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LETTER TO THE EDITOR

Lag inequality for birth–death processes with time-dependent rates

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Abstract

A fluctuation theorem has recently been derived for systems described by univariate birth–death equations or chemical master equations (Seifert U 2004 *J. Phys. A: Math. Gen.* **37** L517–21). We discuss an inequality that follows from this theorem. Focusing on the case of Poissonian stationary distributions, we show that this inequality can also be derived from a deterministic rate equation, in the limit of large system size. We relate these results to recent work on transitions between nonequilibrium stationary states.

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In a recent letter [1], Seifert has derived a fluctuation theorem pertaining to processes that can be described by univariate birth–death equations or chemical master equations, where the system in question is driven away from a stationary state by the external variation of a control parameter. The analysis in [1] is simple and elegant, and serves to emphasize the ubiquity of fluctuation theorems.

The present comment discusses an *inequality* implied by Seifert's fluctuation theorem, which we analyse in detail for the special case when the stationary states of the system are Poissonian. This inequality, given by equation (14), is the mathematical expression of an intuitively obvious notion: when parameters of a system are varied externally, the system needs some time to catch up with the stationary state corresponding to the new parameter values. Equation (14) resembles a thermodynamic inequality, in the sense that it constrains transitions between stationary states, and this constraint is expressed in terms of the net change in a state function. We will show that equation (14) follows immediately from Seifert's fluctuation theorem, and that in the thermodynamic limit—where statistical fluctuations can be ignored—the same result can be obtained from a deterministic rate equation. Finally, we will relate this work to results on transitions between nonequilibrium stationary states, in particular to the work of Shibata [2].

Let us begin with a brief review of the central result of [1]. Consider a system that can exist in any one of a countable number of states, labelled by the integer $n \geqslant 0$. In birth–death

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processes or chemical reactions, n_t represents the number of members contained in some set at time t. This number changes by unit increments as members of the set are born or die, and we assume that the process is governed by the master equation

$$\partial_t p_n = w_{n-1}^+(\lambda) p_{n-1} + w_{n+1}^-(\lambda) p_{n+1} - \left[w_n^+(\lambda) + w_n^-(\lambda)\right] p_n. \tag{1}$$

Here $p_n(t)$ is the probability that the system is in state n at time t; $w_n^\pm(\lambda)$ represent the birth (w^+) and death (w^-) transition rates and λ is some control parameter on which these rates depend. When λ is held fixed, the system relaxes to a stationary state $p_n^s(\lambda)$ that satisfies the detailed balance condition

$$p_n^s \big/ p_{n-1}^s = w_{n-1}^+ \big/ w_n^-. \tag{2}$$

This condition, along with normalization $\left(\sum_n p_n = 1\right)$, determines the set of probabilities, $p_n^s(\lambda)$, characterizing the stationary state[1]. By analogy with the Boltzmann–Gibbs distribution, we can define 'energy levels' associated with this stationary state:

$$\epsilon(n;\lambda) \equiv -\ln p_n^s(\lambda). \tag{3}$$

The fluctuation theorem derived by Seifert then pertains to the statistical ensemble of trajectories obtained by repeatedly initializing the system in the stationary state corresponding to λ_0, and then allowing the system to evolve, stochastically, from $t = 0$ to a final time $t = \tau$, as the control parameter is varied according to some pre-determined protocol λ_t. The theorem is stated by the following equation:

$$\left\langle \exp\left[-\int_0^\tau \epsilon'(n_t;\lambda_t)\dot{\lambda}_t \, \mathrm{d}t\right]\right\rangle = 1. \tag{4}$$

Here $\epsilon' \equiv \partial_\lambda \epsilon$; $\dot{\lambda} \equiv \mathrm{d}\lambda/\mathrm{d}t$; and $\langle\cdots\rangle$ denotes an average over the statistical ensemble of trajectories n_t.

A special case, discussed in detail in [1], occurs when the transition rates obey

$$w_{n-1}^+ \big/ w_n^- = n^s/n, \tag{5}$$

for some positive constant n^s. This condition is equivalent to stating that there exists a positive function $f_n > 0$ such that the transition rates are given by

$$w_n^+ = n^s f_n, \qquad w_n^- = n f_{n-1}. \tag{6}$$

In this case, the stationary distribution is Poissonian,

$$p_n^s = \frac{1}{n!} \mathrm{e}^{-n^s} (n^s)^n, \tag{7}$$

and n^s is the mean of this distribution.

It is convenient to have in mind a simple example described by the above formalism. Consider a closed, flat two-dimensional region (box) of area A, and imagine that particles are born in this region at an average rate νA; thus, ν is the average birth rate per unit area. Once a particle is born, it dies with a probability rate γ: if the particle is alive at a certain time t, then $\gamma\,\mathrm{d}t$ is the probability that it will die within the next infinitesimal time interval $\mathrm{d}t$. Letting n denote the number of particles inside the region, this process is governed by equation (1) with

$$w_n^+ = \nu A, \qquad w_n^- = \gamma n. \tag{8}$$

This set of transition rates obeys equation (5) (equivalently, equation (6) with $f_n = \gamma$), hence the stationary distribution is Poissonian with mean $n^s = \nu A/\gamma$.

[1] In order for a well-defined stationary state to exist, the ratio w_{n-1}^+/w_n^- must decay to zero sufficiently rapidly (as $n \to \infty$) that the normalization condition $\sum_n p_n^s = 1$ can be satisfied. Throughout the letter we assume this condition is satisfied.

This example can be generalized by letting ν and γ depend on n:

$$w_n^+ = \nu_n A, \qquad w_n^- = \gamma_n n. \tag{9}$$

In other words, the probability rate at which particles are born or die is allowed to depend on the current number of particles in the box. In the absence of further assumptions regarding the functions ν_n and γ_n, equation (9) provides a completely general example of the sort of process governed by equation (1). In particular, the stationary distribution need not be Poissonian.

Finally, if we want the process described by the transition rates of equation (9) to lead to a Poissonian distribution, with mean value n^s, then equation (5) implies the existence of a function $f_n > 0$ such that

$$\nu_n A = n^s f_n, \qquad \gamma_n = f_{n-1}. \tag{10}$$

The transition rates given by equation (8) represent a special case ($f_n = \gamma = \nu A/n^s$) of equation (10).

In the preceding four paragraphs, starting with equation (5), we have notationally suppressed the dependence of the transition rates on the control parameter λ. If we now explicitly assume that the functions ν_n and/or γ_n depend parametrically on λ, then we have a situation of the sort addressed in [1], to which equation (4) ought to apply.

By the convexity of the function e^x (see, e.g., [3]), equation (4) implies the inequality

$$\left\langle \int_0^\tau \epsilon'(n_t;\lambda_t)\dot{\lambda}_t \,\mathrm{d}t \right\rangle \geqslant 0. \tag{11}$$

In the remainder of this letter we will analyse this inequality, restricting ourselves to the situation in which the stationary distribution $p_n^s(\lambda)$ is Poissonian for all values of λ. Thus, $\nu_n(\lambda)$ and $\gamma_n(\lambda)$ satisfy equation (10) for some $n^s(\lambda)$ and $f_n(\lambda)$. Combining equations (3) and (7), we get

$$\epsilon(n;\lambda) = n^s(\lambda) - n \ln n^s(\lambda) + \ln n! \tag{12}$$

and

$$\epsilon' = \left(1 - \frac{n}{n^s}\right)\partial_\lambda n^s. \tag{13}$$

Inserting this into equation (11) and rearranging terms yields

$$\int_0^\tau \frac{\dot{n}^s}{n^s}\langle n_t\rangle \,\mathrm{d}t \leqslant \Delta n^s, \tag{14}$$

where $\dot{n}^s = \mathrm{d}n^s/\mathrm{d}t = \dot{\lambda}\partial_\lambda n^s$ and $\Delta n^s = n^s(\lambda_\tau) - n^s(\lambda_0)$.

Equation (14) resembles a thermodynamic inequality with $n^s(\lambda)$ playing the role of a *state function*. Equation (14) tells us that transitions between stationary states are constrained by the net change Δn^s in the value of this state function. As in the case of thermodynamic transitions, this inequality becomes an equality in the limit of infinitely slow (reversible) variation of the control parameter. In that limit, the system evolves through a sequence of stationary states, and we can replace $\langle n_t\rangle$ by its value in the stationary state, $n^s(\lambda_t)$. The two sides of equation (14) are then identically equal.

When λ is varied at a finite rate, equation (14) expresses the 'lag' alluded to in [1] (see the comments following equation (9) therein). For instance, if we change λ so as to make $n^s(\lambda_t)$ increase monotonically with time, then throughout the process the value of n_t will typically be trying to 'catch up' with the (ever-increasing) value of $n^s(\lambda_t)$. The ratio $\langle n_t\rangle/n^s$ will then be less than 1, and therefore the left side of equation (14) will be less than the right side, as predicted. A similar argument can just as easily be made if we change λ so as to cause n^s to decrease monotonically. More generally, equation (14) holds for the less obvious situation in which $n^s(\lambda_t)$ varies non-monotonically.

The inequality expressed by equation (14) pertains to the ensemble average value of n_t. However, as pointed out in [1], equation (4) implies that there must be individual realizations n_t^* for which $\int_0^\tau (\dot{n}^s/n^s) n_t^* \,\mathrm{d}t > \Delta n^s$. In the context of other fluctuation and nonequilibrium work theorems, realizations of this sort are said to 'violate' the second law of thermodynamics[2], and have been observed in recent experimental tests of those theorems [4]. Intuitively, we expect such realizations to become increasingly rare with system size. In particular, in the thermodynamic limit we expect that statistical fluctuations can be ignored altogether, and the behaviour of the system during any particular realization is accurately represented by the ensemble-average behaviour $\langle n_t \rangle$. In that case we can drop the angular brackets in equation (14):

$$\int_0^\tau \frac{\dot{n}^s}{n^s} n_t \,\mathrm{d}t \leqslant \Delta n^s. \tag{15}$$

If statistical fluctuations in n_t are indeed negligible (as we expect in the thermodynamic limit), then the evolution n_t can be described by a deterministic rate equation. This rate equation should have the property that equation (15) is satisfied for any schedule λ_t. Let us now verify that this is the case, for a particular, natural choice of how the transition rates scale with system size.

We will frame our discussion in the context of the previously mentioned example of the birth and death of particles inside a two-dimensional box, and we will treat the area of the box, A, as the scale parameter that defines system size. Since we are restricting ourselves to the case of Poissonian stationary distributions, the coefficients ν_n and γ_n are specified by a function f_n and a constant n^s, as per equation (10). (Both f_n and n^s can depend parametrically on λ.) Let us now assume that these scale as follows with A:

$$n^s = \rho^s A, \qquad f_n = \hat{f}\left(\frac{n}{A}\right), \tag{16}$$

where ρ^s does not depend on A, and $\hat{f}(\cdot)$ is a smooth and positive function of its argument. In terms of the particle density $\rho = n/A$, equation (10) becomes

$$\nu_n \to \hat{\nu}(\rho) = \rho^s \hat{f}(\rho), \qquad \gamma_n \to \hat{\gamma}(\rho) = \hat{f}(\rho), \tag{17}$$

where the arrows indicate the thermodynamic limit: $A, n \to \infty$, with ρ being fixed. With this scaling, the density of particles remains fixed as the area of the box becomes large, and both the birth rate density $\hat{\nu}$ and the death probability rate $\hat{\gamma}$ are functions of the density of particles rather than the size of the system. This is the sort of scaling ordinarily associated with extensive thermodynamic systems.

From equation (17) we have the following rate equation for the particle density, in the thermodynamic limit:

$$\dot{\rho} = \hat{\nu}(\rho) - \hat{\gamma}(\rho)\rho \tag{18}$$

$$= -(\rho - \rho^s)\hat{f}(\rho) \equiv V(\rho). \tag{19}$$

The term $\hat{\nu}$ accounts for the continual birth of new particles, while $\hat{\gamma}\rho$ accounts for the death of old ones.

Since $\hat{f}(\rho)$ is smooth and positive, the dynamics defined by equation (18) have a unique fixed point at $\rho = \rho^s$: $V(\rho) < 0$ whenever $\rho > \rho^s$, and $V(\rho) > 0$ whenever $\rho < \rho^s$. It immediately follows that

$$V(\rho) \ln(\rho^s/\rho) \geqslant 0. \tag{20}$$

[2] The term is used loosely, and does not imply that the second law, properly understood, has in any way been overthrown!

Now let ρ^s and $\hat{f}(\rho)$ depend explicitly on a control parameter λ. Consider the scenario to which equation (14) is meant to apply: we begin in the stationary state corresponding to an initial value of the control parameter, then we allow the system to evolve as this parameter is varied with time. As above, we let λ_t denote the externally imposed time dependence of the control parameter, and the initial and final times are taken to be $t = 0$ and $t = \tau$. Our analysis will be facilitated by imagining that the system continues to evolve after the 'final' time τ, with the control parameter held fixed: $\lambda_t = \lambda_\tau$ for $t \geqslant \tau$. Thus, the system both begins and ends in stationary states:

$$\rho_0 = \rho^s(\lambda_0), \qquad \rho_\infty \equiv \lim_{t\to\infty} \rho_t = \rho^s(\lambda_\tau). \tag{21}$$

Now define a function

$$U(\rho, \lambda) \equiv \ln \rho^s(\lambda) - \ln \rho. \tag{22}$$

Equation (20) is then

$$U(\rho, \lambda)V(\rho, \lambda) \geqslant 0, \tag{23}$$

which is valid for all values of ρ and λ. For ρ_t evolving under equation (18), consider the integral

$$I = \int_0^\infty U_t \dot{\rho}_t \, \mathrm{d}t = \int_0^\infty U_t V_t \, \mathrm{d}t \geqslant 0, \tag{24}$$

where U_t is short for $U(\rho_t, \lambda_t)$ and similarly $V_t = V(\rho_t, \lambda_t)$. Integrating the first expression for I by parts, we get

$$I = U_\infty \rho_\infty - U_0 \rho_0 - \int_0^\infty \left(\frac{\mathrm{d}}{\mathrm{d}t} U_t \right) \rho_t \, \mathrm{d}t \tag{25}$$

$$= \int_0^\infty \left(\frac{\dot{\rho}_t}{\rho_t} - \frac{\dot{\rho}^s}{\rho^s} \right) \rho_t \, \mathrm{d}t \tag{26}$$

$$= \Delta\rho^s - \int_0^\infty \frac{\dot{n}^s}{n^s} \rho_t \, \mathrm{d}t, \tag{27}$$

where $\dot{\rho}^s \equiv \dot{\lambda}\partial_\lambda \rho^s$ is the rate of change of ρ^s under the imposed schedule for varying the control parameter, and $\Delta\rho^s \equiv \rho^s(\lambda_\tau) - \rho^s(\lambda_0) = \rho_\infty - \rho_0$ is the net change in the particle density. The two boundary terms on the right side of the first line vanish ($U_0 = U_\infty = 0$, by equations (21) and (22)), and we have used the definition of U to rewrite the remaining integral in the form shown in the second line. To get to the third line, we have used $\rho^s = n^s/A$ and equation (21). Since $I \geqslant 0$ (equation (24)), we finally get

$$\int_0^\tau \frac{\dot{n}^s}{n^s} \rho_t \, \mathrm{d}t \leqslant \Delta\rho^s, \tag{28}$$

where we have used the fact that λ is held fixed (hence $\dot{n}^s = 0$) for $t > \tau$ to change the upper limit of integration. Multiplying both sides by A, we arrive at equation (15).

For sufficiently large systems, equation (15) can thus be derived in two different ways. In the first approach, this inequality emerges as a consequence of Seifert's fluctuation theorem (equation (4)). In the second approach, we derived equation (15) directly from a deterministic rate equation. In both cases, we made use of the assumption that the stationary distribution is Poissonian. For the derivation based on the fluctuation theorem, this assumption gave us an explicit expression for $\epsilon(n; \lambda)$ (equation (12)), while for the derivation using the rate equation, the Poissonian assumption implied a useful relation between the birth and death rates (equation (17)). Note that in the latter case the assumption can be relaxed considerably. For a process governed by the rate equation $\dot{\rho} = \hat{\nu} - \hat{\gamma}\rho \equiv V(\rho)$, let us assume only that the functions $\hat{\nu}(\rho; \lambda)$ and $\hat{\gamma}(\rho; \lambda)$ are such that this process has a unique fixed point $\rho^s(\lambda)$ for every value of the control parameter λ. This assumption is sufficient to give us equation (20), and therefore equation (15); we do not need to further assume that $\hat{\nu}$ and $\hat{\gamma}$ are related by equation (17).

The analysis here and in [1] is mathematical rather than physical. Equation (1) can be used to model abstract processes for which concepts such as thermal equilibrium have no particular relevance, as emphasized by the example of the birth and death of particles in a box. However, there certainly are situations in which equation (1) describes processes for which thermodynamic concepts are pertinent. In [1], Seifert mentions simple chemical reactions that can be modelled with this master equation, and points out that the stationary states in this case can be either states of thermal equilibrium or genuine nonequilibrium stationary states. Shibata [2] has also considered a general framework for studying transitions between nonequilibrium steady states in chemical reaction systems. In this framework, N independent chemical species interact with one another, and also with M species whose concentrations are controlled externally. The instantaneous state of the system is described by a vector $(n_1, \ldots, n_N)$ specifying the populations of the independent species, and evolving under a multivariate master equation. Equations (13) and (19) of [2] are analogues of equations (4) and (11) above[3]. It would be interesting to see whether the central inequality of [2] (equation (19) therein) could be derived from a set of coupled rate equations.

Shibata's work was motivated by Oono and Paniconi's *steady-state thermodynamics* (or *SST*) [5]. Whereas classical thermodynamics is organized around the concept of equilibrium states, SST is a phenomenological framework in which the state space also includes nonequilibrium steady states. In particular, Oono and Paniconi have suggested that transitions between nonequilibrium steady states are governed by an inequality similar to the Clausius inequality of classical thermodynamics. Shibata's analysis of chemical reaction systems supports this hypothesis [2], as does the work of Hatano and Sasa [6, 7], who have considered systems evolving under stochastic Markov and Langevin processes. Recently, the predictions of [7] have been confirmed by Trepagnier and coworkers [8] in experiments using optically dragged microspheres. Finally, Sasa and Tasaki [9] have further developed the basic philosophy of Oono and Paniconi's approach, by carefully considering specific examples of nonequilibrium steady states.

The basic set-up is the same throughout [1, 2, 6–9]: a system is made to evolve from one nonequilibrium steady state to another by the variation of one or more control parameters. (These parameters might be, for instance, the concentrations of chemical species [2], or the velocity of laser tweezers [8].) In all these situations the response of the system satisfies an *equality* of the form $\langle e^{-Y} \rangle = 1$; this in turn implies the *inequality* $\langle Y \rangle \geqslant 0$, by the convexity of the exponential function[4]. While the physical meaning of the quantity Y depends on the specific context, we always obtain $Y = 0$ when the parameters are varied infinitely slowly (see the discussion following equation (14), and also [2, 6–9]). This suggests that the magnitude of Y reflects the degree of irreversibility of the process. More intuitively, Y can be viewed as a measure of the net amount of *lag* that the system incurs during the process, as it tries to keep up with ever-changing values of the external parameters. When these parameters

[3] In Shibata's framework, if we take $N = 1$ and if we assume that each stoichiometric coefficient $c_{\pm l}$ is either 0 or 1, then we recover the situation considered in [1] and in the present letter, for the case of Poissonian stationary states.

[4] An alternative derivation of this inequality, which makes use of the concavity of the logarithm function, is provided in appendix C of [9].

are varied slowly, the system evolves through a sequence of stationary states (and $Y = 0$); when the parameters are varied rapidly, the system is typically unable to keep pace ($Y > 0$).

In classical thermodynamics, the inequalities that govern transitions between equilibrium states can be derived from the assertion that the combined entropy of the system and its thermal surroundings must never decrease. For the simple model systems studied theoretically and experimentally in [1, 2, 6–9] as well as the present letter, transitions between stationary states are also governed by inequalities, but these inequalities do not seem to be fundamentally related to some global quantity whose value never decreases. Rather, they are a mathematical expression of *lag* as discussed above. Whether these sorts of inequalities apply more generally—for instance, when the system does not evolve as a Markov process—remains an open and very interesting question in nonequilibrium statistical mechanics.

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