

Towards a classification scheme for non-equilibrium steady states and a generalized detailed balance condition

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Abstract. A general classification scheme for nonequilibrium steady states - in terms of their stationary probability distribution and the associated probability currents - is proposed. This scheme allows us to identify all choices of transition rates, based on a master equation, which generate the same nonequilibrium steady state. One important consequence is a generalized detailed balance condition.

1 Introduction

In the study of equilibrium statistical mechanics, the successful Boltzmann-Gibbs framework provides us with *known* (static) distributions. Thus, for a system in equilibrium with a thermal bath at inverse temperature β , the probability to find the system in a given configuration \mathcal{C} is given by $P^{eq}(\mathcal{C}) \propto \exp\{-\beta\mathcal{H}(\mathcal{C})\}$, where $\mathcal{H}(\mathcal{C})$ is the internal energy associated with \mathcal{C} . The main challenge here is to extract macroscopic properties out of this P^{eq} , through appropriate statistical averages, $\langle \bullet \rangle = \sum \bullet P^{eq}(\mathcal{C})$. In a few cases, a number of properties can be computed analytically. For significantly many systems, however, most progress is made through computer simulations. There, a large number of configurations is generated, in such a way that they occur with relative weights according to P^{eq} , and these configurations are exploited in estimating various averages. The crucial task is to generate such sequences of configurations with *high efficiency* and *great accuracy*. It is well established that they can be produced through a dynamical evolution process, if the rates for making transitions from one configuration, \mathcal{C}_i , to another, \mathcal{C}_j , - denoted by w_j^i here - obey “detailed balance.” To be precise, we demand [1]

$$w_j^i P_i^{eq} = w_i^j P_j^{eq} \quad (1)$$

where $P^{eq}(\mathcal{C}_i)$ has been simplified to P_i^{eq} .

In nature, many interesting phenomena do not belong to this class of equilibrium systems. In particular, biological systems cannot survive long under the conditions of thermal equilibrium (i.e., coupled to a single thermal bath, at *any* temperature). Instead, they rely on a steady *flux* - of, e.g., energy or particles - through them. With this important distinction, we refer to these systems as being in *non-equilibrium steady states* (NESS).

Even though a NESS itself may be “stationary” or appear (macroscopically) time-independent, it continues to have a serious effect on its environment. By “environment,” we mean all the reservoirs external to the system being studied. Through its coupling to more than one reservoir of energy, particles, etc., our system is, in a sense, causing sustained changes to its environment. This should be contrasted with an equilibrium system, in either the micro- or the canonical ensemble: On average, no changes occur, either to the system itself or the thermal bath.

In this article, we briefly consider a framework, based on the master equation, that allows us to highlight the differences between equilibrium states and NESS’s. In particular, non-trivial probability currents are distinguishing features in the latter, leading us to postulate that a unique and complete description of all stationary states is provided by not only the stationary probability distribution, P^* , but also the current distribution, K^* . In a following sections, we explore some consequences of this postulate and close with a summary and outlook.

2 The master equation and its stationary distribution

For NESS, we have no general Boltzmann-Gibbs like approach to guide us directly to a distribution like P^{eq} . Instead, the modeling of a typical NESS (e.g., translation in protein synthesis) always begins with an underlying *dynamical* process, rather than immediately accessing a stationary distribution $P_i^*(\mathcal{C})$. Such dynamical models typically consist of a simple set of “rules of evolution,” in the form of, say, a set of rates $\{w_j^i\}$ which govern the time dependence of $P_i(t)$ via the master equation:

$$\partial_t P_i(t) = \sum_{j \neq i} \left[w_i^j P_j(t) - w_j^i P_i(t) \right] \quad (2)$$

Being a simple statement of probability conservation, it is clear that

$$w_i^j P_j(t) - w_j^i P_i(t) \quad (3)$$

is just the *net* probability current from j to i . Now, if the rates are ergodic (every \mathcal{C} is connected to all others), $P_i(t)$ approaches a unique stationary P_i^* (i.e., $\partial_t P_i^* = 0$) at large times. Hence, the associated currents also approach stationary values

$$K_i^{*j} \equiv w_i^j P_j^* - w_j^i P_i^* . \quad (4)$$

This expression shows clearly that, for rates obeying detailed balance (Eqn. 1), all currents are identically *zero*, while $P^* = P^{eq}$. For interesting cases of NESS, the rates *violate* detailed balance. In general, little is known about the associated distributions P_i^* . Indeed, very simple rules can lead to remarkably complex states. A good example is Conway’s game of life [2], in which a vast

zoo of intriguingly complex patterns emerges magically from an *exceedingly simple* 233 rule! Other examples can be found in Refs. [3,4].

Remarkably, a completely general graphic construction of P_i^* (from an arbitrary set of w 's) exists [5–9]. Unfortunately, this construction is so involved that it is typically difficult to gain much insight into the nature of the steady states. Nevertheless, it does provide a connection between the *lack of* detailed balance and the presence of *non-zero* K^* 's [8,9]. Thus, we have a good analogy for the difference between equilibrium and non-equilibrium time-independent states: electrostatics *vs.* magnetostatics. The latter has non-trivial, steady currents (to be precise, current loops). Further, from these microscopic distributions of probability currents, the non-trivial, macroscopic fluxes through our system can be computed [8,9].

3 A postulate and its consequences

In a recent article [8], we proposed that all steady states (associated with a master equation) be completely and uniquely characterised by the pair of distributions and currents, $\{P^*, K^*\}$. As a simple generalization of the characterization of equilibrium states by P^{eq} alone, this brings the distribution of probability currents to the forefront, so that K^* plays a central role along with P^* . Several consequences arise from this postulate.

1. As in the case for equilibrium systems, if we wish a dynamical system to evolve toward a given NESS (i.e., a specific pair $\{P^*, K^*\}$), then we may choose any rates that satisfy a “generalized detailed balance” condition

$$w_i^j P_j^* = w_j^i P_i^* + K^{*j} . \quad (5)$$

2. If *one* set of w 's leads to a NESS (and the associated P^* is known), then we can *add* to these rates arbitrary Δ 's that satisfy

$$\Delta_i^j P_j^* = \Delta_j^i P_i^* .$$

without modifying the original NESS. Note that this resembles Eqn. (1), a condition of “detailed balance with respect to P^* ”. But there is an important distinction: unlike the w 's, Δ_i^j may be negative, as long as the sums $w_j^i + \Delta_j^i$ are all non-negative.

3. Since K^* is antisymmetric, the degrees of freedom in choosing w 's can be regarded as having an arbitrary symmetric part in the matrix $w_j^i P_i^*$. In other words, $S_i^j \equiv (w_j^i P_i^* + w_i^j P_j^*)/2$ can be modified at will, subjected only to some simple constraints [8].
4. Schnakenberg [6] introduced one possible way of thinking about the *entropy* production of a system as well as its environment, in the context of the time-dependent solution of a master equation:

$$\dot{S}_{sys} \equiv \sum_{i,j} W_i^j P_i(t) \ln \frac{P_j(t)}{P_i(t)} , \quad \dot{S}_{env} \equiv \sum_{i,j} W_i^j P_j(t) \ln \frac{W_i^j}{W_j^i} . \quad (6)$$

Recognized as the time derivative of $-\sum_i P_i(t) \ln P_i(t)$, the former is naturally associated with “entropy production of the system”. The latter is attributed to the *environment external* to the system, coupled in a way that prevents the system from reaching equilibrium [6]. Their sum, the “total entropy production”

$$\dot{\mathbf{S}}_{tot} \equiv \sum_{i,j} W_i^j P_j(t) \ln \frac{W_i^j P_j(t)}{W_j^i P_i(t)}, \quad (7)$$

is *non-negative*. In the steady state, $\dot{\mathbf{S}}_{sys}^* = 0$ and

$$\dot{\mathbf{S}}_{env} = \dot{\mathbf{S}}_{tot} = \frac{1}{2} \sum_{i,j} K_i^{*j} \ln(W_i^j P_j^* / W_j^i P_i^*). \quad (8)$$

Through (5), we have

$$\dot{\mathbf{S}}_{tot}^* = \frac{1}{2} \sum_{i,j} K_i^{*j} \ln \frac{S_i^j + K_i^{*j}/2}{S_i^j - K_i^{*j}/2}. \quad (9)$$

Since many choices of S_i^j lead to the same NESS, the implication of this equation is that there are many ways to couple the system to its environment such that the entropy production of the latter can be made arbitrarily large or small!

4 Summary and Outlook

We have addressed a fundamental question associated with non-equilibrium steady states: Within the framework of the master equation, what class, if any, of transition rates $\{w\}$ leads to the same stationary state? For equilibrium systems, the answer is provided by the detailed balance condition. To generalize this answer to NESS, we first postulate that a NESS is completely and uniquely specified by not only its stationary distribution P^* but also the steady currents K^* . We explored a number of consequences of this postulate, including a *generalized* detailed balance condition (Eqn. 5). Several specific examples are provided elsewhere [9]. Numerous open questions remain, so that the outlook for future work is bright. Here, we conclude by listing a few.

(i) At the most simplistic level, we can take known distributions P^* and associate them with a set of non-trivial currents K^* . Since we have provided a way to simulate such systems, we can study the novel properties, if any, associated with the *fluxes*. (ii) In the past, renormalization group analysis has provided much insight into critical phenomena. The properties of a system under scale transformations can be recast as flows in the space of distributions $P^{eq}(C)$ or equivalently, in the space of hamiltonians $\mathcal{H}(C)$. If the pair $\{P^*, K^*\}$ is to characterize systems in NESS, we may study the flows in the space of current distributions, K^* , as well. In particular, the puzzle of

why certain NESS belong to *equilibrium* universality classes [10] while others define *truly novel* universal behavior [11] remains unsolved. Perhaps the perspective presented here will provide a natural arena in which this mystery can be resolved. (iii) Entropy production is another venerable issue. Are there other ways to define entropy production, or even entropy, both for the system and for the reservoirs to which it is coupled? If so, what are the implications of our postulate for these types of entropy production? (iv) Since probability currents are the key features that distinguish a NESS from a system in equilibrium, we are reminded of electric currents being the main distinction between magnetostatics and electrostatics. Does this analogy allow us to define ‘magnetic fields’ in our case? And is there an underlying gauge theory? We hope that the proposal presented here will generate many novel lines of research.

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