



Stochastic thermodynamics across scales: Emergent inter-attractor discrete Markov jump process and its underlying continuous diffusion



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ABSTRACT

We investigate the internal consistency of a recently developed mathematical thermodynamic structure across scales, between a continuous stochastic nonlinear dynamical system, i.e., a diffusion process with Langevin and Fokker–Planck equations, and its emergent discrete, inter-attractor Markov jump process. We analyze how the system's thermodynamic state functions, e.g. free energy F , entropy S , entropy production e_p , free energy dissipation \dot{F} , etc., are related when the continuous system is described with coarse-grained discrete variables. It is shown that the thermodynamics derived from the underlying, detailed continuous dynamics gives rise to exactly the free-energy representation of Gibbs and Helmholtz. That is, the system's thermodynamic structure is the same as if one only takes a middle road and starts with the *natural* discrete description, with the corresponding transition rates empirically determined. By natural we mean in the thermodynamic limit of a large system, with an inherent separation of time scales between inter- and intra-attractor dynamics. This result generalizes a fundamental idea from chemistry, and the theory of Kramers, by incorporating thermodynamics: while a mechanical description of a molecule is in terms of continuous bond lengths and angles, chemical reactions are phenomenologically described by a discrete representation, in terms of exponential rate laws and a stochastic thermodynamics.

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1. Introduction

A quite complete mathematical thermodynamic structure for general stochastic processes has been described recently for both discrete Markov jump processes and continuous Langevin–Fokker–Planck systems [1–9]. In this formalism, the entropy production rate e_p of a Markov dynamics can be mathematically decomposed into two non-negative terms: free energy dissipation rate $-\dot{F}$, corresponding to Boltzmann's original theory on irreversibility of spontaneous change, and house-keeping heat Q_{hk} , corresponding to the Brussels school's notion of irreversibility including nonequilibrium steady states (NESS) [10–14].¹

In almost all applications of stochastic dynamic theories in physics, chemistry and biology, there are multiple time scales often with a significant separation of their magnitudes. Furthermore, when a dynamical system is highly nonlinear, with interactions including strong feedback, multistability with multiple attractors is often the rule rather than an exception.

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¹ This is an interpretation of the mathematical equation $e_p = -\dot{F} + Q_{hk}$ based on a traditional view of thermodynamics. A new view advocated in Ref. [3], noting that both Q_{hk} and e_p are non-negative, is to interpret $\dot{F} = Q_{hk} - e_p$ as a *balance equation* for free energy F ; i.e., the First Law of an open system, with Q_{hk} and e_p being a source and a sink.

Visualizing such a complex system naturally leads to the notion of a landscape, which has become a highly popular metaphor as well as a useful analytical device [15–19]. When stochastic nonlinear dynamical systems of populations of individuals become large, a time scale separation between inter- and intra-attractor dynamics becomes almost obligatory. In cellular biology, they have been called respectively biochemical network and cellular evolution time scales [20].

In chemistry, recognizing a separation of time scales has led to the fundamental understanding of chemical reactions in terms of discrete states of molecules, in addition to the full mechanical description of constitutive atoms in terms of bond lengths and bond angles. In fact, one of the most significant, novel, chemical concepts is that of a transition state which, in terms of the modern nonlinear dynamical systems language, is the saddle point on a separatrix that divides two basins of attraction [21,22]. Recall also that in the application of Gibbs' formalism of statistical mechanics to chemical equilibrium, the conditional free energy plays a central role [23,24]. One usually does not work with the pure mechanical energy of a system; rather, one works with a conditional free energy from a coarse-grained representation and develops a partition function thereafter. An essential notion in this approach is the consistency across scales. We shall expand on these ideas more precisely in the following section.

In the present work we address the question of whether the mathematical thermodynamic structure of a given continuous stochastic nonlinear dynamical system is consistent with the mathematical thermodynamics associated with the emergent discrete Markov jump process. In other words: whether the formal mathematical relations between state functions and process variables remain unchanged when the system is viewed at either a finer- or a coarse-grained scale.

It is important to point out, at the onset, that the state of a stochastic dynamical system has always had two distinctly different meanings: (a) a state of a single, stochastically fluctuating, system; and (b) a state in terms of the distribution over an ensemble. Similarly, in more precise mathematical terms, a state function can be (a) a function of a stochastic process, or (b) a functional of the solution to a Fokker–Planck equation. The deep insight from the theory of probability is that these are two complementary, yet mathematically identical, descriptions of the same *stochastic process*. With this distinction in mind, entropy and free energies are state functionals of the second type, while energy is a state function of the first type. A state function of the first type naturally has fluctuations. Most classical thermodynamic functions, on the other hand, are of the second type.

It is also important to point out that the present analysis starts with the assumption of Markovian dynamics with both continuous and discrete states. We wish to investigate the internal logic of stochastic thermodynamics. All the thermodynamic quantities that appear in the present work, though motivated by physics and using the same names, are mathematically defined quantities based on the stochastic dynamics alone. In particular, our analysis differs from the recent coarse-graining thermodynamic analysis based on a conventional approach [2,9] which reveals a hidden entropy production. An explicit assumption of our mathematical formalism is that one cannot measure entropy production without sufficient time resolution to recognize time irreversibility.²

2. Equilibrium statistical thermodynamic consistency across scales

In equilibrium statistical mechanics, the concept of consistency, or invariance, has a fundamental importance in the study of realistic physical systems at an appropriate scale [23,24]. In a continuous system, the conditional free energy is known as the potential of mean force [26]. The conditional free energy can do work just as the Newtonian mechanical energy; the concept of entropic force is well understood in physical chemistry [27].

For an investigator working on a certain level of description, with discrete states ($i = 1, 2, \dots$) and conditional free energy (A_i), the canonical partition function of the statistical thermodynamic system is [23,24,27]:

$$Z(T) = \sum_{i=1} e^{-A_i/k_B T}. \quad (1)$$

Note that, since A_i is a conditional free energy, it can be decomposed into $A_i = E_i - TS_i$, where $E_i = \partial(A_i/T)/\partial(1/T)$ and $S_i = -\partial A_i/\partial T$. In general, both E_i and S_i are themselves functions of the temperature.

Now, for another investigator who works at a much more refined level, with a continuous variable \mathbf{x} , each state i corresponds to a unique region of the phase space ω_i , with $\omega_i \cap \omega_j = \emptyset$ for $i \neq j$, and $\bigcup_{i=1} \omega_i = \Omega$ covering the entire phase-space region available to the system. Let $V(\mathbf{x})$ ($\mathbf{x} \in \Omega$) be the potential of mean force at this level. Then, the canonical partition function for this observer is

$$\tilde{Z}(T) = \int_{\Omega} d\mathbf{x} e^{-V(\mathbf{x})/k_B T}. \quad (2)$$

We see that $Z(T)$ and $\tilde{Z}(T)$ are equal if the A_i in Eq. (1) are such that

$$A_i(T) = -k_B T \ln \left(\int_{\omega_i} d\mathbf{x} e^{-V(\mathbf{x})/k_B T} \right). \quad (3)$$

² In Ref. [25], it was attempted to introduce entropy as a function of the first type with $\gamma_t = -\ln f_X^s(X_t)$ where X_t is a diffusion process, and $f_X^s(x)$ is the stationary solution to the corresponding Fokker–Planck equation. One sees that entropy really is a population-based concept: it requires $f_X^s(x)$. For diffusion processes with detailed balance, since $f_X^s(x) \propto e^{-\phi(x)}$ where $\phi(x)$ is potential energy, then fluctuating γ_t and fluctuating energy $\phi(X_t)$ are the same.

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