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LETTER TO THE EDITOR

Fluctuation theorem for birth–death or chemical master equations with time-dependent rates

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Abstract
For systems described by univariate birth–death or chemical master equations driven out of equilibrium by externally controlled time-dependent transition rates, a nonlinear fluctuation theorem is derived. For paradigmatic chemical reactions, this theorem acquires a particularly transparent form.

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In a major development in non-equilibrium statistical mechanics, fluctuation theorems have been derived which restrict the possible fluctuations of driven systems beyond the validity of linear-response regimes. First observed in computer simulations of sheared liquids [1], they have later been derived for chaotic and contracting deterministic dynamics [2, 3] as well as for driven diffusive systems [4, 5] and, most recently, for chemical non-equilibrium reactions [6]. Basically these theorems relate the probability of observing a certain entropy production rate to the probability of observing the corresponding entropy 'consumption' rate. They typically apply to stationary non-equilibrium states driven by imposing fluxes through time-independent boundary conditions.

A related but somewhat different approach has been applied to systems driven out of equilibrium by external time-dependent forces or potentials. Jarzynski's relation [7, 8],

$$\langle \mathrm{e}^{-\beta W_{\mathrm{d}}} \rangle = 1, \tag{1}$$

constrains a nonlinear average of the dissipated work W_{d} spent while driving a system from state 1 to state 2 in a surrounding heat bath of inverse temperature β. This relation has found wide-spread applications *inter alia* in the analysis of mechanical single molecule experiments; for a review, see [9]. Both developments ultimately arise from the behaviour of non-equilibrium systems under time reversal; for a coherent presentation, see [10].

The purpose of this letter is to derive and discuss the fluctuation theorem for master equations with transition rates that become time dependent through an external control parameter $\lambda(t)$. If for time-independent rates, i.e. fixed λ, detailed balance is fulfilled, we can derive a fluctuation theorem which restricts nonlinearly the possible fluctuations of the system driven by a time-dependent $\lambda(t)$. While the mere existence of such a relation can be expected

in analogy to the above cases, its general form derived below, in fact, becomes particularly transparent for simple chemical master equations.

We consider the master equation [11]

$$\partial_t p(n) = w^+(n-1,\lambda)p(n-1) + w^-(n+1,\lambda)p(n+1) - [w^+(n,\lambda) + w^-(n,\lambda)]p(n) \quad (2)$$

for the probability $p(n,t)$ to be in state n at time t where only jumps to neighbouring states are allowed. We assume that the rates $w^{\pm}(n,\lambda)$ depend on an external parameter λ later to be controlled according to some protocol $\lambda(t)$. For ease of notation, we will not make the λ-dependence explicit everywhere. In typical applications of birth–death processes or chemical reactions, the phase space is constrained to $n \geqslant 0$. This constraint implies that, for fixed λ, the stationary state $p^s(n)$ necessarily obeys a detailed balance condition

$$p^s(n)/p^s(n-1) = w^+(n-1)/w^-(n), \quad (3)$$

from which one derives easily

$$p^s(n) = p^s(0)\prod_{m=1}^{n} w^+(m-1)/w^-(m), \quad (4)$$

where $p^s(0)$ is determined by the normalization $\sum_{n=0} p^s(n) = 1$. It will be convenient to define 'energy levels' by

$$\epsilon_n(\lambda) \equiv -\ln p^s(n,\lambda). \quad (5)$$

Derivatives with respect to λ will be denoted by a prime such as in $\epsilon_n'(\lambda) \equiv \mathrm{d}\epsilon_n(\lambda)/\mathrm{d}\lambda$.

The fluctuation theorem now applies to stochastic trajectories $n(\tau)$ obtained by starting the system at time $t = 0$ in the stationary state with $\lambda(0)$ and driving it according to some protocol $\lambda(\tau)$ with $0 \leqslant \tau \leqslant t$ from $\lambda(0)$ to $\lambda(t)$. Below we will prove that these trajectories obey the fluctuation theorem

$$\left\langle \exp\left[-\int_0^t \epsilon'_{n(\tau)}\dot{\lambda}(\tau)\,\mathrm{d}\tau\right]\right\rangle = 1, \quad (6)$$

where the average $\langle\cdots\rangle$ is over many realizations of this protocol and $\dot{\lambda} \equiv \mathrm{d}\lambda/\mathrm{d}t$.

This general relation becomes more transparent for processes for which the stationary state is a Poissonian distribution

$$p^s(n) = \mathrm{e}^{-n^s}(n^s)^n/n! \quad (7)$$

with mean $n^s(\lambda)$. With the energy $\epsilon_n = n^s - n\ln n^s + \ln n!$, the fluctuation theorem (6) acquires the appealing form

$$\left\langle \exp\int_0^t \delta n(\tau)\frac{n^{s\prime}(\lambda)}{n^s(\lambda)}\dot{\lambda}(\tau)\,\mathrm{d}\tau\right\rangle = 1 \quad (8)$$

for the fluctuating deviation

$$\delta n(\tau) \equiv n(\tau) - n^s(\lambda(\tau)) \quad (9)$$

from the stationary mean $n^s(\lambda(\tau))$. Here, $n^{s\prime} \equiv \mathrm{d}n^s/\mathrm{d}\lambda$. Note that this fluctuation theorem (as the more general one (6)) holds for arbitrarily fast driving beyond any kind of linear-response regime. In general, one expects $n^{s\prime}(\lambda(\tau))\dot{\lambda}$ and δn to have different signs since, e.g., changing the rates such that $n^s(\lambda(\tau))$ increases will typically lead to $n(\tau)$ lagging behind $n^s(\lambda(\tau))$. The fluctuation theorem shows that there will be realizations for which at least along some parts of the trajectory the fluctuation are 'ahead' of the change of the stationary mean.

A Poissonian distribution is obtained for rates that obey

$$w^+(n-1,\lambda)/w^-(n,\lambda) = n^s(\lambda)/n \quad (10)$$

with some $n^s(\lambda)$. The simplest example is given by the chemical reaction

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} \tag{11}$$

with the rates $w^+(n) = k_1 n_\mathrm{A}$ and $w^-(n) = k_2 n$. Here, n denotes the number of X molecules and the mean is $n^s \equiv k_1 n_\mathrm{A}/k_2$. We assume that the number n_A of A molecules is constant. An example which allows for a genuine non-equilibrium stationary state is given by the scheme

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \mathrm{B} \tag{12}$$

with numbers $n_\mathrm{A}, n_\mathrm{B}$ fixed. The rates are $w^+(n-1) = k_1 n_\mathrm{A} + k_4 n_\mathrm{B}$ and $w^-(n) = (k_2 + k_3)n$. The stationary state is again a Poissonian with $n^s = (k_1 n_\mathrm{A} + k_4 n_\mathrm{B})/(k_2 + k_3)$. Note that full chemical equilibrium, however, is obtained only for $k_1 n_\mathrm{A}/k_2 = k_4 n_\mathrm{B}/k_3 \equiv n^\mathrm{eq}$. If in these two examples any of the rates $k_{1,2(,3,4)}$ and/or the numbers $n_{\mathrm{A}(,\mathrm{B})}$ depend on the external control parameter $\lambda(t)$, the fluctuation theorem (8) restricts the possible trajectories $n(\tau)$.

Characteristic for the fluctuation theorem in the Poissonian case is the linear appearance of δn in the exponent. Such a linear expression also holds more generally for all stationary distributions of the form

$$p^s(n) = c(q) q^n f(n) \tag{13}$$

as long as they derive from a detailed balance condition. The stationary mean value becomes

$$n^s = \sum_n n p^s(n) = -(q/c(q))\partial c/\partial q. \tag{14}$$

Using this expression in (6) and the definition (9), the fluctuation theorem becomes

$$\left\langle \exp \int_0^t \delta n(\tau) \frac{q'(\lambda)}{q(\lambda)} \dot{\lambda}(\tau)\, \mathrm{d}\tau \right\rangle = 1. \tag{15}$$

As an example for this case, consider the isomerization

$$\mathrm{Y} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} \qquad \text{with} \quad n_\mathrm{Y} = N - n, \tag{16}$$

where n is the number of X molecules, and N is the total number of molecules. This scheme is similar to (11) above with an additional conservation law. The rates $w^+(n) = k_1(N-n)$ and $w^-(n) = k_2 n$ no longer fulfil (10). The stationary distribution becomes a binominal one with

$$p^s(n) = (1+q)^{-N} q^n \binom{N}{n} \tag{17}$$

where $q \equiv k_1/k_2$ and the mean $n^s = qN/(1+q)$. If one (or both) of the rates $k_{1,2}$ are changed externally, the fluctuations will obey the theorem (15) with $q(\lambda) \equiv k_1(\lambda)/k_2(\lambda)$.

For the proof of the general form (6) of the theorem, we consider the more general master equation

$$\partial_t p(n) = \sum_m w(m,n)p(m) - w(n,m)p(n) \tag{18}$$

for the time-dependent probability $p(n,t)$ with transition rates $w(m,n,\lambda)$. We assume that for fixed λ the system is in a stationary state $p^s(n)$ obeying detailed balance

$$p^s(n)/p^s(m) = w(m,n)/w(n,m). \tag{19}$$

The proof now resembles Lebowitz and Spohn [5], Crooks [8] and Maes [10] adapted to our system. The probability prob$[n(\tau)]$ for a trajectory $n(\tau) = (n_0, n_1, \ldots, n_k)$ which starts in

state n_0, jumps at time τ_1 to state n_1, jumps at time τ_2 to state $n_2, \ldots,$ finally jumps at time τ_k to n_k where it stays till time t, is given by

$$\begin{aligned}\mathrm{prob}[n(\tau), \lambda(\tau)] = p^s(n_0, \lambda(0)) \times \exp\left[-\int_0^{\tau_1} \sum_{m \neq n_0} w(n_0, m, \lambda(\tau))\,\mathrm{d}\tau\right] \times w(n_0, n_1, \lambda(\tau_1)) \\ \times \exp\left[-\int_{\tau_1}^{\tau_2} \sum_{m \neq n_1} w(n_1, m, \lambda(\tau))\,\mathrm{d}\tau\right] w(n_1, n_2, \lambda(\tau_2)) \times \cdots \\ \times \exp\left[-\int_{\tau_k}^{t} \sum_{m \neq n_k} w(n_k, m, \lambda(\tau))\,\mathrm{d}\tau\right]. \qquad (20)\end{aligned}$$

The probability for the reversed trajectory $\tilde{n}(\tau) \equiv n(t-\tau)$ to occur under the reversed protocol $\tilde{\lambda}(\tau) \equiv \lambda(t-\tau)$ is

$$\begin{aligned}\mathrm{prob}[\tilde{n}(\tau), \tilde{\lambda}(\tau)] = p^s(\tilde{n}_0, \tilde{\lambda}(0)) \times \exp\left[-\int_0^{\tau_1} \sum_{m \neq \tilde{n}_0} w(\tilde{n}_0, m, \tilde{\lambda}(\tau))\,\mathrm{d}\tau\right] \times w(\tilde{n}_0, \tilde{n}_1, \tilde{\lambda}(\tau_1)) \\ \times \exp\left[-\int_{\tau_1}^{\tau_2} \sum_{m \neq \tilde{n}_1} w(\tilde{n}_1, m, \tilde{\lambda}(\tau))\,\mathrm{d}\tau\right] w(\tilde{n}_1, \tilde{n}_2, \tilde{\lambda}(\tau_2)) \times \cdots \\ \times \exp\left[-\int_{\tau_k}^{t} \sum_{m \neq \tilde{n}_k} w(\tilde{n}_k, m, \tilde{\lambda}(\tau))\,\mathrm{d}\tau\right]. \qquad (21)\end{aligned}$$

The crucial quantity is the ratio

$$\mathrm{e}^{-R[n(\tau)]} \equiv \frac{\mathrm{prob}[\tilde{n}(\tau), \tilde{\lambda}(\tau)]}{\mathrm{prob}[n(\tau), \lambda(\tau)]} = \exp\left[-\int_0^t \mathrm{d}\tau\, \epsilon'_{n(\tau)} \dot{\lambda}(\tau)\right], \qquad (22)$$

where the last equality follows by using (19) and (5) and the cancellation of the exponential integral terms. The proof of the fluctuation theorem now follows almost trivially from the following line of identities:

$$1 = \sum_{\tilde{n}(\tau)} \mathrm{prob}[\tilde{n}(\tau), \tilde{\lambda}(\tau)] = \sum_{\tilde{n}(\tau)} \mathrm{e}^{-R[n(\tau)]}\, \mathrm{prob}[n(\tau), \lambda(\tau)] \qquad (23)$$

$$1 = \sum_{n(\tau)} \mathrm{e}^{-R[n(\tau)]}\, \mathrm{prob}[n(\tau), \lambda(\tau)] = \left\langle \exp\left[-\int_0^t \mathrm{d}\tau\, \epsilon'_{n(\tau)} \dot{\lambda}(\tau)\right]\right\rangle. \qquad (24)$$

It is instructive to point out explicitly the relation of the present fluctuation theorem to Jarzynski's [7] which is easily done in the context of diffusive motion. For a particle moving diffusively along a continuous coordinate $x(\tau)$ in a potential $V(x, \lambda)$ that depends on an external control parameter $\lambda(\tau)$, the stationary distribution for fixed λ is given by

$$p^s(x, \lambda) = \exp[-\beta V(x, \lambda)]/Z(\lambda) \qquad (25)$$

with the partition function $Z(\lambda) \equiv \int_{-\infty}^{+\infty} \exp[-\beta V(x, \lambda)]\,\mathrm{d}x$. Substituting the correspondence $n(\tau) \sim x(\tau)$ and

$$\epsilon(n, \lambda) \equiv -\ln p^s(n, \lambda) \sim -\ln p^s(x, \lambda) = \beta V(x, \lambda) + \ln Z(\lambda) \qquad (26)$$

into (6) leads to

$$\left\langle \exp\left[-\beta \int_0^t V'[x(\tau), \lambda(\tau)]\dot{\lambda}(\tau)\,\mathrm{d}\tau\right] \frac{Z(\lambda(0))}{Z(\lambda(t))}\right\rangle = 1. \tag{27}$$

With the definitions of the free energy $F(\lambda) \equiv -(1/\beta)\ln Z(\lambda)$, the applied work $W \equiv \int_0^t \mathrm{d}\tau\, V'[x(\tau), \lambda(\tau)]\dot{\lambda}(\tau)$, and the dissipated work $W_\mathrm{d} \equiv W - [F(\lambda(t)) - F(\lambda(0))]$, one recovers Jarzynski's relation in the form (1). This observation shows that the present fluctuation theorem is akin to Jarzynski's relation. In our case, the 'boundary term' $Z(\lambda(0))/Z(\lambda(t))$ is 1 since definition (5) implies a 'partition function' identically equal to 1.

In summary, we have derived a fluctuation theorem for processes described by master equations with time-dependent rates if the stationary state for fixed rates obeys detailed balance. For a uni-variate birth–death process with one step increments the latter holds always true. If the stationary state is Poissonian or binominal the fluctuation theorem acquires an intriguing simple form. It would be highly desirable to verify the theorem in experiments by using one of the simple chemical reaction schemes discussed in this letter. Likewise, it will be interesting to see for which multivariate (chemical) master equations the general form (6) (which is always true given the detailed balance condition) can be reduced to more transparent expressions such as (8) or (15) derived here for particular classes of rates.

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References

[1] Evans D J, Cohen E G D and Morriss G P 1993 *Phys. Rev. Lett.* **71** 2401
[2] Gallavotti G and Cohen E G D 1995 *Phys. Rev. Lett.* **74** 2694
Gallavotti G and Cohen E G D 1995 *J. Stat. Phys.* **80** 931
[3] Evans D J and Searles D J 1994 *Phys. Rev.* E **50** 1645
[4] Kurchan J 1998 *J. Phys. A: Math. Gen.* **31** 3719
[5] Lebowitz J L and Spohn H 1999 *J. Stat. Phys.* **95** 333
[6] Gaspard P 2004 *J. Chem. Phys.* **120** 8898
[7] Jarzynski C 1997 *Phys. Rev. Lett.* **78** 2690
[8] Crooks G E 2000 *Phys. Rev.* E **61** 2361
[9] Ritort F 2003 *Sém. Poincaré* **2** 63
[10] Maes C 2003 *Sém. Poincaré* **2** 29
[11] Gardiner C W 2004 *Handbook of Stochastic Methods* 3rd edn (Berlin: Springer)