number and entropy:

$$E = \sum_m \epsilon_m P_m = \langle \epsilon_m \rangle, \quad (7)$$

$$N = \sum_m n_m P_m = \langle n_m \rangle, \quad (8)$$

$$S = -k_B \sum_m P_m \ln P_m = \langle -k_B \ln P_m \rangle. \quad (9)$$

It is clear from the above formulas that these state variables can change due to two different mechanisms: a change in occupation of the levels, i.e., a modification of P_m , or a shift of the energy levels, i.e., a change of the energy level ϵ_m . In particular, the rate of energy change is given by:

$$d_t E = \sum_m \{\epsilon_m d_t P_m + d_t \epsilon_m P_m\} \quad (10)$$

$$= \dot{Q} + \dot{W}_{chem} + \dot{W}. \quad (11)$$

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