Transient fluctuation theorems for the currents and initial equilibrium ensembles

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Abstract. We prove a transient fluctuation theorem for the currents for continuous-time Markov jump processes with stationary rates, generalizing an asymptotic result by Andrieux and Gaspard (2007 *J. Stat. Phys.* **127** 107) to finite times. The result is based on a graph-theoretical decomposition in cycle currents and an additional set of tidal currents that characterize the transient relaxation regime. The tidal term can then be removed by a preferred choice of a suitable initial equilibrium ensemble, a result that provides the general theory for the fluctuation theorem without ensemble quantities recently addressed in Bulnes-Cuetara *et al* (2014 *Phys. Rev.* E **89** 052119). As an example we study the reaction network of a simple stochastic chemical engine, and finally we digress on general properties of fluctuation relations for more complex chemical reaction networks.

Keywords: current fluctuations

Contents

1. Introduction

Fluctuation theorems (FT's in the following) have dominated the last twenty years of research in nonequilibrium statistical mechanics. Proceeding from the landmark formulation by Bochkov and Kuzovlev [1], a host of variations on the theme have been elaborated depending on the theoretical setup, the observables of interest and the time specifics. This paper inscribes in the line of inquiry of FT's for stochastic dynamics [2–4], with special regard to the observables related to the cycle decomposition of Markov processes [5].

The relevance of cycle currents and their conjugate affinities to nonequilibrium thermodynamics was investigated by Hill and Schnakenberg [6,7]. The intuitive picture is that a cycling process performed by a system is capable of transducing and transforming energy across the environment. As an example, the Otto cycle in the stationary performance of a car engine transforms the fuel's chemical energy into the vehicle's kinetic energy. Hence, a full characterization of the cycle structure of the system allows for the characterization of the thermodynamic behavior of nonequilibrium steady distributions,

e.g. as regards their insurgence from a minimum entropy production principle [8]. In this setting, Andrieux and Gaspard have derived an asymptotic FT for the now-called Schnakenberg cycle currents [9] and applied it to chemical reactions [10]. Further insights on FT's and large deviations for cycle currents can be found in [11–13].

Under the assumption of local detailed balance [14] for quantum systems coupled with several heat and particle reservoirs, upon which cycle currents acquire a simple physical interpretation, recently Bulnes-Cuetara *et al* [15] have shown that a fluctuation relation for the currents also holds at finite times, provided that the processes are sampled from one specific initial equilibrium ensemble. We also refer to [16] for some earlier results, [17] for an analysis of heat versus work FT's, [18] for further elaboration and [19] for the derivation of a similar result in a deterministic setting.

In this paper we provide the general theory underlying transient FT's for time-homogeneous Markov jump processes. In particular, we generalize the result of Andrieux and Gaspard by including in the description certain tidal currents that complement the cycle currents. The result is based on an algebraic graph-theoretical analysis investigated by one of the authors in [20]. We can then generalize the initial-ensemble result, extending it to time-homogeneous Markov processes on graphs without the requirement of local detailed balance. As an example, we analyze a simple chemical reaction network.

The paper is structured as follows. In section 2 we anticipate the forms taken by the various fluctuation relations. In section 3 we initialize the example of a chemical reaction network. In section 4 we provide preliminary results from graph theory and in section 5 we give the general results from direct manipulations of the probability density of Markov jump processes, while for completeness in appendix the same results are derived in the Feynman–Kac formalism for the moment generating function. In section 6 we look back at the example under a new light, before coming to conclusions.

2. A recap on fluctuation relations

Before moving to the full treatment, it is useful to make the statements in the introduction slightly more precise. The simplest fluctuation relation takes the form

$$\frac{P(\Sigma_t)}{P(-\Sigma_t)} \asymp e^{\Sigma_t}. \tag{1}$$

Here, Σ_t is the value taken by a stochastic variable $\Sigma(t)$ called the reservoir entropy production of a process (sometimes denoted $\Delta_r S$, $-\Delta_e S$ etc), which accounts for the flux of entropy towards the environment. In our setting, the entropy production is a stochastic process with probability $\mathrm{Prob}\{\Sigma(t) \in [\Sigma_t, \Sigma_t + \mathrm{d}\Sigma_t]\} = P(\Sigma_t)\mathrm{d}\Sigma_t$ and $\asymp$ denotes the long time limit (in the following we will not distinguish between probabilities an probability densities). Then equation (1) states that at sufficiently large times the probability of measuring a positive entropy production is exponentially favored with respect to the probability of measuring a negative entropy production. Since the entropy production is odd under time reversal, the fluctuation relation provides a formulation of the second law of thermodynamics and a characterization of the arrow of time.

To the entropy production of a system several mechanisms may contribute. Then, the fluctuation relation can be specialized as follows

$$\frac{P(\boldsymbol{J}_t)}{P(-\boldsymbol{J}_t)} \asymp e^{\boldsymbol{F}\cdot\boldsymbol{J}_t}, \tag{2}$$

where $\boldsymbol{J}_t$ are the values taken by some physical observables that (almost surely) grow linearly in time, e.g. time-integrated heat fluxes, charge or matter currents, or any thermodynamic flux. The quantities $\boldsymbol{F}$ are non-fluctuating intensive variables conjugate to the $\boldsymbol{J}_t$. If one adopts an abstract characterization of thermodynamic processes as generic Markov processes on a discrete state space, then $\boldsymbol{J}_t$ count the net number of times the process has performed certain elementary cyclic paths.

Asymptotic relations can be extended to finite times by conditioning both the forward and the backward processes to some fixed initial state [21],

$$\frac{P(\boldsymbol{J}_t|x_0)}{P(-\boldsymbol{J}_t|x_t)} = e^{\boldsymbol{F}\cdot\boldsymbol{J}_t+\Phi(x_0)-\Phi(x_t)} \tag{3}$$

where Φ is a suitable state function. Unfortunately, from an experimental viewpoint conditioning a process to one exact initial state is problematic. However, notice that if one could sample both the forward and the backward processes with probability $e^{-\Phi}/Z$ (Z the normalization factor) one obtains an exact FT for the currents valid at all times

$$\frac{P(\boldsymbol{J}_t)}{P(-\boldsymbol{J}_t)} = e^{\boldsymbol{F}\cdot\boldsymbol{J}_t}, \tag{4}$$

where we marginalized out x_0, x_t. Yet, again, preparing the system in a given ensemble $e^{-\Phi}/Z$ might also be awkward, unless it is of a very special kind. Indeed, for certain classes of systems it has been found that this ensemble is the equilibrium ensemble of the system where all forces producing cycle currents are momentarily disconnected. Physically, this corresponds to the situation where first one prepares the system by letting it relax to equilibrium and then all of a sudden turns on the external forces.

3. Example: network of chemical reactions

In this section we consider a simple reaction network. We derive a meaningful expression for the total entropy produced after an arbitrary sequence of reactions, writing it in terms of macroscopic physical currents of certain external species called *chemostats* and in terms of an equilibrium initial ensemble. The reader eager to learn the full theory might want to skip this section. For sake of simplicity we set $k_B T = 1$.

Let X_1 and X_2 be two chemical species of observational interest that partake to three reversible chemical reactions, one that produces or consumes X_1, one that produces or consumes X_2 and one that converts X_1 into X_2 and vice versa:

$$\begin{aligned}
Y_1 &\underset{-1}{\overset{+1}{\rightleftharpoons}} X_1 \\
X_2 &\underset{-2}{\overset{+2}{\rightleftharpoons}} Y_2 \\
X_1 + Y_3 &\underset{-3}{\overset{+3}{\rightleftharpoons}} X_2 + Y_4.
\end{aligned} \tag{5}$$

Here $Y_1, \ldots, Y_4$ are (assemblies of) chemostats, that is, substrate species that are independently administered by the environment and whose concentrations do not vary in time. A complete treatment of the thermodynamics of chemostatted networks has been provided by the authors in [22]. This reaction scheme is a simple model of a molecular engine, where reactions 1 and 2 provide the working substances X_1 and X_2 and reaction 3 performs chemical work by transforming molecules of Y_3 into molecules of Y_4, while completing a thermodynamic cycle within the system. The observable of interest is the rate J_3 at which this latter reaction proceeds. The reaction network can be represented by a graph whose edges are the *complexes* of the species of observational interest, as follows

$$
\begin{array}{ccc}
X_1 & \xrightarrow{\ \ 3\ \ } & X_2 \\
& & \\
{\scriptstyle 1} \searrow & & \swarrow {\scriptstyle 2} \\
& \emptyset &
\end{array}
\quad .
\tag{6}
$$

Under several assumptions (Boltzmann's Stosszahlansatz, well-stirred solution etc), the number of variable molecules undergoes a continuous-time Markov jump process satisfying the random-time change equation

$$
\mathbf{X}(t) = \mathbf{X}(0) + \sum_{r=\pm 1}^{\pm 3} J_r(t)\, \boldsymbol{\nu}_r,
\tag{7}
$$

where we collected the two variable species in a vector $\mathbf{X}$ and $\boldsymbol{\nu}_r$ is the vector of stoichiometric coefficients of the r-th reaction,

$$
\boldsymbol{\nu}_{\pm 1} = \pm \begin{pmatrix} +1 \\ 0 \end{pmatrix}, \quad \boldsymbol{\nu}_{\pm 2} = \pm \begin{pmatrix} 0 \\ -1 \end{pmatrix}, \quad \boldsymbol{\nu}_{\pm 3} = \pm \begin{pmatrix} -1 \\ +1 \end{pmatrix}.
\tag{8}
$$

Each time a reaction proceeds the populations increase by an amount $\boldsymbol{\nu}_r$. Hence, the state space where this random process takes place is the lattice (that we call the *chemical lattice*) generated by the three vectors $\boldsymbol{\nu}_{+1}, \boldsymbol{\nu}_{+2}, \boldsymbol{\nu}_{+3}$, limited to the sector of positive populations, as depicted in figure 2(a). Notice that the generating vectors are not independent, as

$$
\boldsymbol{\nu}_{+1} + \boldsymbol{\nu}_{+2} + \boldsymbol{\nu}_{+3} = 0.
\tag{9}
$$

The quantity $J_r(t)$, counting the number of times reaction r occurs up to time t, is distributed with a unit-rate Poisson distribution [23] according to

$$
J_r(t) \sim \mathrm{Pois}\left(\int_0^t w_{\mathbf{X}(s)+\boldsymbol{\nu}_r, \mathbf{X}(s)} \, \mathrm{d}s \right).
\tag{10}
$$

The $\{w_{\mathbf{X}+\boldsymbol{\nu}_r, \mathbf{X}}\}_{\mathbf{X}}$'s are the rates at which reaction r proceeds. By the law of mass-action these rates are proportional to the products of the abundances of the reactants,

$$
\begin{array}{lll}
w_{\mathbf{X}+\boldsymbol{\nu}_1, \mathbf{X}} = Y_1, & w_{\mathbf{X}+\boldsymbol{\nu}_2, \mathbf{X}} = X_2, & w_{\mathbf{X}+\boldsymbol{\nu}_3, \mathbf{X}} = Y_3 X_1, \\
w_{\mathbf{X}-\boldsymbol{\nu}_1, \mathbf{X}} = X_1, & w_{\mathbf{X}-\boldsymbol{\nu}_2, \mathbf{X}} = Y_2, & w_{\mathbf{X}-\boldsymbol{\nu}_3, \mathbf{X}} = Y_4 X_2,
\end{array}
\tag{11}
$$

where for sake of simplicity we set all proportionality constants to unity.

In the following we will drop all explicit time dependencies. We define the currents as the stochastic variables that count the net number of transitions between site $\mathbf{X}$ and a neighboring site,

$$
j_{\mathbf{X}+\boldsymbol{\nu}_r, \mathbf{X}} := \#\,(\text{transitions from } \mathbf{X} \text{ to } \mathbf{X} + \boldsymbol{\nu}_r) - \#\,(\text{transitions from } \mathbf{X} + \boldsymbol{\nu}_r \text{ to } \mathbf{X}). \tag{12}
$$

Notice that $\sum_{\mathbf{X}} j_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} = J_r$. Each transition decreases the Gibbs free energy of the system by an amount

$$f_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} := \ln \frac{w_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}}}{w_{\mathbf{X},\mathbf{X}+\boldsymbol{\nu}_r}}, \tag{13}$$

i.e. $f_{\mathbf{X}+\boldsymbol{\nu}_1,\mathbf{X}} = \ln Y_1/(X_1+1)$, $f_{\mathbf{X}+\boldsymbol{\nu}_2,\mathbf{X}} = \ln X_2/Y_2$, $f_{\mathbf{X}+\boldsymbol{\nu}_3,\mathbf{X}} = \ln(Y_3 X_1)/(Y_4(X_2+1))$. Notice that both the currents and the Gibbs free energy differences are antisymmetric by inversion of the orientation of the transition,

$$j_{\mathbf{X},\mathbf{X}+\boldsymbol{\nu}_r} = - j_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} \tag{14a}$$

$$f_{\mathbf{X},\mathbf{X}+\boldsymbol{\nu}_r} = - f_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}}. \tag{14b}$$

A crucial observation is that the Gibbs free energy differences satisfy Kirchoff's Loop Law (KLL)

$$f_{\mathbf{X},\mathbf{X}-\boldsymbol{\nu}_2} + f_{\mathbf{X}-\boldsymbol{\nu}_2,\mathbf{X}+\boldsymbol{\nu}_3} + f_{\mathbf{X}+\boldsymbol{\nu}_3,\mathbf{X}} = \ln \frac{Y_1 Y_3}{Y_2 Y_4} =: F \tag{15}$$

where the *affinity F* is the total Gibbs free energy decrease around a cyclic process that starts at $\mathbf{X}$ and moves by amount $\boldsymbol{\nu}_3$, then $\boldsymbol{\nu}_1$, then $\boldsymbol{\nu}_2$ to return to $\mathbf{X}$ by virtue of equation (9). Quite importantly, it is peculiar to chemical networks with mass-action law that the affinity does not depend on the state $\mathbf{X}$ where the cycle is based, which will allow a significant simplification.

Finally we introduce the total entropy production

$$\Sigma := \sum_{\mathbf{X}} \sum_{r>0} j_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} \, f_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}}. \tag{16}$$

Notice that we restricted the sum to the positive verse of the reactions to avoid double-counting. This expression simplifies in view of KLL,

$$\Sigma = \sum_{\mathbf{X}} \left[j_{\mathbf{X}+\boldsymbol{\nu}_3,\mathbf{X}} \left(F - f_{\mathbf{X},\mathbf{X}-\boldsymbol{\nu}_2} - f_{\mathbf{X}-\boldsymbol{\nu}_2,\mathbf{X}+\boldsymbol{\nu}_3}\right) + \sum_{r=1,2} j_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} \, f_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} \right]$$

$$= F J_3 + \sum_{\mathbf{X}} \left[\left(j_{\mathbf{X}+\boldsymbol{\nu}_1,\mathbf{X}} + j_{\mathbf{X}-\boldsymbol{\nu}_3,\mathbf{X}}\right) f_{\mathbf{X}+\boldsymbol{\nu}_1,\mathbf{X}} + \left(j_{\mathbf{X}-\boldsymbol{\nu}_2,\mathbf{X}} + j_{\mathbf{X}+\boldsymbol{\nu}_3,\mathbf{X}}\right) f_{\mathbf{X}-\boldsymbol{\nu}_2,\mathbf{X}}\right]$$

$$= F J_3 + \sum_{X_1} J_{X_1} \ln \frac{Y_1}{X_1+1} + \sum_{X_2} J_{X_2} \ln \frac{Y_2}{X_2+1} \tag{17}$$

where we introduced

$$J_{X_1} := \sum_{X_2} \left(j_{\mathbf{X}+\boldsymbol{\nu}_1,\mathbf{X}} + j_{\mathbf{X}-\boldsymbol{\nu}_3,\mathbf{X}}\right) \tag{18a}$$

$$J_{X_2} := \sum_{X_1} \left(j_{\mathbf{X}-\boldsymbol{\nu}_2,\mathbf{X}} + j_{\mathbf{X}+\boldsymbol{\nu}_3,\mathbf{X}}\right) \tag{18b}$$

respectively with the meaning of total increase of species 1 at fixed X_2 and total increase of species 2 at fixed X_1. We now introduce the second crucial ingredient, namely Kirchhoff's Current Law (KCL). Since the trajectory is continuous, the total current out of a given state visited by the trajectory must be zero, but for states $\mathbf{X}_0 = \mathbf{X}(0)$ and $\mathbf{X}_t = \mathbf{X}(t)$ that are respectively a source and a sink of a unit current. KCL can then be employed to obtain

$$J_{X_1} = \theta_{[X_1(0),+\infty)}(X_1) - \theta_{[X_1(t),+\infty)}(X_1) \tag{19a}$$

$$J_{X_2} = \theta_{[X_2(0),+\infty)}(X_2) - \theta_{[X_2(t),+\infty)}(X_2) \tag{19b}$$
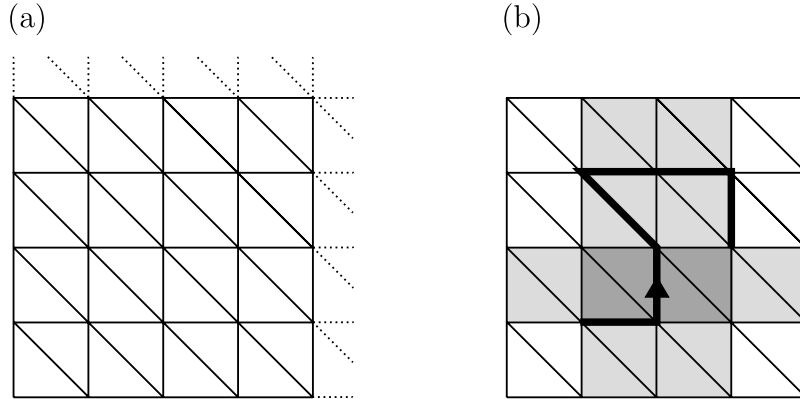
(a) (b)

Figure 1. (*a*) The chemical lattice for the chemical reaction network equation (5). Horizontal edges correspond to reaction 1, vertical edges correspond to reaction 2 and diagonal edges correspond to reaction 3. (*b*) A path. The shaded horizontal region corresponds to $J_{X_2} = +1$, the shaded vertical region corresponds to $J_{X_1} = +1$, white regions correspond to vanishing currents.

where θ is the Heaviside step function on a discrete set[1] (see figure 1(*b*) for clarification). Employing KCL we obtain for the entropy production

$$\Sigma = FJ_3 + \ln \prod_{\mathbf{X}=\mathbf{X}_0+\mathbf{1}}^{\mathbf{X}_t} \frac{Y_1}{X_1} \frac{Y_2}{X_2}. \tag{20}$$

To give an interpretation of the latter term, we resort to the chemical master equation that rules the evolution of the probability of being at $\mathbf{X}$ at time t

$$\frac{\mathrm{d}}{\mathrm{d}t}P_t(\mathbf{X}) = \sum_{\mathbf{X},r} \left[w_{\mathbf{X},\mathbf{X}+\boldsymbol{\nu_r}} P_t(\mathbf{X}+\boldsymbol{\nu}_r) - w_{\mathbf{X}+\boldsymbol{\nu}_r,\mathbf{X}} P_t(\mathbf{X}) \right] =: \mathcal{L}(\mathbf{Y})P_t(\mathbf{X}) \tag{21}$$

where on the right-hand side we introduced the generator $\mathcal{L}(\mathbf{Y})$, which of course depends on the chemostats' concentrations. The claim in section 2 is that the second term in equation (20) should be obtained as the equilibrium distribution of the system where the third reaction is inhibited, which is achieved by setting $Y_3 = Y_4 = 0$. We then look for the solution of

$$\mathcal{L}(Y_1, Y_2, 0, 0)P^{\mathrm{eq}} = 0, \tag{22}$$

which is easily seen to be a Poissonian

$$P^{\mathrm{eq}}(\mathbf{X}) = \mathrm{e}^{-Y_1-Y_2} \frac{Y_1^{X_1}}{X_1!} \frac{Y_2^{X_2}}{X_2!} \tag{23}$$

satisfying detailed balance

$$w_{\mathbf{X}+\boldsymbol{\nu_r},\mathbf{X}} P^{\mathrm{eq}}(\mathbf{X}) = w_{\mathbf{X},\mathbf{X}+\boldsymbol{\nu_r}} P^{\mathrm{eq}}(\mathbf{X}+\boldsymbol{\nu}_r). \tag{24}$$

Finally, we obtain the desired result

$$\Sigma = J_3 F + \ln \frac{P^{\mathrm{eq}}(\mathbf{X}_t)}{P^{\mathrm{eq}}(\mathbf{X}_0)}. \tag{25}$$

[1] Defined as $\theta_A(b) = \sum_{a \in A} \delta_{a,b}$, for $A \subseteq \mathbb{Z}$, δ the Kroenecker delta.

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Fluctuation theorems for the chemical master equation in the form of equations (1)–(4) can be derived by standard techniques, hence supporting the result that exact FT's for the currents hold when the initial state is sampled from the equilibrium ensemble obtained by disconnecting the mechanisms that drive the system to nonequilibrium. In the next sections we will provide the full theory and in section 3 we come back to this example to discuss how the general theory allows to extend these observations to more general chemical networks.

4. Tools: cycle and cocycles in network thermodynamics

We will be involved with continuous-time Markov jump process on a finite state space. The state space of the system can be viewed as an oriented graph, the trajectory followed by the jump process as a sequence of oriented edges connecting vertices. All thermodynamic observables associated to the trajectory (current, free energy increase etc) are weights assigned to every edge of the graph, antisymmetric by inversion of the orientation of the edge. In this section we briefly refresh the ensuing algebraic graph-theoretical picture; a broader treatment can be found in [20].

4.1. Cycle/cocycle decomposition of a graph

The state space of the system is a connected oriented graph $G = (X, E)$ (without loops, allowing multiple edges) with oriented edges $e \in E$ connecting distinct vertices $x \in X$. Let $|E|$ be the number of edges and $|X|$ that of vertices. The orientation is arbitrary, by $-e$ we represent the inverse orientation of an edge. The graph is completely characterized by the $|E| \times |X|$ matrix ∂ prescribing the incidence relations between edges and vertices:

$$\partial_{x,e} = \begin{cases} +1, & \text{if } \xrightarrow{e} x \\ -1, & \text{if } \xleftarrow{e} x \ . \\ 0, & \text{otherwise} \end{cases} \tag{26}$$

We will make constant reference to the following example:

$$\begin{array}{c} x_1 \xrightarrow{e_1} x_2 \\ e_4 \Big\uparrow \ \diagup e_5 \ \Big\downarrow e_2 \\ x_4 \xleftarrow{e_3} x_3 \end{array} \ , \qquad \partial = \begin{pmatrix} -1 & 0 & 0 & +1 & 0 \\ +1 & -1 & 0 & 0 & +1 \\ 0 & +1 & -1 & 0 & 0 \\ 0 & 0 & +1 & -1 & -1 \end{pmatrix}. \tag{27}$$

Real combinations of edges are denoted by a vector in Dirac notation $| \cdot \rangle \in \mathbb{R}^E$. We also introduce the transpose vector $\langle \cdot |$ and the scalar product $\langle \cdot | \cdot \rangle$.

Cycles are, as intuitive, successions of oriented edges (a tail for each tip, at every vertex). Cycles are algebraically characterized as integer right null vectors of the incidence matrix,

$$\partial | c \rangle = 0. \tag{28}$$

Therefore they form a vector space. A preferred basis of cycles can be constructed by a standard procedure that was employed by Schnakenberg for the analysis of network

thermodynamics [7]. We briefly refresh it. A *spanning tree* T is a maximal set of (unoriented) edges that contains no cycles. We choose one such arbitrary spanning tree,

$$\begin{array}{c} \overset{e_1}{\underset{e_3}{\left. \begin{array}{c|c} & \\ e_4 & \diagup e_5 \end{array} \right| e_2}} \end{array} \quad . \tag{29}$$

The choice of a spanning tree is arbitrary from a mathematical point, while physically it corresponds to the choice of a different set of relevant observables. An important property of spanning trees is that there exists a unique oriented path $\gamma_{xx'}$ connecting any vertex x' to any other vertex x of the graph belonging to the spanning tree.

Edges e_α not belonging to the spanning tree are called the *chords* (dotted, above). Their number is given by Euler's formula $|C| = |E| - |X| + 1$. Adding chord e_α to the spanning tree identifies a unique cycle c_α with orientation along the verse of the chord:

$$c_4 = \begin{array}{c} \overrightarrow{} \\ \uparrow \quad \downarrow \\ \overleftarrow{} \end{array} \bigg| \quad , \qquad c_5 = \begin{array}{c} \diagup \\ \overleftarrow{} \end{array} \bigg| \quad . \tag{30}$$

It can be proven that the set of cycles so generated is a basis for the null space of the incidence matrix [24].

Orthogonal to the set of cycles is the set of *cocycles* (or cuts), generated by the corresponding *cochords*. A cochord is an edge e_μ^* belonging to the spanning tree. Their number is $|E| - |C| = |V| - 1$. Removing cochord e_μ^* from a spanning tree disconnects the graph into two basins. The set of edges that connect one basin to the other, oriented in the verse of the generating cochord, is a cocycle:

$$c_1^* = \begin{array}{c} \bullet \longrightarrow \circ \\ \downarrow \qquad \vdots \\ \circ \cdots\cdots \circ \end{array} \quad , \quad c_2^* = \begin{array}{c} \bullet \cdots\cdots \bullet \\ \downarrow \diagup \downarrow \\ \circ \cdots\cdots \circ \end{array} \quad , \quad c_3^* = \begin{array}{c} \bullet \cdots\cdots \bullet \\ \downarrow \diagup \vdots \\ \circ \longleftarrow \bullet \end{array} \quad . \tag{31}$$

In this example, vertices in the source basins are disks, in the target basins are circles, edges of the spanning tree that connect them are dotted.

We can now give a vector representation of chords, cycles, corchords and cocycles as linear combinations of edges of the graph. We denote them respectively $|e_\alpha\rangle, |c_\alpha\rangle, |e_\mu^*\rangle, |c_\mu^*\rangle$. In our example, we have

$$|c_1^*\rangle = \begin{pmatrix} +1 \\ 0 \\ 0 \\ -1 \\ 0 \end{pmatrix}, \quad |c_2^*\rangle = \begin{pmatrix} 0 \\ +1 \\ 0 \\ -1 \\ -1 \end{pmatrix}, \quad |c_3^*\rangle = \begin{pmatrix} 0 \\ 0 \\ +1 \\ -1 \\ -1 \end{pmatrix},$$

$$|c_4\rangle = \begin{pmatrix} +1 \\ +1 \\ +1 \\ +1 \\ 0 \end{pmatrix}, \quad |c_5\rangle = \begin{pmatrix} 0 \\ +1 \\ +1 \\ 0 \\ +1 \end{pmatrix}. \tag{32}$$

A crucial result proven in [20] is that the identity over the edge space can be decomposed as

$$I = \sum_\alpha |c_\alpha\rangle\langle e_\alpha| + \sum_\mu |e_\mu^*\rangle\langle c_\mu^*|. \tag{33}$$

where $|\cdot\rangle\langle\cdot|$ denotes the outer product of two vectors, yielding an $|E|\times|E|$ matrix. We will repeatedly employ this identity in the following sections. As a side comment, $\Pi := \sum_\alpha |c_\alpha\rangle\langle e_\alpha|$ and $\Pi^* := \sum_\mu |e_\mu^*\rangle\langle c_\mu^*|$ are oblique complementary projectors, $\Pi^2 = \Pi$, $\Pi^{*2} = \Pi^*$, $\Pi\Pi^* = \Pi^*\Pi = 0$, which gives rise to an elegant formulation of network thermodynamics based on projectors.

4.2. Tidal and cycle currents and their dual variables

In network thermodynamics one assigns two observables to each oriented edge, the current j_e and its conjugate force f_e. They are required to be antisymmetric by edge inversion, $j_{-e} = -j_e$, $f_{-e} = -f_e$. We collect their values in two vectors $|j\rangle$ and $|f\rangle$. The *entropy production* is the bilinear form

$$\Sigma := \langle j\,|\,f\rangle = \sum_e f_e j_e. \tag{34}$$

We immediately apply the identity decomposition equation (33) to the currents to obtain

$$|j\rangle = \sum_\alpha |c_\alpha\rangle\langle e_\alpha\,|\,j\rangle + \sum_\mu |e_\mu^*\rangle\langle c_\mu^*\,|\,j\rangle. \tag{35}$$

$$=: \sum_\alpha J_\alpha |c_\alpha\rangle + \sum_\mu J_\mu |e_\mu^*\rangle. \tag{36}$$

The second line defines the *cycle currents* J_α and the *tidal currents* J_μ. The former are well-known from Schnakenberg's analysis. They quantify the cycling of a process. The latter give the total flux from a set of source vertices to a set of target vertices, as visualized in equation (31). This decomposition is somewhat analogous to the Helmholtz decomposition of a vector field into a curl and a gradient (modulo a harmonic term).

Now, plugging equation (35) into the entropy production we obtain

$$\Sigma = \sum_\alpha J_\alpha\langle f\,|\,c_\alpha\rangle + \sum_\mu J_\mu\langle f\,|\,e_\mu^*\rangle \tag{37}$$

$$= \sum_\alpha J_\alpha F_\alpha + \sum_\mu J_\mu F_\mu \tag{38}$$

where we introduced the *affinities* F_α as observables conjugate to the cycle currents and the *potential drops* F_μ as observables conjugate to the tidal currents.

5. Results: fluctuation theorems for the currents

5.1. Transient FT for joint tidal and cycle currents

We consider a continuous-time Markov jump process $(\boldsymbol{x}, \boldsymbol{\tau})$, starting at state x_0 and performing n transitions in time t to state x_t. The rate of a jump from state x to x' is $w_{x'x}$. The process visits state x_i for an interval τ_i before jumping to state x_{i+1}, up to time $t = \tau_0 + \ldots + \tau_n$. The joint probability density of the n states visited by the trajectory is given by

$$P_{n,t}(\boldsymbol{x}, \boldsymbol{\tau}) = \delta\Big(t - \sum_{i=0}^n \tau_i\Big)\mathrm{e}^{-w_{x_n}\tau_n}\prod_{i=0}^{n-1} w_{x_{i+1},x_i}\mathrm{e}^{-w_{x_i}\tau_i}, \tag{39}$$

where $\delta(\cdot)$ is the Dirac delta and $w_x = \sum_{x'} w_{x'x}$. The marginal probability density for the states is given by

$$P_{n,t}(\boldsymbol{x}) = \int \ldots \int_0^\infty \mathrm{d}\boldsymbol{\tau}\, P_{n,t}(\boldsymbol{x}, \boldsymbol{\tau}) = Q_{n,t}(\boldsymbol{x}) \prod_{i=0}^{n-1} w_{x_{i+1}, x_i} \tag{40}$$

where

$$Q_{n,t}(\boldsymbol{x}) := \int \ldots \int_0^\infty \mathrm{d}\boldsymbol{\tau}\, \delta\Big(t - \sum_{i=0}^n \tau_i\Big) \prod_{i=0}^n \mathrm{e}^{-w_{x_n}\tau_n}. \tag{41}$$

The actual dependence on t is difficult to compute and not relevant for what follows.

We define the time-reversed process as that process $(\boldsymbol{x}^\dagger, \boldsymbol{\tau}^\dagger)$ where the succession of states and time intervals are inverted, $x_i^\dagger = x_{n-i}$ and $\tau_i^\dagger = \tau_{n-i}$. Notice that for the time-reversed process we have

$$Q_{n,t}(\boldsymbol{x}) = Q_{n,t}(\boldsymbol{x}^\dagger). \tag{42}$$

As a consequence, the following fluctuation relation between forward and backward successions of states holds

$$P_{n,t}(\boldsymbol{x}) = P_{n,t}(\boldsymbol{x}^\dagger) \prod_i \frac{w_{x_{i+1}, x_i}}{w_{x_i, x_{i+1}}}. \tag{43}$$

The above expression can be further marginalized. We define the (time-integrated) edge current along $x \leftarrow x'$ as a stochastic variable counting the net number of transitions from x' to x,

$$j_{xx'}(\boldsymbol{x}) := \sum_i \left(\delta_{x_{i+1}, x}\, \delta_{x_i, x'} - \delta_{x_{i+1}, x'}\, \delta_{x_i, x} \right). \tag{44}$$

It satisfies the antisymmetry relations $j_{x'x}(\boldsymbol{x}) = -j_{xx'}(\boldsymbol{x})$ and $j_{xx'}(\boldsymbol{x}) = -j_{xx'}(\boldsymbol{x}^\dagger)$. Equation (43) can then be written in terms of the currents as follows

$$P_{n,t}(\boldsymbol{x}) = \mathrm{e}^{\langle f\,|\,j(\boldsymbol{x})\rangle}\, P_{n,t}(\boldsymbol{x}^\dagger) \tag{45}$$

where the entries of $|\,f\,\rangle$ are the thermodynamic forces $f_{xx'} := \ln(w_{xx'}/w_{x'x})$. We can then finally marginalize for the currents taking values $|\,j\,\rangle$. It must be here noted that the expressions of the current and of the probability measure are conditioned to a fixed total number of transitions n. Although, experimentally one usually has access to the total number of transitions between two states irrespective of the total number of transitions that the trajectory performs. The probability of observational values of the currents $|\,j\,\rangle$ up to time t is given by

$$P_t(|\,j\,\rangle) = \sum_{n=1}^\infty P_{n,t}(|\,j\,\rangle) P_t(n) \tag{46}$$

where $P_t(n)$ is the probability that a total number of transitions n occurs in time t. Since the time-reversed process performs the same number of jumps, we do not need to compute it and we obtain

$$P_t(|\,j\,\rangle) = \mathrm{e}^{\langle f\,|\,j\,\rangle} P_t(-|\,j\,\rangle). \tag{47}$$

We can now apply the cycle/cocycle decomposition exposed in section 4. To do this, we should first identify a spanning tree of the graph such that the chord currents are currents

of physical relevance to the specific model at hand. We can then define stochastic cycle and tidal currents

$$J_\alpha(\boldsymbol{x}) := \langle e_\alpha | j(\boldsymbol{x}) \rangle \tag{48a}$$

$$J_\mu(\boldsymbol{x}) := \langle c_\mu | j(\boldsymbol{x}) \rangle. \tag{48b}$$

The first counts the number of times the α-th cycle is enclosed, the second counts the number of times the process jumps from the source to the target basin of the μ-th cut. Since cycle and tidal currents are one-to-one to the edge currents, by a simple coordinate transformation (which can be proven, but here is irrelevant, to have unit Jacobian) we can move to the probability of the former, which by equation (38) obeys the joint FT

$$\frac{P_t(\boldsymbol{J}, \boldsymbol{J}^*)}{P_t(-\boldsymbol{J}, -\boldsymbol{J}^*)} = \exp\left(\sum_\alpha F_\alpha J_\alpha + \sum_\mu F_\mu J_\mu \right), \tag{49}$$

where we collected the cycle and cocycle currents into $\boldsymbol{J} = \{J_\alpha\}_\alpha$ and $\boldsymbol{J}^* = \{J_\mu\}_\mu$. This equation generalizes the result of Andrieux and Gaspard to finite times. An important observation is that we do not need to condition this FT to an initial and a final state, since conditioning is implicit. In fact, knowledge of the tidal currents implies knowledge of the initial and final states.

5.2. Asymptotic FT for the cycle currents

We now focus on the tidal term. An important fact is that a Markov jump process on a graph is continuous, i.e. it can be drawn without lifting the pencil. As an important implication, tidal currents can only take values in $\{-1, 0, 1\}$, while cycle currents take values in $\mathbb{Z}$. Intuitively, while a process can wind arbitrarily many times around a cycle in a preferential direction, the only way to increase a tidal current is to move from the source to the target basin of the cocycle, after which by continuity only the inverse can occur, restoring the tidal current to its initial value. In fact, orienting all edges of the graph in such a way that the initial state x_0 is in the source basin of all cocycles, then tidal currents can only take values in $\{0, 1\}$.

Let $\langle \partial_x |$ be the rows of the incidence matrix. Then by continuity of the trajectory

$$\langle \partial_x | j(\boldsymbol{x}) \rangle = \delta_{x,x_t} - \delta_{x,x_0}. \tag{50}$$

This also shows that knowledge of the complete set of currents retains the infomation about the initial and final states, that is, *de facto* the FT equation (49) is conditioned to its boundary states. Since by definition the kernel of ∂ is the cycle space, then the row space of the incidence matrix spans the cocycle space. Then there exists a linear transformation M such that $\langle c_\mu | = \sum_x M_{\mu,x} \langle \partial_x |$, given by

$$M_{\mu,x} = \begin{cases} -1/2, & x \in \text{source } c_\mu \\ +1/2, & x \in \text{target } c_\mu. \end{cases} \tag{51}$$

The $\pm 1/2$ terms are given by the fact that the rows of the incidence matrix are not linearly independent, and therefore one has to adjust a double counting. Then

$$J_\mu(\boldsymbol{x}) = \sum_x M_{\mu,x} \langle \partial_x | j(\boldsymbol{x}) \rangle = M_{\mu,x_t} - M_{\mu,x_0}, \tag{52}$$

which is 0 if both x_0 and x_t are in the target or in the source, +1 if x_0 is in the source and x_t in the target and -1 vice versa.

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It follows from this discussion that tidal currents are bounded, while cycle currents typically increase with time according to

$$J_\alpha(\boldsymbol{x}) \asymp t\,\mathrm{J}_\alpha(\boldsymbol{x}), \tag{53}$$

where J_α is the current per time and when referred to a stochastic variable $\asymp$ means asymptotically, almost surely. Then in the long time limit the asymptotic FT of Andrieux and Gaspard is obtained

$$\lim_{t\to+\infty} \frac{1}{t} \ln \frac{P_t(t\,\mathrm{J})}{P_t(-t\,\mathrm{J})} \asymp \sum_\alpha F_\alpha\,\mathrm{J}_\alpha. \tag{54}$$

Unless a restoring force intervenes (e.g. periodic driving, time-dependent protocols etc), tidal forces are doomed to disappear. Indeed, their effect is so weak that they do not affect any statistical property of the currents [11].

5.3. Unconditional transient FT for the cycle currents (without ensembles)

Let us define a function over the vertices

$$\Phi_x := -\sum_\mu F_\mu M_{\mu,x}. \tag{55}$$

After equation (52) we obtain

$$\sum_\mu F_\mu J_\mu(\boldsymbol{x}) = \Phi_{x_0} - \Phi_{x_t}, \tag{56}$$

which means that the tidal contribution is a state function. An intuitive way to picture this is the following. Suppose the trajectory moves from state x_0 to x_t along the spanning tree. Then the tidal term is increased by the potential drops within the tree and the cycle term is untouched. Now, instead, suppose that x_0 and x_t are connected by a chord and that the trajectory travels along that chord. Then, one will account one full cycle and consequently will have to subtract terms from the tidal accounting. As far as the cocycle term is concerned, the result of these two operations is the same, that is, the tidal term only cares about where the trajectory is and not how it got there, because every time a cycle is enclosed that contribution is thrown in the cycle term.

Then, we can express the joint FT in terms of the cycle currents, conditioned to the boundary states:

$$\frac{P_t(\boldsymbol{J}|x_0)}{P_t(-\boldsymbol{J}|x_t)} = \exp\left(\sum_\alpha F_\alpha J_\alpha + \Phi_{x_0} - \Phi_{x_t}\right). \tag{57}$$

Now suppose the initial state x_0 is sampled with probability $P_0(x_0)$ and that the initial state of the time-reversed processes is sampled with probability $P_t(x_t)$. The choice

$$P_0(x) = P_t(x) = Z^{-1}\mathrm{e}^{-\Phi_x} \tag{58}$$

clearly de-conditions the above expression with respect to the boundary states, which can then be marginalized yielding the finite time FT for the cycle currents, with given initial ensemble

$$\frac{P_t(\boldsymbol{J})}{P_t(-\boldsymbol{J})} = \exp \sum_\alpha F_\alpha J_\alpha. \tag{59}$$

Finally, let us give a clear interpretation of the special distribution from which boundary states must be sampled to attain an exact finite-time FT. By definition F_μ

is the potential drop across the generating cochord, which belongs to the spanning tree. Fixing a reference state $\bar{x}$, let $|\gamma_{x\bar{x}}\rangle$ be the vector representative of the unique oriented path in the spanning tree that connects $\bar{x}$ to x. Then one has

$$\Phi_x = \langle\,\gamma_{x\bar{x}}\,|\,f\,\rangle. \tag{60}$$

It is then well known that the ensemble $Z^{-1}e^{-\Phi_x}$ is the equilibrium steady distribution of the network where the chords are completely removed. Changing reference state $\bar{x}$ amounts to shifting the potential Φ by a constant ground value.

Let us recapitulate this important message. Consider a continuous-time Markov jump process on a graph. Choose a spanning tree of the graph. The criterium is that the currents flowing across the chords (i.e. edges not belonging to the spanning tree) should be of particular physical relevance. Then, such cycle currents satisfy an exact transient fluctuation relation if the processes are sampled from the equilibrium ensemble reached by the Markov process with all rates along chords set to zero.

Finally, as is well-known equilibrium ensembles can be obtained by a maximum entropy procedure [25] with suitable constraints that incorporate the information available about the system before the experiment is conducted, which is used to build up a prior probability (on the role of priors in nonequilibrium statistical mechanics at a foundational level, see [26, 27] by one of the authors). Then, it is interesting to note that the ensemble that needs to be prepared for an observation of the FT at all times is precisely the maximum entropy ensemble (the distribution of lowest information) with respect to the experimental apparatus that is going to measure the currents. The initial ensemble is dictated uniquely by the topology of the graph, expressed by equation (51), and by the potential equation (55) whose average plays the role of the maximum entropy constraint according to the theory pioneered by Jaynes [25].

6. Example: network of chemical reactions revisited

The graph-theoretical method exposed in sections 4 and 5 can be fruitfully applied to the chemical network analyzed in section 3, conjecturing that all results can be extended to the infinite case in some mathematically rigorous way. The chemical lattice admits an infinite number of spanning trees, most of which have no regularity. We choose the *comb* depicted in figure 2(a), consisting of the edges along the X_1 axis and of all the vertical edges. With reference to figure 2(b), there are two kinds of cycles: Cycles of kind c_0 generated by chords $\mathbf{X} \to \mathbf{X} + \boldsymbol{\nu}_1$ have null affinity; Cycles of kind c_3 generated by chords $\mathbf{X} \to \mathbf{X} + \boldsymbol{\nu}_3$ have affinity $F = \ln\frac{Y_1 Y_3}{Y_2 Y_4}$. Hence the cycle term reads

$$\sum_\alpha F_\alpha J_\alpha = F \sum_{\mathbf{X}} j_{\mathbf{X}+\boldsymbol{\nu}_3,\mathbf{X}} = F J_3 \tag{61}$$

yielding the first term in equation (20).

There are two types of cocycles. Horizontal cochords $(X_1, 0) \to (X_1 + 1, 0)$ carrying potential drop $\ln Y_1/(X_1 + 1)$ generate cocycles of type c_1^* in figure 2(c) with current J_{X_1}. As regards the vertical set of cochords of type $\mathbf{X} \to \mathbf{X} + \boldsymbol{\nu}_2$, notice that all those that are based at the same X_2 carry the same potential drop $\ln X_2/Y_2$. Then a resummation occurs, as depicted in figure 2(d) and one obtains an effective cocyle carrying current J_{X_2}.
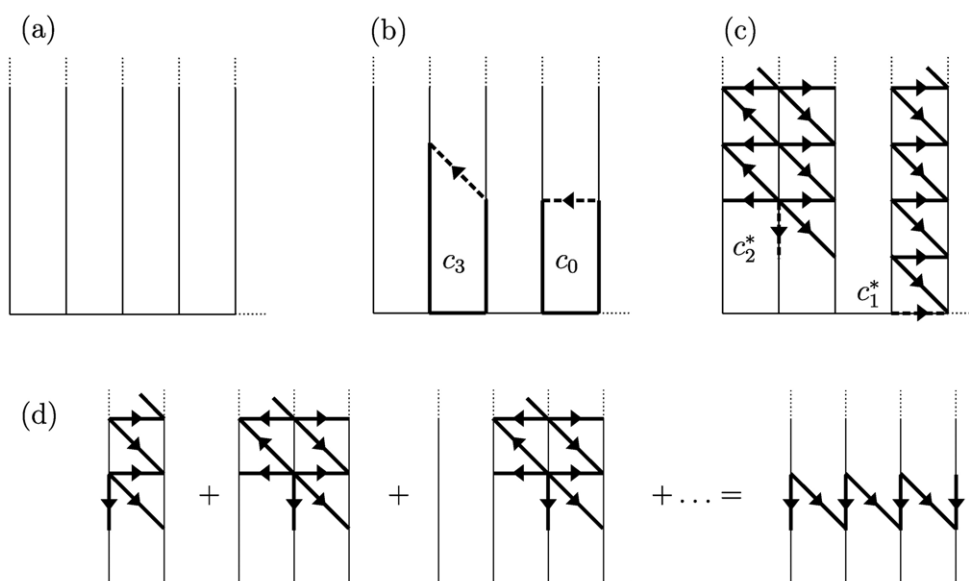
Figure 2. (*a*) An infinite spanning tree. (*b*) Two cycles; the generating chords are dashed. (*c*) Two cocycles; the generating cochords are dashed. Cocycle c_2^* is generated by a vertical cochord, cocycle c_1^* is generated by a horizontal cochord. (*d*) Linear combination of cocycles of type c_2^* at given X_2.

We then obtain

$$\sum_\mu F_\mu^* J_\mu^* = \sum_{X_1} J_{X_1} \ln \frac{Y_1}{X_1 + 1} + \sum_{X_2} J_{X_2} \ln \frac{Y_2}{X_2 + 1} \qquad (62)$$

which is the second term in equation (17).

Finally, the initial equilibrium ensemble that makes the finite-time FT for the currents hold is the steady distribution of a Markov process occurring on the comb, which is obtained by eliminating reaction 3 from the reaction scheme. It is interesting to note that, due to the fact that the affinities of type 0 in figure 2 all vanish, any spanning tree that only consists of reaction steps of kind 1 and 2 will give rise to the same initial ensemble. Hence, while in principle the choice of spanning tree affects the FT, chemical networks enjoy certain regularity properties that boil down the great generality of Schnakenberg's analysis to actual physical currents. In the specific case of chemical networks, this possibility is granted by the mass-action law and by the fact that the topology of the chemical lattice in figure 2(*a*) is simply obtained by shifting and reproducing the chemical reaction network in equation (6). While we postpone a full discussion of chemical networks to a future publication, it is interesting to note that not all chemical reaction schemes allow for such great simplification depending on certain topological properties related to the concept of *deficiency* of the network [28].

7. Conclusions

In this paper we collected several results about finite-time FT's for the currents for stationary Markov jump processes on a finite state space, giving a unified framework

based on certain algebraic graph-theoretical techniques that allow to decompose any thermodynamic observable in terms of cycle and cocycle observables, by virtue of the fundamental identity equation (33). In particular, we generalized the result of Andrieux and Gaspard [9] for the so-called Schnakeberg currents to finite times, both by direct manipulation of the probability density function of Markov jump trajectories and by the generating function approach exposed in appendix.

One major limitation of our results that calls for further generalization is the requirement that transition rates are time-independent. Indeed, the FT without ensemble quantities discussed by Bulnes-Cuetara *et al* [15] was formulated for time-dependent protocols. We mention, without further discussion, that a full generalization of their result to arbitrary Markov processes on finite state spaces in terms of cycles and cocycles is significantly more complicated. The resulting expressions defy a clear physical interpretation. Partial results can be obtained under more restrictive assumptions, e.g. that the affinities are constant in time. Furthermore, as regards linear chemical networks we point out that there exists a finite-time FT with the initial state sampled from the steady nonequilibrium ensemble, with a time-dependent effective affinity [30]. We leave these issues and the treatment of general chemical reaction networks to future inquiry.

Acknowledgments

Appendix. Generating function approach

As an *addendum*, we will prove the 'initial ensemble' FT exposed in section 5.3 by the commonly employed method of the generating function, generalizing the treatment explored by Bulnes-Cuetara in [29] and by Andrieux *et al* in [16].

Let $\boldsymbol{\lambda} = (\lambda_\alpha)_\alpha$ be a set of counting fields defined on the chords of the graph and $\mathbf{1} = (1, \ldots, 1)$ the unit vector of length $|V|$. It is well-known [9] that the moment generating function for the cycle currents is given by

$$Z(\boldsymbol{\lambda}, t) = \sum_x P_x(\boldsymbol{\lambda}, t) = \mathbf{1} \cdot P(\boldsymbol{\lambda}, t), \tag{A.1}$$

where $P(\boldsymbol{\lambda}, t)$ evolves by the Feynman–Kac type of equation

$$\frac{\mathrm{d}}{\mathrm{d}t} P(\boldsymbol{\lambda}, t) = \mathcal{L}(\boldsymbol{\lambda}) P(\boldsymbol{\lambda}, t). \tag{A.2}$$

Here, $\mathcal{L}(\boldsymbol{\lambda})$ is the *tilted* generator with entries

$$\mathcal{L}_{xx'}(\boldsymbol{\lambda}) = \begin{cases} -w_x, & \text{if } x = x' \\ w_{xx'}\mathrm{e}^{\lambda_\alpha}, & \text{if } x \neq x', x \leftarrow x' = e_\alpha \\ w_{xx'}\mathrm{e}^{-\lambda_\alpha}, & \text{if } x \neq x', x \rightarrow x' = e_\alpha \\ w_{xx'} & \text{otherwise} \end{cases} \tag{A.3}$$

and the initial condition is given by

$$P(\boldsymbol{\lambda}, 0) = P(\boldsymbol{0}, 0), \tag{A.4}$$

where $P(\boldsymbol{0}, 0)$ is the initial probability density over states. It is important that $P(\boldsymbol{\lambda}, 0)$ does not depend on $\boldsymbol{\lambda}$. Physically, this reflects the fact that the preparation of the system cannot depend on the output of the counting experiment.

The tilted generator obeys a crucial time-reversal symmetry relation. Let us consider the generator $\mathcal{L}(\boldsymbol{F} - \boldsymbol{\lambda})^T$ with entries

$$[\mathcal{L}(\boldsymbol{F} - \boldsymbol{\lambda})^T]_{xx'} = \begin{cases} -w_x, & \text{if } x = x' \\ w_{x'x} \mathrm{e}^{F_\alpha - \lambda_\alpha}, & \text{if } x' \neq x, x' \leftarrow x = e_\alpha \\ w_{x'x} \mathrm{e}^{\lambda_\alpha - F_\alpha}, & \text{if } x' \neq x, x' \rightarrow x = e_\alpha \\ w_{x'x} & \text{otherwise.} \end{cases} \tag{A.5}$$

By definition, the α-th affinity is the circulation of the force around a cycle comprising chord $e_\alpha = x \leftarrow x'$ and the unique path $\gamma_{x'x}$ that is internal to the spanning tree T and that goes from state x to state x'. Then,

$$F_\alpha = \ln \frac{w_{xx'}}{w_{x'x}} + \langle \gamma_{x'x} \,|\, f \rangle = \ln \frac{w_{xx'}}{w_{x'x}} + \Phi_{x'} - \Phi_x, \qquad x \leftarrow x' = e_\alpha. \tag{A.6}$$

Moreover, notice that for all edges internal to the spanning tree

$$\Phi_{x'} - \Phi_x = \ln \frac{w_{x'x}}{w_{xx'}}, \qquad x \leftarrow x' \in T. \tag{A.7}$$

We then obtain

$$[\mathcal{L}(\boldsymbol{F} - \boldsymbol{\lambda})^T]_{xx'} = \begin{cases} -w_x, & \text{if } x = x' \\ w_{x'x} \mathrm{e}^{\Phi_{x'} - \Phi_x - \lambda_\alpha}, & \text{if } x' \neq x, x' \leftarrow x = e_\alpha \\ w_{x'x} \mathrm{e}^{\Phi_{x'} - \Phi_x + \lambda_\alpha}, & \text{if } x' \neq x, x' \rightarrow x = e_\alpha \\ w_{xx'} \mathrm{e}^{\Phi_{x'} - \Phi_x} & \text{otherwise} \end{cases} \tag{A.8}$$

yielding the symmetry relation

$$\mathcal{L}(\boldsymbol{F} - \boldsymbol{\lambda})^T = \Theta \mathcal{L}(\boldsymbol{\lambda}) \Theta^{-1}, \tag{A.9}$$

where $\Theta = \mathrm{diag}\left(\mathrm{e}^{-\Phi_x}/Z\right)_x$, $Z = \sum_x \mathrm{e}^{-\Phi_x}$ being the normalization factor.

Finally, we can go back to the moment generating function. Integrating equation (A.2), in view of equation (A.1), we obtain

$$Z(\boldsymbol{\lambda}, t) = \boldsymbol{1} \cdot \mathrm{e}^{t\mathcal{L}(\boldsymbol{\lambda})} P(\boldsymbol{0}, 0) = \boldsymbol{1} \cdot \Theta^{-1} \mathrm{e}^{t\mathcal{L}(\boldsymbol{F} - \boldsymbol{\lambda})^T} \Theta P(\boldsymbol{0}, 0). \tag{A.10}$$

Let us also consider

$$Z(\boldsymbol{F} - \boldsymbol{\lambda}, t) = \boldsymbol{1} \cdot \mathrm{e}^{t\mathcal{L}(\boldsymbol{F} - \boldsymbol{\lambda})} P(\boldsymbol{0}, 0). \tag{A.11}$$

In general, the two are not related unless

$$P(\boldsymbol{0}, 0) = \Theta^{-1} \boldsymbol{1}, \tag{A.12}$$

in which case

$$Z(\boldsymbol{\lambda}, t) = Z(\boldsymbol{F} - \boldsymbol{\lambda}, t). \tag{A.13}$$

Equation (A.12) is nothing but the requirement that the initial state is the equilibrium state described in section 5.3, equation (A.13) is well-known to imply the fluctuation relation when moving from the generating function picture to the probability density picture.

References

[1] Bochkov G N and Kuzovlev Y E 1981 Nonlinear fluctuation-dissipation relations and stochastic models in nonequilibrium thermodynamics: I. Generalized fluctuation-dissipation theorem *Physica* A **106** 443

Bochkov G N and Kuzovlev Y E 1981 Nonlinear fluctuation-dissipation relations and stochastic models in nonequilibrium thermodynamics: II. Kinetic potential and variational principles for nonlinear irreversible processes *Physica* A **106** 480

[2] Kurchan J 1998 Fluctuation theorem for stochastic dynamics *J. Phys. A: Math. Gen.* **31** 3719

[3] Maes C 1999 The fluctuation theorem as a Gibbs property *J. Stat. Phys.* **95** 367

[4] Lebowitz J L and Spohn H 1999 A Gallavotti-Cohen-type symmetry in the large deviation functional for stochastic dynamics *J. Stat. Phys.* **95** 333

[5] Kalpazidou S 1995 *Cycle Representations of Markov Processes* (Berlin: Springer)

[6] Hill T L 2005 *Free Energy Transduction and Biochemical Cycle Kinetics* (New York: Dover)

[7] Schnakenberg J 1976 Network theory of microscopic and macroscopic behavior of master equation systems *Rev. Mod. Phys.* **48** 571

[8] Polettini M 2011 Macroscopic constraints for the minimum entropy production principle *Phys. Rev. E* **84** 051117

[9] Andrieux D and Gaspard P 2007 Fluctuation theorem for currents and Schnakenberg network theory *J. Stat. Phys.* **127** 107

[10] Andrieux D and Gaspard P 2004 Fluctuation theorem and Onsager reciprocity relations *J. Chem. Phys.* **121** 6167

[11] Wachtel A, Vollmer J and Altaner B 2014 Determining the statistics of fluctuating currents: general Markovian dynamics and its application to motor proteins (arXiv:1407.2065)

[12] Faggionato A and Di Pietro D 2011 Gallavotti–Cohen-type symmetry related to cycle decompositions for Markov chains and biochemical applications *J. Stat. Phys* **143** 11

[13] Bertini L, Faggionato A and Gabrielli D 2014 Flows, currents and cycles for Markov Chains: large deviation asymptotics (arXiv:1408.5477)

[14] Van den Broeck C and Esposito M 2010 Three faces of the second law. I. Master equation formulation *Phys. Rev. E* **82** 011143

[15] Bulnes-Cuetara G, Esposito M and Imparato A 2014 Exact fluctuation theorem without ensemble quantities *Phys. Rev. E* **89** 052119

[16] Andrieux D, Gaspard P, Monnai T and Tasaki S 2009 The fluctuation theorem for currents in open quantum systems *New J. Phys.* **11** 043014

[17] Kim K, Kwon C and Park H 2014 Heat fluctuations and initial ensembles *Phys. Rev. E* **90** 032117

[18] Fogedby H C and Imparato A 2014 Heat fluctuations and fluctuation theorems in the case of multiple reservoirs (arXiv:1408.0537)

[19] Campisi M, Hänggi P and Talkner P 2011 Colloquium: quantum fluctuation relations: foundations and applications *Rev. Mod. Phys.* **83** 771

[20] Polettini M 2014 Cycle/cocycle oblique projections on oriented graphs (arXiv:1405.0899)

[21] Seifert U 2008 Stochastic thermodynamics: principles and perspectives *Eur. Phys. J. B* **64** 423

[22] Polettini M and Esposito M 2014 Irreversible thermodynamics of open chemical networks I: emergent cycles and broken conservation laws *J. Chem. Phys.* **141** 024117

[23] Ethier S N and Kurtz T G 1986 *Markov Processes: Characterization and Convergence* (New York: Wiley)

[24] Nakanishi N 1971 *Graph Theory and Feynman Integrals* (New York: Gordon and Breach)

[25] Jaynes E T 1957 Information theory and statistical mechanics *Phys. Rev.* **106** 620

[26] Polettini M 2013 Of dice and men. Subjective priors, gauge invariance and nonequilibrium thermodynamics *Proc. 12th Joint European Thermodynamics Conf. (Brescia, Italy, 1–5 July 2013)*

[27] Polettini M 2012 Nonequilibrium thermodynamics as a gauge theory *Eur. Phys. Lett.* **97** 30003

[28] Feinberg M 1987 Chemical reaction network structure and the stability of complex isothermal reactors—I. The deficiency zero and deficiency one theorems *Chem. Eng. Sci.* **42** 2229

[29] Bulnes-Cuetara G 2013 Fluctuation theorem for quantum electron transport in mesoscopic circuits (arXiv:1310.0620)

[30] Andrieux D and Gaspard P 2008 Temporal disorder and fluctuation theorem in chemical reactions *Phys. Rev. E* **77** 031137