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Stochastic thermodynamics: From principles to the cost of precision

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HIGHLIGHTS

- The basic principles of stochastic thermodynamics are developed.
- The thermodynamic uncertainty relation between dissipation, currents and their dispersion is introduced.
- Examples for thermodynamic inference are presented.

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ABSTRACT

In these lecture notes, the basic principles of stochastic thermodynamics are developed starting with a closed system in contact with a heat bath. A trajectory undergoes Markovian transitions between observable meso-states that correspond to a coarse-grained description of, e.g., a biomolecule or a biochemical network. By separating the closed system into a core system and into reservoirs for ligands and reactants that bind to, and react with the core system, a description as an open system controlled by chemical potentials and possibly an external force is achieved. Entropy production and further thermodynamic quantities defined along a trajectory obey various fluctuation theorems. For describing fluctuations in a non-equilibrium steady state in the long-time limit, the concept of a rate function for large deviations from the mean behavior is derived from the weight of a trajectory. Universal bounds on this rate function follow which prove and generalize the thermodynamic uncertainty relation that quantifies the inevitable trade-off between cost and precision of any biomolecular process. Specific illustrations are given for molecular motors, Brownian clocks and enzymatic networks that show how these tools can be used for thermodynamic inference of hidden properties of a system.

1. Introductory remarks

Over the last about ten to twenty years, stochastic thermodynamics has emerged as a comprehensive framework for describing small driven systems in contact with (or embedded in) a heat bath like colloidal particles in laser traps or biomolecules and biomolecular networks. As an essential concept, the notions of classical thermodynamics like work, heat and entropy production are identified on the level of fluctuating trajectories. The distributions of these quantities obey various universal exact fluctuation relations.

In the first part of these lecture notes, these concepts will be developed for a driven system obeying a Markovian dynamics on a discrete set of states which implicitly also contains the case of overdamped motion on a continuous state space usually described by Langevin equations. Since this part is well established by now, only a few selected references to the original

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key papers will be given. A more comprehensive guide to the vast literature concerning refinements and theoretical and experimental case studies, can be found, inter alia, in several recent reviews [1–4].

The second part deals with a more recent development concerning the fluctuations in non-equilibrium steady states for which a family of inequalities were found among which the most prominent one constrains the mean and variance of currents in terms of the overall entropy production. This universal relation can also be expressed as the inevitable trade-off between cost and precision of any thermodynamically consistent process which has been dubbed the thermodynamic uncertainty relation. Its proof follows from a universal bound on the large deviations of any current. Stronger bounds on these fluctuations follow with somewhat more knowledge about the driving forces and the topology of the underlying network. With these relations, measured fluctuations allow to infer otherwise hidden properties of these systems. This presentation is not intended to be an exhaustive review of these recent (and ongoing) developments but rather a pedagogical introduction to them.

2. Closed system in contact with a heat bath

2.1. Meso-states

Starting on a very general level, we consider a closed system with micro-states $\{\xi\}$ and energy $H(\xi)$ in contact with a heat bath at inverse temperature β. In equilibrium, free energy, internal energy and entropy are given by

$$F = -(1/\beta)\ln\sum_{\xi}\exp[-\beta H(\xi)], \quad E = \partial_\beta(\beta F), \quad S = \beta^2\partial_\beta F = \beta(E-F), \tag{1}$$

respectively.

We then partition the total phase space into a set of observable meso-states $\{I\}$. Each micro-state ξ is assumed to belong to one and only one meso-state I to which many micro-states $\xi \in I$ contribute. In equilibrium (superscript^e), the probability to find the system in meso-state I is then given by

$$P_I{}^e = \sum_{\xi\in I}\exp[-\beta(H(\xi)-F)] \equiv \exp[-\beta(F_I - F)] \tag{2}$$

where the last equality defines the free energy F_I of the state I. This identification is justified, first, since the mean energy in state I can be expressed as

$$E_I = \sum_{\xi\in I} P(\xi|I)H(\xi) = \partial_\beta(\beta F_I), \tag{3}$$

where

$$P(\xi|I) = \exp[-\beta(H(\xi)-F)]/P_I{}^e = \exp[-\beta(H(\xi)-F_I)] \tag{4}$$

is the conditional probability for the micro-state ξ given the meso-state I. Second, defining an "intrinsic" entropy S_I from F_I as in (1) leads to

$$S_I \equiv \beta^2\partial_\beta F_I = \beta(E_I - F_I) = -\sum_{\xi\in I} P(\xi|I)\ln P(\xi|I) \equiv S[P(\xi|I)], \tag{5}$$

which is the Shannon entropy of the conditional probability.[1] With these expressions, in equilibrium, mean energy, entropy and free energy of the system can also be written as

$$E = \sum_I P_I{}^e E_I, \quad S = \left\{\sum_I P_I{}^e S_I\right\} + S[P_I{}^e], \quad F = \left\{\sum_I P_I{}^e F_I\right\} - (1/\beta)S[P_I{}^e], \tag{6}$$

respectively.

2.2. Trajectory, time-scale separation, transition rates and master equation

In the course of time, the system moves along a trajectory $I(t)$ of meso-states. While in principle any partition into meso-states is formally possible, such a separation makes physical sense, and will lead to stochastic thermodynamics, if transitions between meso-states are slow while transitions between the micro-states belonging to one meso-state are fast. As a necessary condition, obviously, the heat bath has to relax at least as fast. Ideally, the dynamics along such a trajectory then becomes Markovian, which means that there is a (constant) transition rate K_{IJ} for the system in state I to jump to state J

[1] Throughout this presentation, entropy is dimensionless, i.e., Boltzmann's constant is set to 1, and $S[p_i] \equiv -\sum_i p_i \ln p_i$ denotes the Shannon entropy of an arbitrary discrete probability distribution.