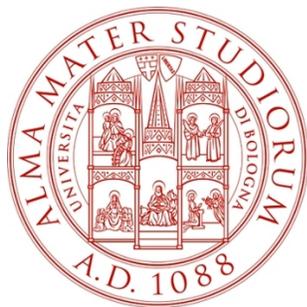


ALMA MATER STUDIORUM - UNIVERSITÀ DI BOLOGNA



Dottorato di Ricerca in Fisica
XXIV Ciclo

Settore concorsuale: 02/B3. Settore scientifico-disciplinare: FIS/07.

Geometric and Combinatorial Aspects of NonEquilibrium Statistical Mechanics

Presentata da: Dott. Matteo Polettini

Coordinatore: Prof. Fabio Ortolani

Relatore: Prof. Armando Bazzani

Esame finale anno 2012

Contents

0.1	Introduction	5
0.2	Results	11
0.3	Aknowledgements	14
1	Network theory	15
1.1	Examples first	15
1.2	Which system?	21
1.3	Algebraic graph theory in a nutshell	22
1.4	Mesoscopic and macroscopic observables	34
1.5	Discretizing continuous theories	38
1.6	Duality of graphs	39
1.7	Linear regime	43
2	Applications: duality and variational principles	51
2.1	System/Environment Duality: example	52
2.2	System/Environment Duality: discussion	53
2.3	Minimum entropy production	59
2.4	Maximum entropy production?	66
3	Master equation: dynamics	69
3.1	Master equation	69
3.2	Reduced dynamics	71
3.3	Semigroup propagator	72
3.4	Jump trajectories and the path measure	74
3.5	Appying the path measure	76
3.6	Ergodic theorems	77
3.7	Path inversion	78

4	Master equation: thermodynamics	81
4.1	Entropy production	82
4.2	Path entropies	84
4.3	Fluctuation theorems	87
4.4	Local detailed balance	93
4.5	Clausius circuitations	96
4.6	Linear regime for the heat fluxes	100
4.7	Green-Kubo relations for the heat fluxes	102
4.8	Independent reservoirs in open quantum systems	103
5	Steady states	111
5.1	Matrix-tree theorems	111
5.2	Proof of steady state formula	115
5.3	Cycle fluxes	117
5.4	Recovering equilibrium partition functions	121
6	Nonequilibrium Geometry	125
6.1	On information and entropy	126
6.2	Priors	128
6.3	Implementing gauge invariance	131
6.4	Parallel transport and Wilson loops	135
6.5	Time-dependent gauge transformations	139
6.6	Microscopic analysis	140
7	Decay modes	145
7.1	Eigenvalues and decay modes	146
7.2	The time-reversal generator	146
7.3	Normal generators	148
7.4	The Fisher matrix	150
7.5	Relative entropy and monotonicity	154
7.6	Convexity: an overview	157
7.7	Finding counterexamples to convexity	159
7.8	A class of non-equilibrium phase transitions?	163
7.9	Information-geometric interpretation	166

0.1 Introduction

We can say nothing about the thing in itself, for we have eliminated the standpoint of knowing, i.e. of measuring. A quality exists for us, i.e. it is measured by us. If we take away the measure, what remains of the quality? What things are is something that can only be established by a measuring subject placed alongside them.

Friedrich Nietzsche [1].

Sonja: *Morality is subjective.*

Russian gentleman: *Subjectivity is objective.*

Sonja: *Moral notions imply attributes to substances which exist only in relational duality.*

Russian gentleman: *Not as an essential extension of ontological existence.*

Sonja: *Can we not talk about sex so much?*

Woody Allen, *Love and Death*.

This thesis gathers and tidies up three years of speculations and results on several aspects of Non-Equilibrium Statistical Mechanics, some of which have been made public on the arXiv and eventually have been published or are in the process of being published in peer-reviewed journals [2–5]:

- M.P., *Macroscopic constraints for the minimum entropy production principle*, Phys. Rev. E **84**, 051117 (2011),
- M.P., *Nonequilibrium thermodynamics as a gauge theory*, accepted for publication on Eur. Phys. Lett. (13 dec. 2011),
- M.P., *System/environment duality of nonequilibrium network observables*, arXiv:1106.1280 (2011),
- M.P., *Equivalence Principle and Critical Behaviour for Nonequilibrium Decay Modes*, arXiv:1105.4134 (2011).

The rest of the material is work in progress that the author is elaborating, in part by himself and in part in collaboration with Massimiliano Esposito

and his group in Brussels, where the author spent a period of three months (winter 2011). Many of the basic raw ideas behind this work have been shared and discussed with the Ph.D. advisor professor Armando Bazzani. The author spent another period of three months (spring 2010) in Marseille as a host in the Quantum Gravity group of Carlo Rovelli. These are the three persons which — scientifically — I am mostly grateful to, for various reasons: moral support and intellectual intimacy, independence and familiarity with the community, liberty of thought and discussion.

Non-Equilibrium Statistical Mechanics (NESM) is a broad subject. As a matter of fact, it possibly embraces all physical systems, as it can be argued that no physical system is truly isolated: environmental noise, external forcing, measuring apparatuses, emergent phenomena from complexity, unknown fundamental theories entail that dissipation occurs at all levels of description of reality. Equilibrium Statistical Mechanics (ESM) is the small portion of NESM that studies thermalized systems, i.e. systems that have already relaxed to an equilibrium state where no in- or out-flows occur, be them flows of matter, energy, charge or, more abstractly, entropy. As to the ambitions, NESM overreaches ESM in many respects: (i) Describing systems in the process of thermalization (ii) Describing systems which have relaxed to steady states which display constant entropy flows towards the environment; (iii) Describing systems in the process of relaxation to non-equilibrium steady states; (iv) Describing forced systems which do not relax at all. As to the results, it is fair to say that ESM exceeds NESM both in theoretical control of its models and in experimental validation, and that in the 20th century NESM has best succeeded in the close-to-equilibrium regime. However, the last twenty years have witnessed a burst in the development of driven lattice models, stochastic thermodynamics, spin glasses, thermostatted dynamical systems, systems with long-range interactions, complex systems, and applications to nanophysics, biophysics, climatology, complex networks and many other diverse fields, fostering some (cautious) optimism about the future of NESM and of its experimental reach.

Given the immense realm of NESM, a host of techniques and approaches are employed in the theoretic literature to attack simplified models and generic systems. This makes it difficult to define exactly what NESM is. In this respect, a perfect example is the problem of the attribution of the so-called fluctuation theorems, that were derived in a variety of contexts, from Axiom A dynamical systems [6] to Markov processes [7] to hamiltonian driven systems [8, 9], but which actually can be backdated to the work of

Bochkov and Kuzovlev [10]. Basically, the body of literature on the fluctuation theorems (and on NESM in general) is divided in two main segments: deterministic vs. stochastic descriptions. This thesis inscribes in the literature on stochastic systems, although many of the considerations in Ch.1 have a wider scope.

Ch.1 is devoted to the network theory of macroscopic thermodynamical observables, initiated by Julian Schnakenberg [11, 12]. Schnakenberg engaged in the definition of the fundamental macroscopic observables of Non-Equilibrium Statistical Mechanics, grossly conceived as a theory of the internal flows of a system. He worked with conjugate variables (currents and forces) defined over a finite state space, founding his theory on an analogy with the theory of electrical circuits and generalizing it, in some respects, to regimes where Ohm's law does not hold. For this reason the other great scientist that we gladly tribute is Gustav Robert Kirchhoff [13], whose laws and theorems are ubiquitous in this thesis. Schnakenberg's theory was born out of the study of biophysical systems [12, 15], and recently it is finding growing applications to chemical reaction networks, molecular motors and transport phenomena [16–23]. It has already been recognized in the literature that Schnakenberg's analysis has a deep geometrical and combinatorial content [24, 25]. It is the backbone for the comprehension of Non-Equilibrium Steady States (NESSs) [24, 26], to which the theory was so-far restricted. The aim of this chapter is to illustrate the theory and to go beyond NESSs, generalizing Schnakenberg's construction to arbitrary states and providing a detailed survey of the linear regime constitutive relations.

The complete theory of nonequilibrium observables turns out to enjoy a duality which exchanges forces with currents, the concept of steadiness with that of detailed-balancing of the external constraints, and ultimately properties of the environment with properties of the system. This is the subject matter of Ch.2, where it is also shown that Schnakenberg's observables serve as constraints for a formulation of the Minimum Entropy Production Principle that marries well with Prigogine's original formulation [27].

Ch.3 introduces continuous-time Markov processes on a finite state space, through the master equation. We choose to spare useless details and only introduce the pieces of machinery that are essential for the rest of the thesis.

The thermodynamics of master equation systems is discussed in Ch.4. We first define the internal, environmental and total entropy production rates for the master equation, then introduce their microscopic analogues along single jump trajectories. These definitions are used to prove fluctuation theorems.

Although this is standard material, we tried to give a rather personalized perspective on the problem. In particular we make a strong claim about fluctuation theorems for systems with incommensurable rates. The second part of the chapter discusses the Local Detailed Balance *ansatz*, which was recently proposed by Esposito and Van den Broeck in the attempt to give a more physical grasp on the nonequilibrium thermodynamics of master equation systems [46]. Local Detailed Balance permits to make direct contact with 18th century thermodynamics; in particular, we show that the notion of Schnakenberg affinity coincides with Clausius’s measure of irreversibility along a cyclic process.

Spanning trees are one major graph-theoretical ingredient of this thesis. They participate in our network analysis, as the choice of one spanning tree allows to find basis of cycles and of dual cocycles whereupon we define a set of macroscopic observables. They appear in the enumerative polynomials which provide expressions for the determinant of the linear response matrices. Finally, they are used to define the steady-state solution of the master equation. In Ch.5 we prove the spanning-tree formula for the steady state, briefly illustrate the content and spirit of the so-called matrix-tree theorems and discuss a few combinatorial properties and applications.

The material developed in Ch.6 constitutes the most conceptual and at the same time consistent part of this thesis. In accordance with our modern understanding of Quantum Mechanics and Quantum Field Theory, where adiabatic phases and Wilson loops play an ever more prominent role [14], in Schnakenberg’s theory the constraints which prevent a system from relaxing to equilibrium are circuitations of certain “connection” variables. We make this observation into a gauge principle. In particular, we observe that thermostatics, that is, the quantification of the internal entropy of a system, depends on a prior probability that one assigns to microstates of the system (for example, microcanonical equiprobability of certain degrees of freedom). We interpret this arbitrariness as a gauge freedom, and prove that Schnakenberg’s theory is consistent with the requirement of a gauge invariant theory of thermodynamics. In Sec.6.6 we give a microscopic interpretation of gauge invariance as the choice of a stochastic process representing a given jump trajectory, something akin to the choice of coordinates for the representation of the motion of bodies in classical mechanics. The discrete setup allows to give an intuitive and self-contained treatment of the geometrical aspects of gauge theory, without delving into the differential geometry of principal and tangent bundles. However, from time to time geometrical jargon will make

its appearance in this thesis.

Geometry is also involved in the interpretation of the results presented in Ch.7, where certain orthogonality relations between eigenmodes of a generator are shown to be related to the Fisher-Rao metric on the space of probability measures. Using a motto, we can state that equilibrium systems are to thermodynamics what inertial frames are to gravity, as their modes trivialize the metric at one point on the manifold, corresponding to the steady state. The phenomenology of nonequilibrium systems in the light of the Fisher matrix is very rich; besides equilibrium systems, we analyze nonequilibrium p -normal systems, with complex spectrum and a peculiar behavior under time-reversal, and systems with a degenerate spectrum. In this latter case the Fisher metric seems to signal the insurgence of a class of non-equilibrium phase transitions — even on a finite state-space. Apart from the geometrical interpretation, the formalism seems to be rich and of direct physical application; in fact, we use it to prove that relative entropy with respect to the steady state is not a convex function of time, thus refuting a tempting conjecture and a potential principle of thermodynamics.

In the conclusive chapter we briefly describe possible directions of research where this material might be employed.

Four broad and important subjects related to this work are completely absent: Equilibrium Statistical Mechanics, Stochastic Differential Equations, diffusion equation of continuous systems (Fokker-Planck Equation), and Large Deviation Theory. Nevertheless, all of these topics have been a major concern of the author.

This brief overview will probably leave the impression of a patchwork rather than an organic thesis. In many respects it is so. The author spent the last three years doing “research” in the literary sense of the word, searching for motivations, results, interpretations, always digging out new material, considering its relevance, abandoning lines, opening new projects and so on. This thesis should be considered as a recollection of thoughts and results and not as an encyclopedia of the things that he studied. Therefore it reflects the author’s style and gait in doing research. In particular, by no means should this thesis be considered as a manual or an introduction to NESM, not even to network theory or to the geometry and combinatorics of NESM. As a matter of fact, we give nearly no background on geometry, combinatorics and NESM besides what is strictly necessary for the derivation of the results, nor do we really employ mathematically sophisticated instruments, that would require further explanation and deserve several chapters on their own. We consider

this thesis more like a report-in-progress, susceptible of future modifications, a momentary repository where it is useful to pin-point what has been done so far and put some order into ideas and partial results that are in constant re-elaboration, in view of possible future publication. However, there is an underlying question connecting all considerations in this report: To what extent are non-equilibrium systems different from equilibrium ones, and which geometrical instruments can be used to quantify the distance between them? Along this thread, we tried to give a consequential and self-contained outline, in such a way that a sufficiently elastic and willing reader will in principle be able to go through the whole work, without resorting to other material.

This thesis is a rather theoretical work, even though it is the final output of a Ph.D. program in applied physics. Its style reflects the author's interests, ambitions and even his ideas on the utility and scope of science. At this point it should be incumbent to prospect viable applications. Unfortunately, the author's expertise does not allow for a deep insight into the fascinating physics of real-world complex and non-equilibrium systems. A friend and colleague of the author, a sharp physicist who recently left the academia, appended to his latest article the following (all-too-bitter) disclaimer: "This paper is not intended for journal publication. Therefore, it lacks the delusional claims typically found in published papers about its (simultaneous) relevance to drug design, nanoelectronics, photonics, spintronics or any other fashionable application [...]". We think that avoiding propagandistic fireworks helps clarifying contents and allows a serious evaluation the true scientific value of a piece of research. Applications might well be around the corner, but they are not the subject matter of this thesis.

Finally, let us briefly comment on the quotations at the head of this introduction. At the time of writing, the author subscribes to what might be called the "informationism" interpretation of statistical mechanics. This is not just a marginal note, as this point of view sustains the findings described in Ch.6, which would otherwise have marginal relevance. Informationists take very seriously the fact that physics produces statements about measurements that observers perform on a system and prescriptions about how they confront results. Physics is about acquisition of information, information storage and processing, and communication. This viewpoint does not exhaust itself with the trite recognition that experimental validation, in all of its variants, is the unquestioned arbiter of the physical nature of a theory. It rather refers to the crucial role that information has come to play in the logical foundation of theories. No assertion whatsoever is made about the existence of the

world, which is an ontological issue which transcends physics: informationism is equidistant both from realism and from solipsism. Paraphrasing Nietzsche: “Existence is nonsensical without interpretation”. Although this might appear as an extremist point of view, it is instead very laic, prudent and even conventional. By its own statute, it does not aim at telling how the world *is* on the whole, but it is only concerned with how we deal with the portion of the world that is empirically accessible to us. However, discussions about objectivity and subjectivity, ontological existence and relational duality tend to become wars of religions. With Allen, we prefer to only lightly touch upon philosophy and soon plunge into more “physical” discourses.

0.2 Results

Some of the results that are original (at least to a certain degree, and up to our knowledge) in this thesis are conceptual, and even of a foundational character; some others are of a rather technical nature, mainly involving graph theory. Technical results might be part of a greater picture or might be isolated yet.

From our point of view, the most interesting conceptual proposals are:

- The generalization of Schnakenberg’s observables to non-steady states of non-equilibrium systems, accounting for internal and external conjugate macroscopic currents and forces (Sec.1.4).
- The duality between observables characterizing the state of the system and those characterizing the state of the environment, and the analysis of special instances where system/environment duality comes into play (Sec.2.1 and Sec.2.2).
- The implementation of macroscopic observables as constraints in the Minimum Entropy Production Principle (MINEP) and the connection to Prigogine’s original formulation of the principle and to his expectation that MINEP should be cast in the form of a gaussian principle of least constraint (Sec.2.3).
- Schnakenberg’s circuitations as a tool for understanding the thermodynamics of locally detailed balanced master equation systems (Sec.4.5), and the emergence of Clausius’s measure of irreversibility along a cyclic process as the fundamental macroscopic force.

- Thermodynamics of master equation systems as a gauge theory, and the interpretation of gauge transformations as changes of prior probability measure (Ch.6).
- The relevance of the Fisher-Rao metric for the analysis of the decay modes of the master equation. In particular: the geometrical interpretation of equilibrium systems as those systems which satisfy a sort of statistical equivalence principle (Sec.7.9), and the critical behavior of systems with defective generator (Sec.7.8).
- The confutation of conjectures on the convexity of the relative entropy as a function of time by means of a counterexample (Sec.7.7).

A list of more technical results:

- The definition of macroscopic observables as cycles and cocycles starting from one spanning tree, Eqs.(1.27), and the consequent decomposition of the entropy production in terms of the generalized set of observables, Eqs.(1.12a,1.35).
- In the linear regime, the decomposition of the entropy production as a quadratic form of the external macroscopic forces and currents, Eq.(1.53).
- The invariance of the determinant upon modification on the fundamental set of observables.
- The formula for the number of spanning trees of a graph as the volume of the parallelotope formed by cycles (or cocycles) in a fundamental set, Eq.(1.55).
- The discrete electro-magnetic duality between fields and sources, Eq.(2.2), as an example of system/environment duality.
- Using affinities as Lagrange multipliers for the minimization of the entropy production, Eq.(2.8).
- The Transient Fluctuation Theorem for the currents Eq.(4.24), which generalizes a result by Andrieux and Gaspard [21], and the Fluctuation Theorem for the heat flows, Eq.(4.48).

- A proof that Local Detailed Balance is not restrictive, i.e., that all master equations can be given a Local Detailed Balance interpretation with a cyclomatic number of heat reservoirs (in Sec.4.4).
- The Schnakenberg analysis of locally detailed balanced systems in terms of topological and non-topological cycles, Eqs.(4.40,4.41).
- The analysis of the linear-regime for the heat fluxes, Sec.(4.6) and (4.7).
- The derivation of the Local Detailed Balance assumption from the markovian dynamics of Open Quantum Systems, and consequently a viable definition of the entropy production rate for quantum Lindblad Equations, Eq.(4.59).
- A simple graphical proof of the matrix-tree theorem for master equations, Eq.5.1, and a new proof based on the Fluctuation Theorem of a result by Hill on cycle fluxes, Eq.(5.12).
- A proof that the entropy production, Eq.6.22, is gauge invariant, and that it is the simplest gauge-invariant completion of the time derivative of the Gibbs-Shannon's entropy.
- A proof that the evolution equation for the moment generating function of a suitable stochastic process, Eq.(6.39), coincides with the time-dependent gauge-transformed master equation, Eq.(6.32).
- The definition of the Fisher's correlation matrix for decay modes of a master equation, which is shown to be diagonal for equilibrium and p -normal systems (Sec.7.9); time-reversal generators have inverse Fisher matrix.
- A counterexample to convexity of the relative entropy, Eq.(7.22), and a discussion on how to generate counterexamples with initial state sampled arbitrarily close to the steady state.
- In Sec.(7.8), the analysis of a simple three-state system which displays critical behavior in time, and for which the Fisher matrix becomes degenerate at the critical line.

Results are not given in the form of theorems, as mathematical accuracy has not been pursued.

0.3 Acknowledgements

Besides the persons credited in the introduction, carved in my memories are the profound discussions about almost anything from quantum gravity to nonequilibrium statistical mechanics with the people that I met at Quantum Gravity Group in Marseille, in particular Francesca Vidotto, Eugenio Bianchi, Matteo Smerlack, Harold Haggard and Antonino Marcianò. I am very thankful to Marcello Dalmonte for many precious advices and for showing me the way to publication, and to Afshin Montakhab for vivacious discussion on the informationist viewpoint.

1

Network theory

1.1 Examples first

We espouse Gowers’s principle that examples should precede the theory for a better understanding [28].

Consider a discrete state space consisting of four states, which exchange between one another some physical quantity, be it mass, energy, charge, spin etc., at certain rates. For sake of abstractness, we will suppose that these physical quantities are coded in bits, so that from the comparison of two nearby snapshots of the system an observer will be able to measure a certain flux of raw “information” at a certain time. States of the system are depicted with vertices (or sites) of a graph, and the channels of communication with oriented edges e connecting the states, as is shown in Fig.1.1a. Currents j_e might have positive or negative sign, according to the direction of the flow — concordant or opposite to the edges’ orientations. Notice that not all states need to be connected. We further suppose that the currents are induced by conjugate mesoscopic forces a_e , which have the same sign $\text{sign } a_e = \text{sign } j_e$, and finally we introduce the entropy production (rate)¹,

$$\sigma[j, a] = j_1 a_1 + j_2 a_2 + j_3 a_3 + j_4 a_4 + j_5 a_5. \quad (1.1)$$

A comment is needed on the usage of the scale words. Schnakenberg referred to j_e ’s as a microscopic currents, and to the observables we are going to

¹In this chapter we will talk of entropy production meaning entropy production rate, in later chapters we will be more careful with the terminology.

build as macroscopic. However, later developments in the stochastic thermodynamics of master equation systems (see Ch.3 and references therein) allow us to identify single-trajectory analogues of thermodynamical quantities whose averages over paths return j_e, σ , etc. This suggests to reserve the word “microscopic” for this further layer, and to adopt “mesoscopic” for j_e and a_e , irregardless of their spatial dimension.

We first consider steady states. This is the original reach of Schnakenberg’s theory. The configuration of currents is steady if the total inflow at the nodes is null, yielding the conservation laws

$$j_4^{ss} = j_1^{ss}, \quad j_2^{ss} = j_3^{ss}, \quad j_1^{ss} + j_5^{ss} = j_2^{ss}, \quad j_3^{ss} - j_4^{ss} = j_5^{ss}. \quad (1.2)$$

Eqs.(1.2) are known as Kirchhoff’s Current Laws. One of them is redundant. The others allow us to express all of the steady currents in terms of, e.g., j_1^{ss} and j_3^{ss} . Replacing the solution into the expression for the entropy production

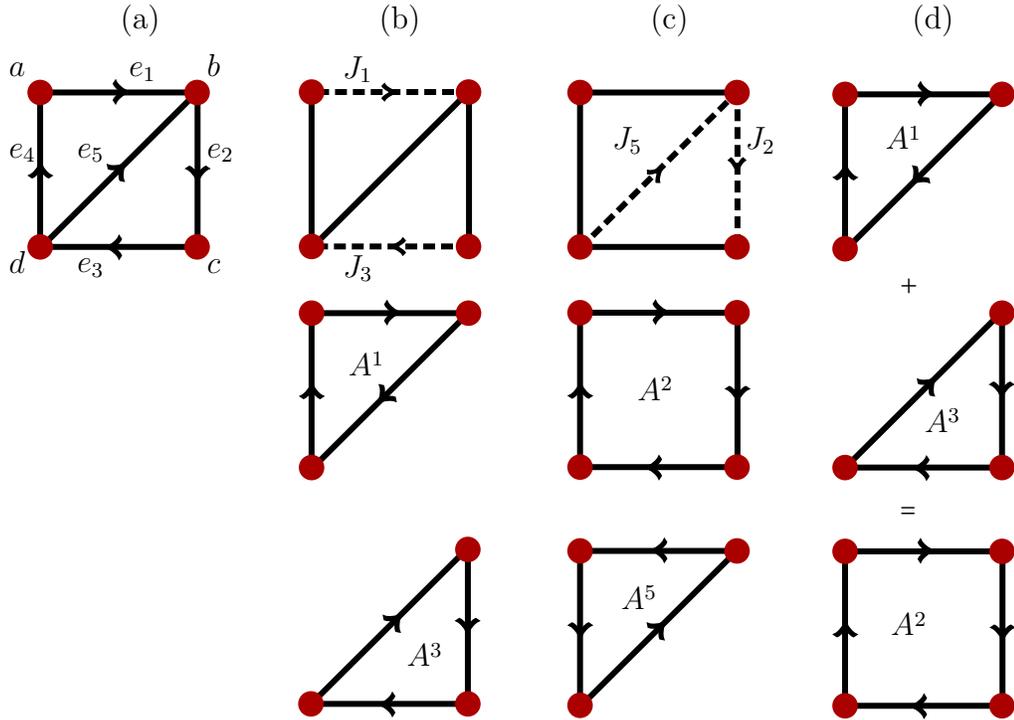


Figure 1.1: (a) An oriente graph. (b,c) Internal currents and external forces corresponding to different spanning trees. (d) Composition of affinities.

yields

$$\sigma[j^{ss}, a] = j_1^{ss} \overbrace{(a_1 + a_4 - a_5)}^{A^1} + j_3^{ss} \overbrace{(a_2 + a_3 + a_5)}^{A^3}. \quad (1.3)$$

Overbraces are used to define the macroscopic external forces or affinities. They form pairs of conjugate variables together with the fundamental internal currents $J_1 = j_1^{ss}$ and $J_3 = j_3^{ss}$. A system is said to satisfy detailed balance when affinities vanish

$$A^1 = A^3 = 0. \quad (1.4)$$

These are known Kirchhoff's Voltage Laws. When both Kirchhoff's Current Law and Voltage Law hold, the system displays null entropy production, and we talk of an equilibrium steady state. Near the equilibrium steady state, the linear regime constitutive relations are now assumed: currents and forces are related by $a_e = \ell_e j_e^{ss}$, with ℓ_e a positive local (i.e., edge-by-edge) linear response coefficients. This regime corresponds to a small perturbation of an equilibrium steady state into a non-equilibrium steady state. We obtain for the macroscopic forces

$$\begin{aligned} A^1 &= \ell_1 j_1^{ss} + \ell_4 j_4^{ss} - \ell_5 j_5^{ss} = \overbrace{(\ell_1 + \ell_4 + \ell_5)}^{L^{11}} J_1 + \overbrace{(-\ell_5)}^{L^{13}} J_3 \\ A^3 &= \ell_2 j_2^{ss} + \ell_3 j_3^{ss} + \ell_5 j_5^{ss} = \overbrace{(\ell_2 + \ell_3 + \ell_5)}^{L^{33}} J_3 + \overbrace{(-\ell_5)}^{L^{31}} J_1. \end{aligned}$$

The right-and side defines the macroscopic linear response coefficients, which satisfy Onsager's reciprocity relations [29],

$$L_{13} = L_{31}.$$

Moreover, response coefficients satisfy

$$\det L \geq 0, \quad L = \begin{pmatrix} L_{11} & L_{13} \\ L_{31} & L_{33} \end{pmatrix}, \quad (1.6)$$

which corresponds to Eq.(1.3) in the original paper by Onsager [29], by him attributed to Boltzmann. So, affinities and internal currents are good thermodynamical observables.

Notice that the choice of J_1 and J_3 as boundary currents in terms of which all other steady state currents are expressed was arbitrary. A different equivalent choice would be, for example, $J_2 = j_2^{ss}$ and $J_5 = j_5^{ss}$. Solving Eqs.(1.2) we obtain $j_1^{ss} = j_4^{ss} = J_2 - J_5$, $j_3^{ss} = J_2$, and the entropy production now reads

$$\sigma[j^{ss}, a] = J_2 \overbrace{(a_1 + a_2 + a_3 + a_4)}^{A^2} + J_5 \overbrace{(-a_1 - a_4 + a_5)}^{A^5}, \quad (1.7)$$

where again we identified conjugate external forces. There is a simple graph-theoretical description of the internal currents and the affinities. With reference with Fig.1.1.b, notice that removing the edges e_1 and e_3 corresponding to the chosen boundary currents J_1 and J_3 yields a spanning tree, that is a set of edges which contains no cycles and which spans the graph. A spanning tree is such that when we add either e_1 or e_3 (which are called the chords of the spanning tree), a unique cycle is generated. Then the conjugate affinities A^1 and A^3 are defined as circuitations of the mesoscopic forces along the cycles. Similarly for the new currents and forces, which are defined starting from a different spanning tree (Fig.1.1.c). Obviously, the new currents can be expressed in terms of the old ones by a linear transformation. So can the new affinities in terms of the old ones,

$$A^2 = A^1 + A^3, \quad A^5 = -A^1.$$

These rules correspond to an intuitive composition of cycles, Fig.1.1.d. In particular, the property of detailed balance, Eq.(1.4), is independent of the set of fundamental observables (fundamental set) chosen.

The choice of a spanning tree allows to identify a set of conjugate variables characterizing nonequilibrium steady states. Affinities are circuitations, internal currents flow along preferred edges of the graph. Spanning trees arise in the theory in another very notable respect. We can now consider the linear regime with respect to J_2, A^2, J_5, A^5 . We do not perform the direct calculation explicitly. One can verify that the determinant of the new linear response matrix coincides with the one calculated in Eq.(1.6),

$$\begin{aligned} \det \begin{pmatrix} L_{11} & L_{13} \\ L_{31} & L_{33} \end{pmatrix} &= \det \begin{pmatrix} L_{22} & L_{25} \\ L_{52} & L_{55} \end{pmatrix} \\ &= l_1 l_2 + l_1 l_3 + l_1 l_4 + l_2 l_4 + l_3 l_4 + l_3 l_5 + l_2 l_5 + l_4 l_5. \end{aligned} \quad (1.8)$$

The homogeneous polynomial in the right-hand side is the so-called spanning co-tree polynomial. It is calculated by taking the product of the linear response coefficients along chords of trees, summing over all possible spanning trees that the graph admits. There are eight such trees in our example; they are depicted in Fig.1.6.

To resume, conservation laws at the nodes can be used to express the entropy production in terms of a certain number of boundary currents and of conjugate affinities, which are circulations of the mesoscopic forces along oriented cycles of the graph. Assuming the linear regime constitutive relations yields a symmetric linear response matrix between affinities and fundamental currents, satisfying Boltzmann's relation. Different choices of internal currents and of external forces can be performed by a graph-theoretical procedure, after we choose a spanning tree. However, the determinant of the linear response matrix is independent of the fundamental observables chosen.

An analogous (and, in a very precise sense, dual) theory can be developed for systems which satisfy detailed balance. Eqs.(1.4) furnish a criterion, due to Kolmogorov [30], for systems to satisfy detailed balance. A more physical criterion is that there exists a potential $(v_i)_{i \in V}$ defined over vertices, such that the mesoscopic affinities are potential drops between vertices

$$a_1^{db} = v_a - v_b, \quad a_2^{db} = v_b - v_c, \quad a_3^{db} = v_c - v_d, \quad a_4^{db} = v_d - v_a, \quad a_5^{db} = v_d - v_b.$$

For example, this is the case for electrical networks with no electromotive forces. The potential is determined up to a ground value $v_i \rightarrow v_i + u$; considering that there are four values of v_i , only three mesoscopic forces are independent. In fact Eqs.(1.4) can be used to express detailed balanced mesoscopic forces in terms of three boundary values, for example $A_2^* = a_2^{db}$, $A_4^* = a_4^{db}$ and $A_5^* = a_5^{db}$, with

$$a_1^{db} = A_5^* - A_4^*, \quad a_3^{db} = -A_2^* - A_5^*. \quad (1.9)$$

We call A_2^* , A_4^* and A_5^* macroscopic internal forces. We can plug these expressions into the entropy production to obtain

$$\sigma[j, a^{db}] = A_2^* \overbrace{(j_2 - j_3)}^{J_*^2} + A_4^* \overbrace{(j_4 - j_1)}^{J_*^4} + A_5^* \overbrace{(j_5 + j_1 - j_3)}^{J_*^5}. \quad (1.10)$$

Overbraces define the external macroscopic, or injected, currents. Let us develop the linear regime for detailed balance systems. Physically, in this

case, we perturb an equilibrium steady state into a detailed balance non-steady state, obtaining

$$\begin{pmatrix} J_*^2 \\ J_*^4 \\ J_*^5 \end{pmatrix} = L_* \begin{pmatrix} A_2^* \\ A_4^* \\ J_5^* \end{pmatrix} = \begin{pmatrix} \ell_2^{-1} + \ell_3^{-1} & 0 & \ell_3^{-1} \\ 0 & \ell_1^{-1} + \ell_4^{-1} & -\ell_1^{-1} \\ \ell_3^{-1} & -\ell_1^{-1} & \ell_1^{-1} + \ell_3^{-1} + \ell_5^{-1} \end{pmatrix} \begin{pmatrix} A_2^* \\ A_4^* \\ J_5^* \end{pmatrix}.$$

One can verify that the following relation between determinants of the response matrices holds,

$$\frac{\det L}{\det L_*} = \prod_e \ell_e. \quad (1.11)$$

Hence the linear response of steady states and of detailed balance systems out of equilibrium are related in a subtle way. The author has not yet gained a sufficient physical insight into Eq.(1.11), which could pose limits to the simultaneous optimization of the entropy production contributions.

While most of what has been said so far is collected from known facts in graph theory [31], electrical circuit theory [32], and the theory of Feynman diagrams [33], to our knowledge the forthcoming result might indeed be original. The following formula is crucial in that it paves the way to the results that will be discussed in the rest of this thesis. It turns out that the two expressions for the entropy production of steady state and detailed balanced systems (1.7,1.10) can be put together even for generic non-steady states of unbalanced systems,

$$\sigma[j, a] = \overbrace{J_1 A^1 + J_3 A^3}^{\sigma_{ss}[j, a]} + \overbrace{J_*^2 A_2^* + J_*^4 A_4^* + J_*^5 A_5^*}_{\sigma_{ab}[j, a]}, \quad (1.12a)$$

$$= j_1 a_1 + j_2 a_2 + j_3 a_3 + j_4 a_4 + j_5 a_5 \quad (1.12b)$$

where the fundamental set of macroscopic observables, internal and external currents and forces, is given by

$$\begin{aligned} J_1 &= j_1, & A^1 &= a_1 + a_4 - a_5, \\ J_3 &= j_3, & A^3 &= a_2 + a_3 + a_5, \\ J_*^2 &= j_2 - j_3, & A_2^* &= a_2, \\ J_*^4 &= j_4 - j_1, & A_4^* &= a_4, \\ J_*^5 &= j_5 - j_3 + j_1, & A_5^* &= a_5. \end{aligned}$$

Overbraces in Eq.(1.12a) define the steady entropy production and the transient (or detailed balance) entropy production. The steady entropy production vanishes for detailed balanced systems, the transient entropy production vanishes at steady states:

$$\sigma_{ss}[j, a^{db}] = 0 = \sigma_{db}[j^{ss}, a].$$

They both vanish at an equilibrium steady state.

In the linear regime, less intuitive result is that an analogous superposition holds if we express the entropy production in terms of the external observables,

$$\sigma[j, \ell j] = \sigma[\ell^{-1}a, j] = A^T L^{-1}A + J_*^T L_*^{-1}J_*, \quad (1.13)$$

where $A^T = (A^1, A^3)$ and $J_*^T = (J_*^2, J_*^4, J_*^5)$. We will show that external forces and external currents can be varied independently. The fact that there are no cross-terms in Eq.(1.13) is not obvious, and further supports the point of view that external forces and currents are fundamental macroscopic observables. Moreover, this expression allows to derive the minimum entropy production principle near equilibrium steady states, in two different, and dual, acceptations. Steady states minimize the entropy production at given fixed affinities, as the entropy production in the linear regime is a positive quadratic form, and setting the first variation to zero yields

$$\left. \frac{\delta\sigma[j, \ell j]}{\delta j} \right|_A = \frac{\delta\sigma[j, \ell j]}{\delta J_*} = 2L_*^{-1}J_* \equiv 0, \quad (1.14)$$

i.e., vanishing external currents. Analogously, detailed balanced systems minimize the entropy production at given fixed injected currents,

$$\left. \frac{\delta\sigma[\ell^{-1}a, a]}{\delta a} \right|_{J_*} = \frac{\delta\sigma[\ell^{-1}a, a]}{\delta A} = 2L^{-1}A \equiv 0. \quad (1.15)$$

Finally, there is a precise sense in which observables A, J are dual to observables J_*, A^* . We leave this topic to Sec.1.6.

1.2 Which system?

We append to the previous section some considerations on the notion of system and state. The task of identifying the correct states of a system

is delicate. One can always complete the system with further states so as to modify the definition of steadiness and balancing. An example will do. Suppose p_A and p_B are the populations of two sectors of the world: say, the Austral hemisphere and the Boreal hemisphere. Macroscopic internal currents between the two hemispheres are due to migrational fluxes. The force which drives migrational fluxes might be identified with – say – the wealth gap between the two hemispheres, $a_{AB} = v_B - v_A$, and we might suppose that to a first approximation the migrational flux is proportional to the wealth gap. The population of each hemisphere is also subject to nativity and mortality rates, which in this picture represent external currents. Then the steady state occurs when each state has equal nativity and mortality rates, and there is no migrational flux whatsoever. However, populations are also stationary when migrational fluxes are compensated by an excess natality in one hemisphere and an excess mortality in the other, in such a way as to keep the overall world population constant. Then one can complete the system with one further state C (where souls wait for reincarnation, or else for predestination/heavenly retirement). Natality and mortality can be seen as migrational fluxes to and from C , external currents become internal currents, and the notion of steady state is much broader, as it allows for the net circulation of non-null currents.

1.3 Algebraic graph theory in a nutshell

Roughly speaking, algebraic graph theory is graph theory where graph elements (edges, vertices, cycles, trees) are vectors, their incidence relations are matrices and enumeration problems can be turned into algebraic problems. All the elements of graph theory that we will employ in this section are re-elaborated from standard material. The author suggests the books by Biggs [31] and by Godsil-Royle [34]. Graphs can also be seen as skeletons of cell complexes; therefore, here and there some algebraic-topological considerations will come into play; in this perspective we referred to Giblin’s old book [35].

A graph (V, E) consists of a set V of vertices $i \in V$ that are pairwise connected by edges $e \in E$. Edges can be thought of as couples of vertices, $E \subseteq 2^V$. In the following we shall denote with V, E both the vertex and edge sets and their cardinality, without possibility of confusion. A graph might consist of more than one connected component when two or more subsets of

V are not joint by any edge; here we exclude this possibility and suppose that the graph is connected.

A graph *per se* is an abstract combinatorial object; however, some of the properties that we are going to discuss depend on the possibility to embed it in a plane (or more generally on an orientable surface) and on the peculiar way it is embedded. An embedding of a graph is a map that sends edges to continuous paths and vertices to points, in such a way that the images of two edges only cross at the image of a vertex. It is a standard result that any graph can be embedded in \mathbb{R}^3 ; those that can be embedded in \mathbb{R}^2 are called planar. Not all planar embeddings are topologically equivalent, in the sense that two embeddings of the same graph might not be continuously deformable one into the other, as Fig.1.2.a illustrates.

An arbitrary orientation can be assigned to each edge $e \in E$ (see Fig.1.3). An orientation is the choice of a source vertex $s(e)$ from which the edge emanates, and of a target vertex $t(e)$ at which the edge points. By inverting source and target one obtains the inverse edge $-e$. All the information about graph topology and edge orientation is resumed in the $V \times E$ incidence matrix ∂ with entries

$$\partial_i^e = \begin{cases} +1, & \text{if } \xleftarrow{e} i \\ -1, & \text{if } \xrightarrow{e} i \\ 0, & \text{elsewhere} \end{cases} . \quad (1.16)$$

When an orientation is chosen, we talk of an oriented graph $G = (V, E, \partial)$. Row-vectors of the incidence matrix will be denoted ∂_i . These vectors are not all independent: since each edge has exactly one source vertex (with matrix

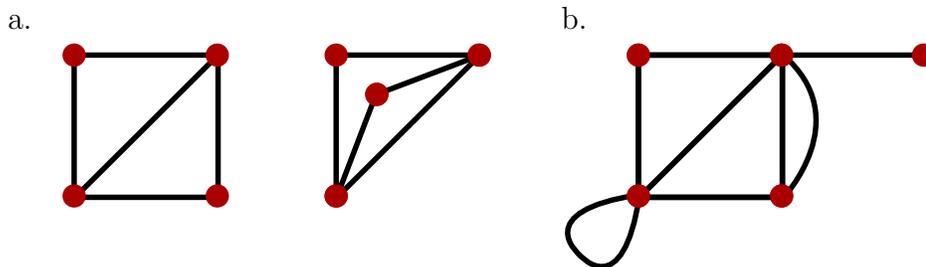


Figure 1.2: (a) Nonequivalent embeddings of the same graph in a plane. (b) A graph with a loop, a pendant edge and multiple edges.

entry -1) and one target vertex (with matrix entry $+1$), summing over all vertices gives zero

$$\sum_i \partial_i = 0. \tag{1.17}$$

Therefore the incidence matrix has at least one left eigenvector relative to eigenvalue zero. In fact, when G is connected it has exactly one such independent left eigenvector: it is a well-known fact that the rank of the incidence matrix of a connected graph is $V - 1$. The incidence matrix does not account for loops (edges whose source and target vertices coincide). We hypothesize that G is loopless for the moment. Instead, we allow for multiple edges between two given vertices (see Fig.1.2.b). The set of loop-less graphs and of viable incidence matrices coincide.

We now allow ourselves to take integer linear combinations of edges, and define a 1-chain (or simply a subgraph) of G an element of the additive group \mathbb{Z}^E . An example, with reference to Fig.1.3: we can graphically represent the integer linear combination $2e_1 - e_2$ by drawing two arrows for edge e_1 pointing towards its target vertex, according to the chosen convention on the orientation, and one arrow which runs opposite to e_2 . Notice that the algebraic representative of a collection of edge e_5 and its inverse — which we call an edge-cycle — gives a null 1-chain; we drew dotted edges.

In the following we shall need to perform linear algebra on vectors in \mathbb{Z}^E , even though strictly speaking \mathbb{Z}^E is not a vector space; we can always think of 1-chains as special vectors in \mathbb{R}^E which take integer components in the basis of individual oriented edges — rigorously speaking, we work on a lattice. The incidence matrix defines a linear operator that to any 1-chain

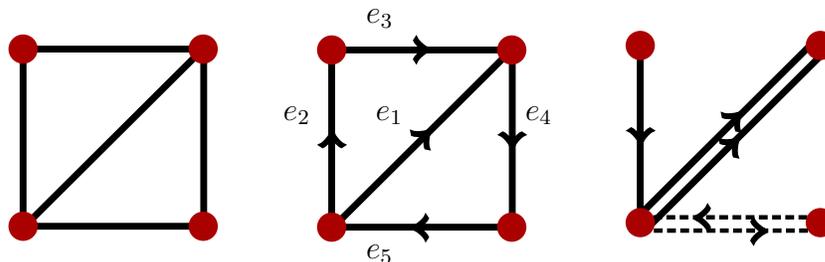


Figure 1.3: A graph, an arbitrary orientation, subgraph $2e_1 - e_2 + e_5 - e_5$.

$g \in \mathbb{Z}^E$ associates a linear combination of vertices in \mathbb{Z}^V (also called a 0-chain), which constitutes the boundary of g . The degree of a vertex in g is the number of outgoing edges minus the number of incoming ones,

$$\text{deg}_i g = \partial_i g.$$

The support $[g]$ of an oriented subgraph is obtained by replacing all oriented edges of g with their unoriented counterparts. We call the bare degree of i in g

$$\text{deg}_i[g] = \sum_{e \in g} [\delta_{s(e),i} + \delta_{t(e),i}],$$

which is simply the number of edges which are incident at a given vertex. A vertex is a leaf if it has bare degree one in E ; its only incident edge is said to be pendant (see Fig.1.2.b).

An oriented cycle c (or, simply, a cycle) is a subgraph whose vertices all have null degree in c , that is, it has null boundary. This means that for any incoming edge at a vertex, if any, there exists an outgoing one. This definition coincides with the algebraic condition

$$\partial c = 0. \tag{1.18}$$

Therefore, as vectors in \mathbb{R}^E , cycles belong to $C = \ker \partial$, which is a closed vector space called the cycle space. The dimension of C (which we also denote with C) is an important topological invariant of graphs called the cyclomatic number,

$$C = E - V + 1. \tag{1.19}$$

This formula follows from the rank-nullity theorem, which for any linear operator A on a E -dimensional vector space states that $\text{rk } A + \text{null } A = \dim E$. Applying the theorem to the incidence matrix, and considering that $\text{rk } \partial = V - 1$, we obtain the cyclomatic number. As elements of the additive group \mathbb{Z}^E , cycles belong to the first homology group of any embedding of G into \mathbb{R}^n . In this context the cyclomatic number is interpreted as the first Betti number, the zero-th Betti number being the number of connected components.

To summarize, the cyclomatic number is the maximum number of independent oriented cycles that are not edge-cycles; all others are integer combinations of these. Notice that the support of a cycle $[c]$ is a graph

whose vertices all have an even bare degree. In general, it might consist of multiple copies of the same edge and have crossings, that is, vertices of bare degree > 2 . If we restrict to vertices of bare degree 2 in $[c]$ we then talk of simple cycles, which are represented by multiplsets in $\{-1, 0, 1\}^E$. Simple cycles are not closed under addition, so that they do not form an additive group. However, we will mainly be interested in simple cycles, as we will show that there always exist basis for C consisting of simple cycles.

A simple cocycle (also called cut or bond in the literature) is a subgraph of G whose removal disconnects the vertex set. A simple cocycle is uniquely identified by the vertex set of one of the two components. If we orient all edges of a simple cocycle so that they emanate from vertices of one of the two components pointing towards vertices of the other, we obtain an oriented simple cocycle c_* ; we will omit to specify “oriented” from now on. A simple cocycle is uniquely identified by the source set $S(c_*) \subset V$; vice versa, the simple cocycle whose source vertex subset is $S \subseteq V$ will be denoted $c_*(S)$. Let us emphasize that, like for simple cycles, simple cocycles form a subset of $\{-1, 0, 1\}^E$ which is neither a vector space nor an additive group. Again, we can take linear combinations of simple cocycles to generate the cocycle vector space C_* . Vectors in C_* with integer entries are called cocycles. The number of simple cocycles in a connected graph is equal to the number of bipartitions of the vertex set. In general, they are not independent: the dimension of the cocycle space is $V - 1$. Let us sketch an argument proving this fact. An interesting addition law holds: the sum of two cocycles with disjoint source sets S_1 and S_2 , $S_1 \cap S_2 = \emptyset$, is the cocycle which emanates from the union $S_1 \cup S_2$ of the source sets. As a consequence, a cocycle with source $S = \cup_m \{i_m\}$ is the sum of the cocycles which emanate from single vertices $\{i_m\} \subset S$. These are not all independent though, since the cocycle

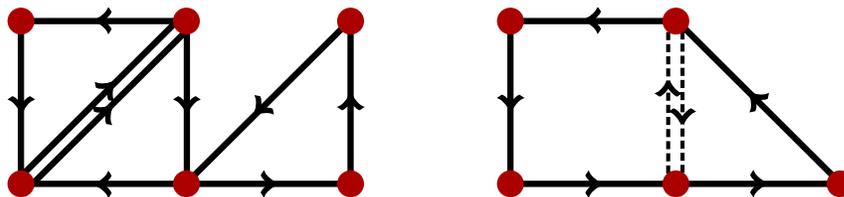


Figure 1.4: (a) An oriented cycle with multiple edges and crossing. (b) A simple cycle that is a linear combination of two simple cycles.

emanating from the full vertex set V is zero by definition

$$c_*(V) = 0. \tag{1.20}$$

A single-vertex-sourced cocycle $c_*(\{i\})$ is the sum of the oriented edges whose source is i . By definition of the incidence matrix, this coincides with the i -th row-vector of ∂ :

$$c_*(\{i\}) = \partial_i.$$

Notice that relation (1.20) implies that the sum of the rows of ∂ is null, confirming Eq.(1.17). This bounds the dimension of C_* to be at most $V - 1$ and further implies that the cocycle space is spanned by an arbitrary choice of $V - 1$ rows of the incidence matrix, which are linearly independent; hence the dimension of C_* is exactly $V - 1$.

Finally, we can prove the extremely important fact that cycles and cocycles are orthogonal with respect to the euclidean scalar product over the edge set

$$(g, g')_E := \sum_{e \in E} g_e g'_e.$$

Orthogonality follows from the definition of cycle, Eq.(1.18), which implies $(\partial_i, c) = 0$, and from the fact that the row vectors of the incidence matrix ∂_i span the cocycle space. We then have

$$C \perp C_*.$$

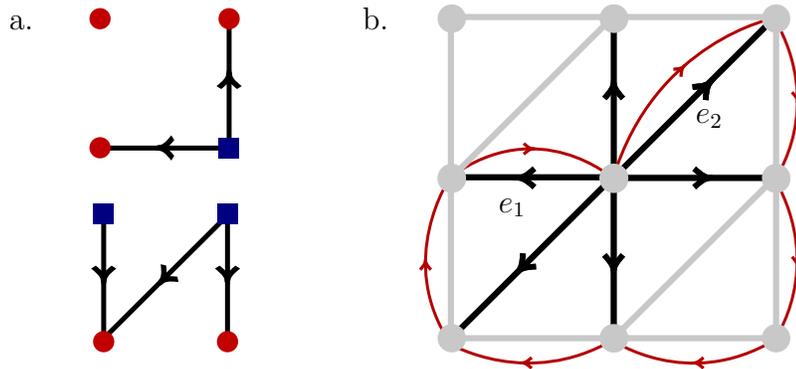


Figure 1.5: a) Two oriented cocycles. Squares and bullets respectively denote the source and target vertices. b) Superposition of a cycle and a cocycle.

Cycles and cocycles are independent and orthogonal, consistently with the formula for the cyclomatic number, Eq.(1.19). In algebraic terms, C is the kernel of ∂ , C_* is its co-image (or row space), whence orthogonality follows. Their dimensions are related by the rank-nullity theorem. From a graphical point of view, orthogonality of C and C_* means that a cycle and a cocycle can only share an even number of edges or none, half of them with the same orientation and half of them with opposite orientation. For example, in Fig.1.5.b the drawn cycle and cocycle share edge e_1 , in opposite direction, and e_2 , in concordant direction, hence their scalar product vanishes.

Let us summarize and generalize the relevant facts about cocycles. Let $S_1, S_2 \subset V$ be vertex subsets in G . The oriented cocycles which emanate from S_1 and S_2 obey the sum rule

$$c_*(S_2) + c_*(S_1) = c_*(S_1 \cup S_2) + c_*(S_1 \cap S_2). \quad (1.21)$$

Any choice of $V - 1$ rows of ∂ is a basis for the cocycle space,

$$C_* = \bigoplus_{m=1}^{V-1} \partial_{i_{\sigma(m)}},$$

where $\sigma : V \rightarrow V$ is an arbitrary permutation of the indices. Then $\dim C_* = V - 1$. The cycle and cocycle spaces furnish an orthogonal decomposition of the vector space of 1-chains,

$$\mathbb{R}^E = C \oplus C_*.$$

There's a standard procedure to construct suitable basis of simple cycles and cocycles. The basis we are going to construct are peculiar in that each element c^α or c_*^μ is uniquely associated to a different conjugate edge e_α or e_μ^* . We call these edges respectively chords and cochords. Moreover, oriented overlaps between cycles, cocycles, chords and cochords satisfy

$$(c^\alpha, e_\beta) = \delta_\beta^\alpha, \quad (e_\mu^*, c_*^\nu) = \delta_\mu^\nu, \quad (c^\alpha, c_*^\mu) = 0, \quad (e_\mu^*, e_\alpha) = 0. \quad (1.22)$$

A basis of simple cycles and cocycles which come with a set of conjugate chords and cochords satisfying these relations will be called a fundamental set. Spanning trees allow to generate fundamental sets. A spanning tree is a subset T of the edge set of a graph which satisfies the following properties:

- Contains no cycles;

- Has $V - 1$ edges;
- Connects all vertices.

Any two of the above suffice to characterize a spanning tree (see Fig.1.6). Spanning trees are a fundamental ingredient in many different respects in this thesis work. They allow to define a basis of fundamental observables, to express the determinant of the linear response matrices, to write an explicit expression for the steady state of the master equation (see Ch.5). The following recipe generates cycles of a fundamental set:

- (i) Choose a spanning tree T ;
- (ii) Add one of the remaining oriented edges e_α (called a chord): this will produce exactly one cycle;
- (iii) Remove all edges which do not belong to the cycle;
- (iv) Orient all edges in the cycle along the direction of e_α to obtain an oriented cycle c^α .

A similar procedure can be used to generate cocycles of a fundamental set starting from the same spanning tree T :

- (i') Define the cotree $T^* = E \setminus T$ as the complement of T in E ;
- (ii') Add to T^* one of the remaining oriented edges e_μ^* (called a cochord): this will produce exactly one cocycle;

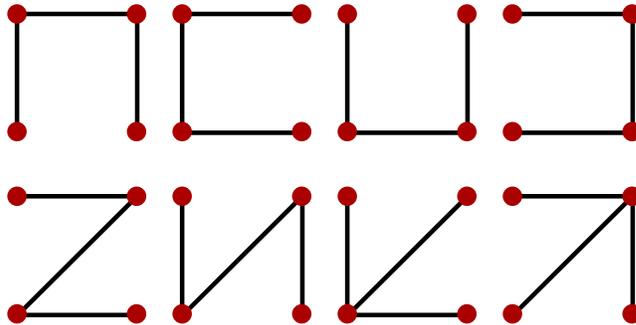


Figure 1.6: All possible spanning trees of the graph in Fig.1.3.

- (iii') Remove all edges which do not belong to the cocycle;
- (iv') Orient all edges in the cocycle accordingly with e_μ^* so to get an oriented cocycle c_μ^* .

Seen from another perspective, a set of cocycles is found by removing one edge of the spanning tree at a time, thus disconnecting the vertex set into two components. Then the cocycle generated is that which connects the two components. In Fig.1.7 we give a graphical step-by-step construction of a fundamental set of cycles and cocycles. The fundamental sets of cycles and cocycles defined above form a basis respectively for C and C_* .

$$C = \bigoplus_{\alpha=1}^{E-V+1} c^\alpha, \quad C_* = \bigoplus_{\mu=1}^{V-1} c_\mu^*.$$

By construction, these are in fact fundamental sets as they satisfy the relations in Eq.(1.22). Interestingly, besides these relations, another interesting superposition rule holds:

$$(c^\alpha, e_\mu^*) + (c_\mu^*, e_\alpha) = 0, \tag{1.23}$$

that is, if cycle α contains cochord e_μ^* , then cocycle c_μ^* contains chord e_α . In fact, notice that a fundamental cycle contains one chord and several cochords, and that a cocycle contains one cochord and several chords. The source and

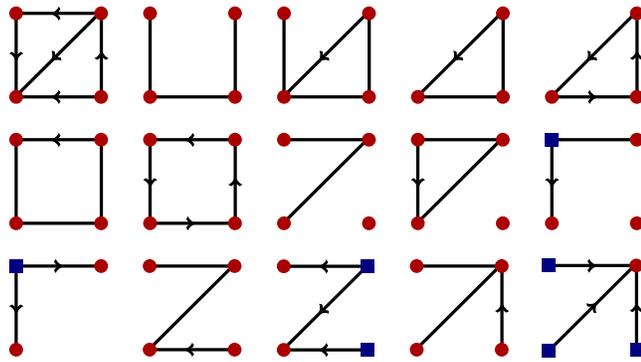


Figure 1.7: Constructing fundamental sets: an arbitrary orientation is assigned, then steps (i), (ii), (iii), (iv), (ii), (iv), (i'), (ii'), (iii'), (iv'), (ii'), (iv'), (ii'), (iv') described above are performed.

target vertices of a chord e_α either belong to distinct source and target subsets of a cocycle c_*^μ , or else they belong to the same sets. In the second case, c^α and c_*^μ do not overlap, as c^α cannot contain the generating cochord e_μ^* : if it did, then c^α and c_*^μ should share another edge, which is not e_α and which cannot be another cochord (as every cocycle only contains one cochord); therefore it should be another chord, and c^α would contain two different chords, which is impossible. The same argument holds when c^α and c_*^μ do overlap.

Using the sum rules for cocycles we can produce explicit transformation formulas from a fundamental set to the incidence matrix rows,

$$c_*^\mu = \sum_{i \in S(c_*^\mu)} \partial_i^T, \quad (1.24a)$$

$$\partial_i^T = \sum_{\substack{\mu: \\ i \in S(c_*^\mu)}} c_*^\mu - \sum_{\substack{\nu: \\ i \in V \setminus S(c_*^\nu)}} c_*^\nu. \quad (1.24b)$$

We now give a general summary of the definitions of this section and the construction of a fundamental set of cycles/cocycles. Let $G = (V, E, \partial)$ be a connected graph with V vertices $i \in V$ and E edges $e \in E$. Edges carry an arbitrary orientation (a choice of source and target vertices), with $-e$ designating the inverse edge. With the exception of loops, the topology of the graph is completely described by the incidence matrix, Eq.(1.16). We use a rather algebraic approach to graph theory, working with integer linear combinations of edges in the lattice \mathbb{Z}^E , upon which ∂ acts as a boundary operator. It is a standard result that ∂ induces an orthogonal decomposition of $\mathbb{Z}^E = C \oplus C_*$ into the cycle space $C = \ker(\partial)$ and the cocycle space $C_* = \text{rowspace}(\partial)$. The dimension of the cycle space is given by the cyclomatic number $C = E - V + 1$, whence by the rank-nullity theorem the cocycle space has dimension $V - 1$.

From a graphical point of view, cycles c are chains of oriented edges such that each vertex is the source and the target of an equal number of edges (possibly none). It is simple if it is connected, has no crossings or overlapping edges. A simple cycle can exist in two opposite orientations. A simple cocycle c_* is a collection of edges whose removal disconnects the vertex set into two components; it might carry one of two possible orientations when all edges point from one of the two components, called the source set $S(c_*)$, towards the other. Of all possible integral basis of \mathbb{Z}^E , we concentrate on fundamental sets, which satisfy the algebra of relations in Eq.(1.22). Fundamental sets are generated starting from a spanning tree. Let $T \subseteq E$ be a spanning tree of

the graph, i.e. a maximal subset of E containing no cycles; we call its edges e_μ^* the cochords. The remaining edges $e_\alpha \in E \setminus T$ are called chords. There are $V - 1$ cochords and C chords. When a chord e_α is added to a spanning tree, a simple cycle c^α is generated, which can be oriented accordingly with e_α . The fundamental set of cycles $\{c^\alpha\}_\alpha$ so generated is a basis for C . Similarly, when a cochord e_μ^* is removed, the spanning tree is disconnected into two components, which identify a simple cocycle c_μ^* , with orientation dictated by e_μ^* . Again, the fundamental set of cocycles $\{c_\mu^*\}_\mu$ is a basis for C_* . The crucial peculiarity of fundamental sets is that no chord is shared by two cycles, and no cochord is shared by two cocycles. Moreover, any of the sets $\{e_\alpha, e_\mu^*\}$, $\{c^\alpha, e_\mu^*\}$, $\{c^\alpha, c_\mu^*\}$, $\{e_\alpha, c_\mu^*\}$ forms a basis for \mathbb{Z}^E .

We conclude this section with an inessential question: how many different choices of fundamental basis there exist? Notice that a set of cycles can be generated by more than one spanning tree, and the same is true of the cocycle space. Moreover, not all collections of independent simple cycles and cocycles can be generated starting from a spanning tree; a simple calculation shows that there are 3 possible cycles in the example graph and 6 possible cocycles (with connected source sets), which would give $18 > 8$ combinations. We conjecture that fundamental sets are one-to-one with spanning trees (up to orientation of the chords and cochords). Find in Fig.(1.8) an example of a basis of simple cycles and cocycles which is not a fundamental set, and which cannot be generated starting from a spanning tree.

The matrix-tree theorem (see Sec.5.1) states that the number of spanning trees in a graph is given by the product of the non-null eigenvalues $\{\lambda_i\}_{i=1}^{V-K}$ of the Kirchhoff matrix $\Delta = \partial\partial^T$, where T denotes matrix transposition. They coincide with the non-null eigenvalues of the co-Kirchhoff matrix $\Delta' = \partial^T\partial$

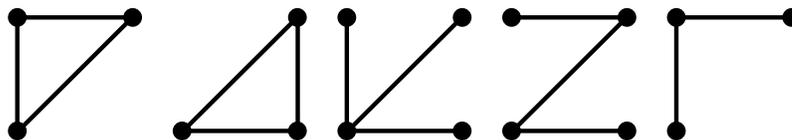


Figure 1.8: A basis of simple cycles and cocycles which is not a fundamental set. Notice that the third cocycle is not associated to its own cochord.

(our definition). We have

$$\# \text{ (fund. sets) } = \prod_{i=1}^{V-K} \lambda_i,$$

where we momentarily allow for K disconnected components. Let us detour a little. We redefine $\partial_1 = \partial$. Let V_1, \dots, V_K be the sets of vertices of the disconnected components of a graph. We introduce the $V \times K$ boundary operator ∂_0 which assigns each vertex to its component:

$$(\partial_0)_k^i = \begin{cases} 1, & \text{if } i \in V_k \\ 0, & \text{if } i \notin V_k \end{cases}.$$

It is such that $\partial_0 \partial_1 = 0$ (the boundary of a boundary is zero). Then we can start building an exact sequence of vector spaces

$$\mathbb{R}^K \xleftarrow{\partial_0} \mathbb{R}^V \xleftarrow{\partial_1} \mathbb{R}^E$$

such that $\text{im } \partial_1 = \ker \partial_0$. The homology groups of G are defined to be $H_j(G) = \ker \partial_j$. Then we have a topological characterization of the cycle space as an homology group. We are now able to introduce one special case of a powerful tool which in algebraic topology takes the name of laplacian (analogous to a discretized Hodge laplacian),

$$\Delta_0 = \partial_0^T \partial_0 + \partial_1 \partial_1^T.$$

By construction it is a non-degenerate $V \times V$ matrix. The matrix-tree theorem then states that the number of spanning trees is given by

$$\# \text{ (fund. sets) } = \frac{\det \Delta_0}{\prod_k |V_k|^2}.$$

The point of Schnakenberg's theory is that the physically relevant observables are defined over fundamental sets. However, there are many ways to choose the set of observables with which to describe the system; this is a sort of gauge freedom, and one can fix the gauge by choosing a preferred spanning tree and an orientation. It is no novelty in physics that the number of ways by which one can fix the gauge is given by the determinant of a laplacian operator: think for example of the Faddeev-Popov determinant in QFT. In that case the measure over the group orbits is complicated by the non-abelian

structure group. The abelian nature of our theory (i.e. the fact that we are dealing with observables which are real numbers) makes the counting purely topological. Were we to construct a functional integral for our theory, we could easily factor out the determinant and absorb it into the normalization constant.

1.4 Mesoscopic and macroscopic observables

A system has a finite set of states V . A couple of states might exchange “information” in the form of a current j_e , whose flow is ignited by a conjugate force a_e ; here e ranges over all possible ordered couples of states which communicate.

We suppose that both real-valued variables are skew-symmetric under reversal of the order in which the states are considered, that they have the same sign, that when forces vanish currents vanish altogether, and that when forces are small, currents are small and they are linearly related to their corresponding forces in a local way, i.e., edge-by-edge.

All of these assumptions are verified for the simplest special example of an electrical network, where forces are voltage differences between nodes of a circuit or electromotive forces, and they are linearly related to currents via Ohm’s law. Motivated by this analogy, we define the entropy production as

$$\sigma = \sum_e a_e j_e, \tag{1.25}$$

quantifying the amount of dissipation.

To resume, along the edges of an oriented graph $G = (V, E, \partial)$, we introduce:

- (i) Real mesoscopic currents, antisymmetric by edge inversion, $j_{-e} = -j_e$;
- (ii) Antisymmetric real conjugate forces $a_e = -a_{-e}$, with $\text{sign } a_e = \text{sign } j_e$;
- (iii) The entropy production (rate)

$$\sigma[j, a] = \sum_e j_e a_e = (j, a)_E. \tag{1.26}$$

Here and there, we will adopt in this section a geometrical jargon borrowed from discrete differential geometry [36,37]. Being antisymmetric, mesoscopic

currents and forces are discrete differential 1-forms; the entropy production is a scalar. The scalar product is the inner product of 1-forms, induced by Hodge's duality. This implies that either the current or the affinity are the Hodge duals of some more primitive quantities. We will discuss this briefly in Sec.1.5.

We choose a spanning tree T , which comes with a fundamental set of simple cycles and cocycles. We define the macroscopic observables:

$$\text{internal currents : } J_\alpha = (e_\alpha, j); \quad (1.27a)$$

$$\text{external forces : } A^\alpha = (c^\alpha, a); \quad (1.27b)$$

$$\text{external currents : } J_*^\mu = (c_*^\mu, j); \quad (1.27c)$$

$$\text{internal forces : } A_\mu^* = (e_\mu^*, a). \quad (1.27d)$$

More explicitly,

$$J_\alpha = j_{e_\alpha}, \quad A^\alpha = \sum_{e \in c^\alpha} a_e, \quad J_*^\mu = \sum_{e \in c_*^\mu} j_e, \quad A_\mu^* = a_{e_\mu^*}. \quad (1.28)$$

Internal currents flow along fundamental chords, external currents are the total flow out of the source set of a cocycle, external forces are circuitations of forces along the fundamental cycles, internal forces are exerted along the internal edges of the spanning tree. We will also refer to external forces as affinities, for reasons that will become clear in Ch.4. Internal variables are local, in that they are defined edge-wise, while external variables are non-local and additive. For this reason one might also refer to the former as intensive variables and to the latter as their conjugate extensive variables.

We say that a system is in a steady state when Kirchhoff's Law holds

$$\partial j^{ss} = 0. \quad (1.29)$$

From a geometrical viewpoint, we might say that j^{ss} is divergenceless. Steady-state currents belong to the kernel of the incidence matrix. We know from the discussion in the previous section that there exists a cyclomatic number of boundary currents J_α such that

$$j^{ss} = J_\alpha^{ss} c^\alpha, \quad (1.30)$$

where repeated indices are implicitly summed over. Notice that we assume Einstein's convention on index contraction when working with macroscopic

observables. The J_α^{ss} 's are steady macroscopic internal currents. By the orthogonality relations Eq.(1.22), projecting the steady mesoscopic current (1.30) along chord e_α yields

$$J_\alpha^{ss} = (e_\alpha, j^{ss}),$$

consistently with Eq.(1.27a). A condition equivalent to Kirchoff's Law (1.29) is the vanishing of all external macroscopic currents (1.27c),

$$J_*^{\mu,ss} = (c_*^\mu, j^{ss}) = 0. \quad (1.31)$$

Plugging Eq.(1.30) into the entropy production, we obtain

$$\sigma[j^{ss}, a] = (a, j^{ss})_E = A^\alpha J_\alpha^{ss} \quad (1.32)$$

This is Schnakenberg's main result: entropy production at the steady state can be expressed in terms of macroscopic conjugate variables. Out of the steady state, Eq.(1.32) suggests the definition of the steady state contribution to the entropy production

$$\sigma_{ss}[j, a] := A^\alpha J_\alpha. \quad (1.33)$$

The (environmental influence on a) system is said to satisfy detailed balance when the affinities vanish,

$$A^{\alpha,db} = (c^\alpha, a^{db}) = 0.$$

In geometrical terms, we say that a^{db} is a closed 1-form (its curl vanishes). As we saw in Sec.1.1, by the Kolmogorov criterion vanishing of the affinities is equivalent to the existence of a potential, or in other words a^{db} is also an exact 1-form. On a graph, closed 1-forms are exact (there is no topology at work). By the orthogonality between cycles and cocycles, it follows that detailed balance forces are a linear combination of cocycles,

$$a^{db} = \sum_\mu A_\mu^{*db} c_*^\mu. \quad (1.34)$$

Plugging into the entropy production yields

$$\sigma[j, a^{db}] = A_\mu^{*db} J_*^\mu.$$

Out of the detailed balance class of systems, we call the transient contribution to the entropy production the term

$$\sigma_{db}[j, a] := A_\mu^* J_\mu^*$$

On the one hand, entropy production boils down to the steady entropy production when the system is in a steady state. On the other, it becomes the transient entropy production when the system satisfies detailed balance. In fact, the entropy production always splits in these two contributions

$$\sigma[j, a] = \sigma_{ss}[j, a] + \sigma_{db}[j, a]. \quad (1.35)$$

This is the central result of this chapter, and possibly of the whole thesis. It is a significative extension of Schnakenberg's original result Eq.(1.32). We now furnish the proof. The strategy is to find the general solution to the following continuity equation with sources

$$\dot{p} + \partial j = 0, \quad (1.36)$$

where \dot{p}_i is the current injected at vertex i . Such currents are constrained by $\sum_{i \in V} \dot{p}_i = 0$. Since any $V - 1$ rows of ∂ span the cocycle space, \dot{p}_i is expressible as a linear combination of a fundamental set of external currents, and vice versa. Given the identities (1.24a), one obtains

$$J_\mu^* = - \sum_{i \in S(c_\mu^*)} \dot{p}_i. \quad (1.37)$$

The flow out of a source set is equal to (minus) the sum of the injected currents at the vertices of the set. The general solution of Eq.(1.36) can be found as a particular solution plus the general solution of the homogeneous equation associated to it. Solving $\partial j = 0$ yields a superposition of cycles $\sum_\alpha \lambda_\alpha c^\alpha$. We look for a particular solution such that the internal currents along chords vanish, $(e_\alpha, j) = 0$. Since chords and cochords are a basis for the edge set, we only need to specify the particular solution along cochords, obtaining

$$j = \lambda_\alpha c^\alpha + \lambda_\mu^* e_\mu^*. \quad (1.38)$$

Inserting Eq.(1.38) into the definitions Eqs.(1.27), and using the orthonormality relations Eq.(1.22), we identify $J_\alpha = \lambda_\alpha$, and $J_\mu^* = \lambda_\mu^*$. Plugging this solution into Eq.(1.26) yields

$$\sigma[j, a] = \sum_\alpha A^\alpha J_\alpha + \sum_\mu A_\mu^* J_\mu^*.$$

This proves our result. Notice that Eq.(1.38) reads

$$j = J_\alpha c^\alpha + J_\mu^* e_\mu^*. \quad (1.39)$$

Similarly, for the affinities the following expression is found:

$$a = A_\mu^* c_\mu^* + A^\alpha e_\alpha. \quad (1.40)$$

1.5 Discretizing continuous theories

Let us briefly go back to the geometrical interpretation of edge variables as differential forms. We might suppose that our theory is a discretized version of a more general continuous theory on a manifold M , with $\dim M = m$. We choose $m = 3$ for ease. Typically a continuity equation reads $\dot{p} + dj$, where d is the exterior differential, p is a volume form $p = p(x)dx^1 \wedge dx^2 \wedge dx^3$, and $j = \varepsilon_{ijk} j^i(x)dx^j \wedge dx^k$ is a 2-form. We introduce the conjugate force 1-form $a = a_i(x)dx^i$. The wedge product \wedge allows to compose a k_1 -form with a k_2 -form returning a $(k_1 + k_2)$ -form. Then $j \wedge a$ is a volume form, and it can be integrated over the manifold to yield the entropy production

$$\sigma = \int_M a \wedge j.$$

We now inscribe a three-dimensional lattice L in M , consisting of volumes v separated by surfaces s which share edges e which meet at vertices i . As j has the meaning of a current and it is a 2-form, it can be integrated over surfaces

$$j_s = \int_s j = \int_s \vec{j} \cdot \hat{n}_\Sigma d\Sigma, \quad (1.41)$$

where $\vec{j} = (j^1, j^2, j^3)$, $d\Sigma$ is the area element, \hat{n}_Σ is the normal to the area element and we used the euclidean scalar product. Notice that the scalar product allows to represent the 2-form as a vector by virtue of Hodge duality. The current j_s has the obvious meaning of total flux of current out of surface s . By contrast, a 1-form's destiny is to be integrated over edges. Therefore we define

$$a_e = \int_e a = \int_e \vec{a} \cdot \dot{\gamma}_t dt,$$

where $\dot{\gamma}_t$ is the tangent vector to the curve at time t .

To define the current along an edge we need to turn to the dual lattice L^* . We draw a vertex i_v^* within each volume v , an edge e_s^* puncturing each surface s , a surface s_e^* punctured by each edge and a volume v_i^* surrounding each vertex i . Then there is a one-to-one correspondence between dual elements of the two lattices, and we can finally define

$$j_e = \int_{s_e^*} j$$

and discretize the entropy production according to

$$\sigma \approx \sum_e a_e j_e.$$

Duality will be the subject matter of the next section. In that case, we restrict to planar graphs (2-dimensional manifolds) and only touch on possible generalizations. It is a work in progress of the author to generalize the complete Schnakenberg's analysis to higher-dimensional lattices (or, more generally, cellular complexes) and to put the geometrical discretization at work for the actual discretization of diffusion equations (Fokker-Planck). The development of such procedure would be more than an academic exercise, as the geometrical discretization maintains the affinities,

$$\oint_{c^\alpha} a = \sum_{e \in c^\alpha} a,$$

so that the thermodynamical character of the theory would be respected.

1.6 Duality of graphs

A graph is planar if it can be drawn on a plane (or, equivalently, on the surface of a sphere) with non-intersecting edges, but at vertices. Planar embeddings are characterized by vertices, edges and faces $f \in F$, which are open neighbors of the plane which cannot be path-connected without crossing an edge. One "outer" face f_F surrounds the full graph; all other "inner" faces $f_m, m < F$ are bounded by cycles of the graph. On the surface of a sphere, there is no difference between inner and outer faces. Euler's formula in algebraic topology prescribes the number of faces to be

$$F = E - V + 2.$$

The dual graph $G^* = (V^*, E^*, \partial^*)$ is obtained with a simple graphical procedure. Draw a dual vertex within each face, including the outer face. If two faces share an edge e at their boundary, draw a dual edge e^* between their correspondent vertices. The dual edge e^* crosses e : to assign an orientation, counterclockwise rotate e until it overlaps with e^* (see Fig.1.9.a). The resulting graph has F vertices connected by E edges. Edges are sent to edges, faces to vertices and vertices to faces.

Crucial facts about the duality transformation $*$ are:

- (i) Up to a reorientation $E \rightarrow -E$, it is involutive;
- (ii) Different embeddings might yield non-isomorphic duals (with different incidence relations);
- (iii) Duality maps the cycle space to the cocycle space, and vice versa. Moreover, it maps a spanning tree T to the complement $T^* = E \setminus T_*$ of a spanning tree $T_* \subseteq E^*$, in such a way that the fundamental sets generated by T_* are the duals of the fundamental sets generated by T , according to the scheme (see Fig.1.9.b)

chords \leftrightarrow cochords,
cycles \leftrightarrow cocycles.

So far we listed a few facts about duality. We now give a more detailed algebraic characterization. An orientation can be assigned to each face f ,

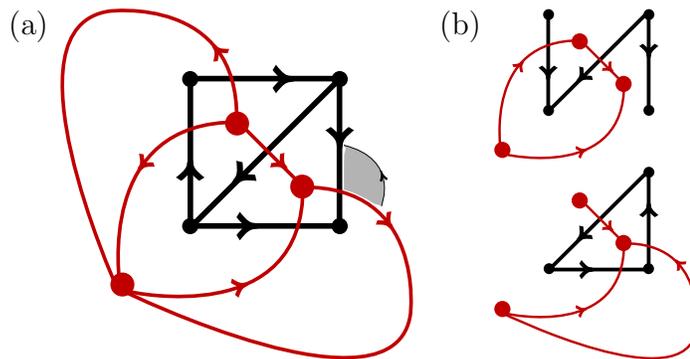


Figure 1.9: (a) The dual graph; the grey angle depicts the assignment of an orientation to a dual edge. (b) The dual of a cocycle and of a cycle.

either clockwise (denoted \circlearrowright) or counterclockwise (denoted \circlearrowleft). An oriented edge which belongs to the boundary of f can be concordant to f if, intuitively, its direction is tangent to the orientation of f ($e \downarrow_{\circlearrowright} f$ or $e \uparrow_{\circlearrowleft} f$), or opposite to it ($e \uparrow_{\circlearrowright} f$ or $e \downarrow_{\circlearrowleft} f$). Let us pick for definitiveness all counterclockwise orientations. We define the face-edge incidence matrix

$$(\partial_2)_e^f := \begin{cases} +1, & e \downarrow_{\circlearrowleft} f \\ -1, & e \uparrow_{\circlearrowleft} f \\ 0, & \text{elsewhere} \end{cases}$$

which can be thought of as an operator on the vector space \mathbb{R}^F of linear combinations of oriented faces that yields their oriented boundary. In fact, the f -th column $\partial_2^f = \partial_2 f$ is an oriented cycle. On the other hand, every oriented cycle is the boundary of some oriented inner face; since $C = F - 1$ we conclude that

$$\text{im } \partial_2 = C = \ker \partial_1, \quad (1.42)$$

where we renamed the incidence matrix $\partial_1 := \partial$. By the rank-nullity theorem we know that $\dim \ker \partial_2 = F - C = 1$. In fact each edge belongs to the boundary of exactly two faces, with which it is in opposite relative orientation. Each row of the boundary operator then has only two non-null elements, one +1 and one -1, so that

$$\sum_f (\partial_2)_e^f = 0. \quad (1.43)$$

This property also reflects the fact that the boundaries of the inner faces are all independent, while the boundary of the outer face is inverse to the sum of the boundaries of the inner faces. The crucial fact is that ∂_2^T is a good incidence matrix. We then define the dual graph G^* to be that graph whose incidence matrix is²

$$\partial_1^* := \partial_2^T.$$

²From a slightly formal point of view, along with matrix ∂_0 defined at the end of Sec.1.3, we can define the $F \times 1$ matrix $\partial_3 = (1, \dots, 1)$, such that $\partial_3 \partial_2 = 0$. Then we have an exact sequence of vector spaces

$$0 \xleftarrow{\partial_0} \mathbb{R}^V \xleftarrow{\partial_1} \mathbb{R}^E \xleftarrow{\partial_2} \mathbb{R}^F \xleftarrow{\partial_3} 0, \quad (1.44)$$

meaning that $\ker \partial_m = \text{im } \partial_{m+1}$. Taking the transpose of $\partial_m \partial_{m+1} = 0$, we obtain $\partial_{m+1}^T \partial_m^T = 0$. Duality inverts the sequence.

Notice that this characterization of duality retains no information on loops, which are dual to pendant edges, as Fig.1.10.a shows. From a thermodynamical point of view, loops and pendant edges are redundant and inessential, and can be eliminated. In Fig.1.10.b it is shown how different embeddings might give rise to non-isomorphic duals.

Both by graphical or algebraic construction, it is straightforward that the dual of cycle ∂_2^f which encloses face f is the collection of edges which emanate from the dual vertex f^* ; therefore, it is a cocycle of the dual graph. Since there are $F - 1$ independent cocycles in G^* and $F - 1$ independent cycles in G , we can already conclude that the dual of the cycle space of a graph is the cycle space of the dual graph and the other way around,

$$C_*(G) = C(G^*), \quad C(G) = C_*(G^*).$$

There is a tight correspondence between simple cycles and simple cocycles. A clockwise oriented simple cycle c encloses a surface which is a composition of clockwise-oriented faces; a counterclockwise oriented cycle can be seen as enclosing the outer faces, with respect to which it is in concord relative orientation. In both cases such cycle is defined by the set of enclosed faces, which we can denote $S^*(c)$. Viceversa, we write $c(S^*)$ to indicate the cycle enclosing $S^* \subset F$. Let $S_1^*, S_2^* \subset F$ be face subsets in G . The oriented cycles which enclose S_1^* and S_2^* obey the sum rule

$$c(S_2^*) + c(S_1^*) = c(S_1^* \cup S_2^*) + c(S_1^* \cap S_2^*).$$

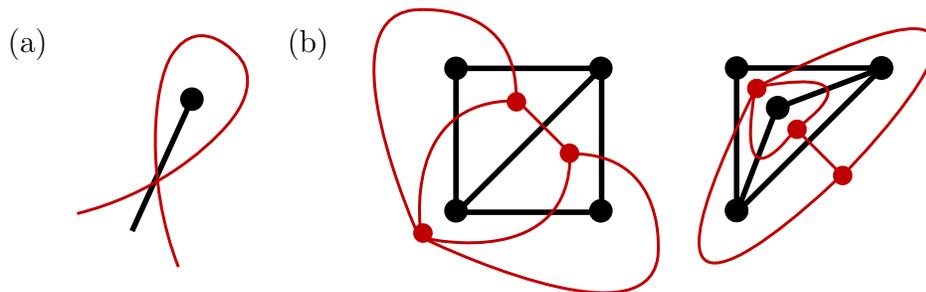


Figure 1.10: (a) The dual of a pendant edge is a loop. (b) Different embeddings give rise to nonisomorphic dual graphs (no degree-4 vertex in the first example, one degree-4 vertex in the second).

This is exactly the same rule as Eq.(1.21) for cocycles. Then not only are the cycle and cocycle space dual one to the other, but each simple cycle is dual to one simple cocycle. The same holds for spanning trees and for cotrees, and therefore for the fundamental basis of cycles and cocycles [33].

Not all graphs can be embedded on the plane or, equivalently, on the surface of a sphere. The two important examples are the complete graph on five vertices K_5 and the complete bipartite graph on 6 vertices, $K_{3,3}$ (see Fig.1.11.a), which are the cornerstones of any non-planar graph as implied by Kuratowski's and Wagner's theorems. However, both these graphs can be embedded in a torus with non-intersecting edges (see Fig.1.11.b). In fact, every graph can be embedded on an orientable (Riemann) surface of high enough genus [38]. The lowest-genus surface defines the genus g of the graph. Euler's formula dictates the number of faces:

$$F = E - V + 2 - 2g.$$

1.7 Linear regime

One major clue that led Schnakenberg to the identification of chords and cycles as good conjugate thermodynamic observables is the fact that, in the linear regime, Onsager's reciprocity relations arise. By "linear regime" it is meant that mesoscopic currents and forces satisfy Ohm's law

$$a = \ell j + O(j^2), \tag{1.45}$$

where

$$\ell = \text{diag}\{\ell_1, \dots, \ell_E\}, \quad \ell_e > 0,$$

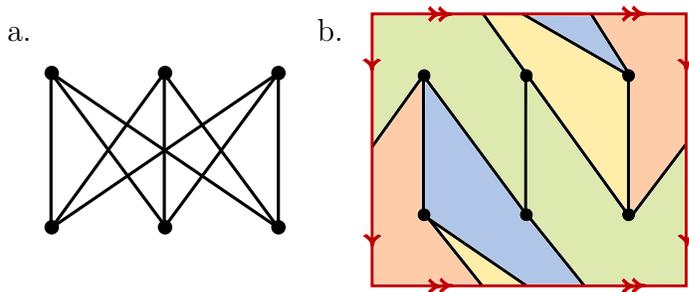


Figure 1.11: (a) The nonplanar graph $K_{3,3}$. (b) An embedding of $K_{3,3}$ in a torus (opposite sides of the bounding rectangle are identified).

is a positive local linear response matrix. By “local” we mean that ℓ is diagonal, that is, that linearly perturbed currents and forces depend on each other edge-by-edge. There are three acceptance of linear regime that we will focus on, separately:

- (i) A system, initially at an equilibrium steady state, is perturbed to a nearby nonequilibrium steady state, while the macroscopic external currents are held fixed

$$J_*^\mu = 0.$$

- (ii) A system is in a non-steady state near the equilibrium steady state and its affinities satisfy detailed balance

$$A^\alpha = 0.$$

- (iii) Linear regime with no constraints.

Schnakenberg only referred to the first case. He furnished the macroscopic linear relation $A^\alpha = L^{\alpha\beta} J_\beta$, proving that the matrix $L = (L_{\alpha\beta})_{\alpha,\beta}$ is symmetrical. In our algebraic formalism the derivation is straightforward. Using the definition of the macroscopic affinity Eq.(1.27b) and the integrated Kirchhoff’s Current Lat, Eq.(1.30), we obtain

$$A^\alpha = (c^\alpha, \ell j) = L^{\alpha\beta} J_\beta, \tag{1.46}$$

where

$$L^{\alpha\beta} := (c^\alpha, \ell c^\beta) \tag{1.47}$$

are the phenomenological coefficients. We will call L the resistance matrix. The resistance matrix is a weighted superposition of cycles. It is obviously symmetrical, hence it satisfies Onsager’s relations. For master equation systems, this insight is complemented by Andrieux and Gaspard’s proof of a Green-Kubo-type of formula for L [16].

Case (ii) is analogous. Definition (1.27c) and Eq.(1.34) yield

$$J_*^\mu = (c_*^\mu, \ell^{-1} a) = L_*^{\mu\nu} A_\nu^* \tag{1.48}$$

where

$$L_*^{\mu\nu} := (c_*^\mu, \ell^{-1} c_*^\nu)$$

is the symmetrical response matrix, which we call the conductance matrix.

The response matrices L and L_* are Gramian matrices: their entries are non-degenerate scalar products of collections of vectors. Gramian matrices are always positive semi-definite. Their determinant is non-null if and only if the vectors are linearly independent. The determinant of a Gramian matrix is the square of the volume of the parallelotope formed by these vectors,

$$\sqrt{\det L} = \|v^1 \wedge \dots \wedge v^{E-V+1}\| > 0, \quad (1.49a)$$

$$\sqrt{\det L_*} = \|v_*^1 \wedge \dots \wedge v_*^{V-1}\| > 0, \quad (1.49b)$$

where \wedge is the exterior product between vectors, $v^\alpha = \ell^{1/2} c^\alpha$ and $v_*^\mu = \ell^{-1/2} c_*^\mu$. Therefore the linear response matrices are positive definite. Eqs.(1.49a,1.49b) furnish a generalization of Boltzmann's relation Eq.(1.6).

The general case (iii) is more complicated. Working out Eqs.(1.39,1.40), we obtain the following linear response relations for the currents

$$\begin{aligned} J_\alpha &= (e_\alpha, \ell^{-1} c_*^\mu) A_\mu^* + (e_\alpha, \ell^{-1} e_\beta) A^\beta, \\ J_*^\mu &= L_*^{\mu\nu} A_\nu^* + (c_*^\mu, \ell^{-1} e_\alpha) A^\alpha, \end{aligned}$$

and analogous relations for the forces

$$\begin{aligned} A^\alpha &= L^{\alpha\beta} J_\beta + (c^\alpha, \ell e_\mu^*) J_*^\mu, \\ A_\mu^* &= (e_\mu^*, \ell c^\alpha) J_\alpha + (e_\mu^*, \ell e_\nu^*) J_*^\nu. \end{aligned}$$

We define the following matrices, which contain information about the weighted overlap of cycles with cochords, chords with chords and so on:

$$\begin{aligned} H_\mu^\alpha &= (c^\alpha, \ell e_\mu^*), & D_{\mu\nu}^* &= (e_\mu^*, \ell e_\nu^*) = \delta_{\mu\nu} \ell e_\mu^*, \\ H_{*\alpha}^\mu &= (c_*^\mu, \ell^{-1} e_\alpha), & D_{\alpha\beta} &= (e_\alpha, \ell^{-1} e_\beta) = \delta_{\alpha\beta} \ell e_\alpha^{-1}. \end{aligned}$$

Compressing indices in vector notation, the linear response eqs. read

$$\begin{pmatrix} J \\ J_* \end{pmatrix} = \begin{pmatrix} D & H_*^T \\ H^* & L^* \end{pmatrix} \begin{pmatrix} A \\ A^* \end{pmatrix}, \quad (1.50a)$$

$$\begin{pmatrix} A \\ A^* \end{pmatrix} = \begin{pmatrix} L & H \\ H^T & D^* \end{pmatrix} \begin{pmatrix} J \\ J_* \end{pmatrix}. \quad (1.50b)$$

Onsager's reciprocity relations are satisfied also in this general case. Since the above equalities coincide, we can derive a host of relationships between linear response matrices imposing

$$\begin{pmatrix} D & H_*^T \\ H^* & L^* \end{pmatrix} \begin{pmatrix} L & H \\ H^T & D^* \end{pmatrix} = \begin{pmatrix} L & H \\ H^T & D^* \end{pmatrix} \begin{pmatrix} D & H_*^T \\ H^* & L^* \end{pmatrix} = \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix}.$$

Indeed, these combinatorial matrices are interrelated in many interesting ways. We now multiply Eq.(1.50a) on the left by (A, A^*) , and we multiply Eq.(1.50b) on the left by (J, J_*) , obtaining two parallel expressions for the entropy production,

$$\sigma = A^T D A + 2A_*^T H^* A + A_*^T L_* A_*, \quad (1.51a)$$

$$\sigma = J^T L J + 2J^T H J_* + J_*^T D^* J_*. \quad (1.51b)$$

Completing the square, and keeping Eqs.(1.50a,1.50b) in mind:

$$\sigma = J_*^T L_*^{-1} J_* + A^T (D - H^{*T} L_*^{-1} H^*) A$$

$$\sigma = A^T L^{-1} A + J_*^T (D^* - H^T L^{-1} H) J_*.$$

Since A^α and J_*^μ can be made to vanish independently, we necessarily have

$$L^{-1} = D - H^{*T} L_*^{-1} H^*,$$

$$L_*^{-1} = D^* - H^T L^{-1} H.$$

Finally we obtain the central result of this section,

$$\sigma = (L^{-1})_{\alpha\beta} A^\alpha A^\beta + (L_*^{-1})_{\mu\nu} J_*^\mu J_*^\nu, \quad (1.53)$$

which pairs with the original definition Eq.(1.26), which we rewrite as

$$\sigma = (\Delta^{*-1})^{\mu\nu} A_\mu^* A_\nu^* + (\Delta^{-1})^{\alpha\beta} J_\alpha J_\beta. \quad (1.54)$$

The entropy production in the linear regime can be written as a bilinear form either of the internal observables, as in Eq.(1.54), or else of the external variables, as in Eq.(1.53), in such a way that there are no mixed terms of currents and affinities. Notice instead that if we express the entropy production in terms of the affinities only, as in Eq.(1.51a), or of the currents only, as in Eq.(1.51b), we obtain cross-terms.

As we commented above, the determinants of both the resistance and the conductance matrices are positive; their value has been related to the volume of the polytope generated by the (deformed) cycle and cocycle vectors respectively. A crucial fact is that these values turn out to be independent of the fundamental set chosen; we might call them linear response invariants. This is far from being an obvious consequence of linear algebra, since both matrices were not constructed as linear operators on the cycle/cocycle space,

but rather as combinatorial objects, strictly depending on graph topology. In fact, the trace of both matrices does depend on the fundamental basis set³.

An intriguing explicit formula for their determinants exists. Let $\mathcal{T}(G)$ denote the set of spanning trees of a weighted graph G , that is a graph with a weight function $w : E \rightarrow \mathbb{R}$ which is symmetric under edge inversion (such is $\ell = (\ell_e)_{e \in E}$, for example). We build two important graph polynomials, the weighted spanning tree polynomial $T_G(w)$, and its dual $T_G^*(w)$:

$$T_G(w) = \sum_{T \in \mathcal{T}(G)} \prod_{e \in T} w_e, \quad T_G^*(w) = \sum_{T \in \mathcal{T}(G)} \prod_{e \notin T} w_e.$$

The first is homogeneous of degree $V - 1$ in w , and the second is homogeneous of degree $E - V + 1$. They are dual one to the other in the sense that the category of spanning trees is dual to the category of spanning co-trees. However, graph G needs not be planar in order for both polynomials to be well-defined. If G is planar, then $T_G^*(w) = T_{G^*}(w)$. This is another situation where duality occurs even when graph duality is not realizable.

It is known [33] that the determinants of L and L^* are given by

$$\det L_* = T_G(\ell^{-1}), \quad \det L = T_G^*(\ell).$$

Notice that the right-hand side of both does not depend on the fundamental set chosen to define L and L_* , so we conclude that the determinants of the response matrices are linear response invariants. As a consequence, setting $\ell_e = 1, \forall e \in E$, Eqs.(1.49a) tell us that the square of the volume enclosed by a fundamental set of simple chords or cochords is independent of the fundamental set chosen and enumerates all spanning trees,

$$\#(\text{spanning trees}) = \left\| \bigwedge_{\alpha} c^{\alpha} \right\|^2 = \left\| \bigwedge_{\mu} c_{*}^{\mu} \right\|^2. \quad (1.55)$$

Consider two different basis of simple cycles, and let A be the endomorphism from one basis to the other. A simple argument (see the previous footnote)

³More precisely, let $U = \{u_{\nu}^{\mu}\}$ be an invertible endomorphism of the cut space which induces a change of basis, $c_{\nu}^{*} = \sum_{\mu} u_{\nu}^{\mu} c_{\mu}^{*}$. Then the conductance matrix takes the form

$$L_*^{\mu\mu'} = \sum_{\nu\nu'} u_{\nu}^{\mu} u_{\nu'}^{\mu'} L_*^{\nu\nu'} = (U L_* U^T)^{\mu\mu'}$$

which is not the formula for a matrix change of basis, unless we restrict to orthogonal transformations $U^T = U^{-1}$, which is too restrictive in our case.

shows that $\det A = \pm 1$, where the sign depends on the orientation of the volume element. We orient all simple cycles so that they have the same orientation. Entries of A must be integers, since all simple cycles are integer linear combinations of simple cycles; then from a mathematical point of view A belongs to the special linear discrete group over the integers, $\text{SL}(C, \mathbb{Z})$. Its generators are the transvection matrices T_{ij} with all 1's on the diagonal and other entries all null but for a +1 in the (i, j) -position [39].

If we choose a basis of cocycles $(c_*^i)_{i \neq l}$ which correspond to the edges emanating from each of the $V - 1$ vertices $i \neq l$, expliciting the conductance matrix's entries we obtain

$$L_*^{ij} = (c_*^i, \ell^{-1} c_*^j) = \begin{cases} \sum_l \ell_{ij}^{-1}, & i = j \\ -\ell_{ij}^{-1}, & i \sim j \\ 0, & \text{elsewhere} \end{cases}. \quad (1.56)$$

In the r.h.s we recognize the matrix obtained by removing l -th row and column from the weighted laplacian of the weighted graph (see [40] for a review on the laplacian of graphs). All first-minors of the weighted laplacians coincide, and by the matrix-tree theorem they enumerate weighted spanning trees. So the dual response matrix is a generalization of the concept of weighted laplacian of a graph which describes the overlapping of some basis of cocycles, rather than the neighboring of vertices.

The spanning tree polynomial is a special case of an extremely powerful construct which is built as a sum over weighted subsets of the edge set of a graph, namely the weighted Tutte polynomial (see [41] for a comprehensive and comprehensible review). A consequence of this correspondence is promptly derived using formula (4.11) from §4.2 in Sokal's review [41]. The determinants of L and L^* satisfy

$$\frac{\det L}{\det L_*} = \prod_{e \in E} \ell_e = \frac{\det D^*}{\det D}. \quad (1.57)$$

Finally, it is evident that linear response matrices are dual one to the other under graph duality. More precisely, sending $\ell \leftrightarrow \ell^{-1}$ and taking the dual graph we obtain

$$L \leftrightarrow L_*, \quad \Delta \leftrightarrow \Delta^*, \quad H \leftrightarrow H^*. \quad (1.58)$$

In particular, due to Eq.(1.23), matrices H and H^* are self-dual. We will describe the physical nature of duality in Sec.(1.6). The analysis of duality in

the linear regime might help find more practical applications. For example, Eq.(1.57) might put constraints on the ability to maximize or minimize its detailed balance or steady state entropy production.

To resume, entries of the response matrix L and of its dual L_* are weighted superpositions of cycles and cocycles. Both matrices L and L_* are symmetric, and under $\ell \leftrightarrow \ell^{-1}$ they are dual one to the other. Similar matrices are employed in electrical circuit analysis [32] and in the parametric formulas for Feynman diagrams (see [33, §3] [42, §18.4] [43, Ch.3]), where they are known as Kirchhoff-Symanzik matrices. In this contest planar-graph duality has been related to duality between momentum and position representations [44]. Possibly, the most intriguing properties of L and L_* are that their determinants are independent of the fundamental sets chosen, that they obey the relation $\det L / \det L_* = \det \ell$, and that they are related to the 0-state Potts-model partition function [41, 45].

Finally, we motivate the choice of names for the resistance and the conductance matrices, showing that the linear response coefficients obey series and parallel reduction rules analogous to the rules for electrical circuits. A vertex is a knee when it has bare degree 2 in G ; it is the target or source of only two edges. A double edge is a couple of edges between the same pair of vertices, enclosing a cycle between them. Let us orient both edges in the same direction, in both cases. It is a simple fact that for planar graphs, duality sends knees to double edges and viceversa (see Fig.1.12.a). Series reduction consists in the replacement of a knee with a single edge, thus eliminating a vertex. Parallel reduction is obtained by replacing a double edge with a single edge, thus eliminating a cycle.

Let us analyze the effect of series reduction on entropy production. At a steady state, there is no current injected in the middle vertex of a knee, so

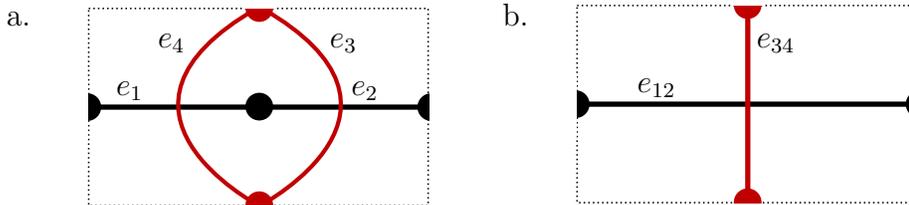


Figure 1.12: (a) A knee and its dual. (b) The result of series and parallel reduction.

that the current flowing along its two edges e_1 and e_2 is the same, $j_1 = j_2 = j_{12}$. Entropy production then reads

$$\sigma[a, j^{ss}] = \sum_{e \neq e_1, e_2} j_e a_e + j_{12}(a_1 + a_2).$$

This suggests to define the reduced force $a_{12} = a_1 + a_2$, so that, in the linear regime, we have $a_{12} = \ell_{12} j_{12}$ where the reduced linear response coefficient is

$$\ell_{12} = \ell_1 + \ell_2,$$

leaving the entropy production unaltered. For detailed-balanced systems, the macroscopic force $a_3 - a_4$ is null, $a_3 = a_4 = a_{34}$. Proceeding as above, the entropy production reads

$$\sigma[a^{db}, j] = \sum_{e \neq e_3, e_4} j_e a_e + (j_3 + j_4) a_{34}$$

giving the parallel reduction rule

$$\ell_{34} = \frac{\ell_3 \ell_4}{\ell_3 + \ell_4}.$$

Of course, the inverse linear coefficients ℓ^{-1} obey inverted parallel and series reduction rules. While the ℓ 's behave like resistances in an electrical circuit, the ℓ^{-1} s behave like condensators. On the other hand, it can be shown that series and parallel reduction leave respectively the spanning co-tree and the spanning tree polynomials unaltered.

Finally, a generalization of the linear regime is feasible, by considering non-local linear response relations

$$a_e = \sum_f \ell_{ef} j_f \tag{1.59}$$

where $\ell = (\ell_{ef})_{e,f}$ is a positive definite matrix. Then most of the arguments in this section can be replied, including positivity of the linear response matrices, Eqs.(1.50a,1.50b) and Eq.(1.53). We do not know whether generalized linear response matrices have combinatorial properties related to spanning trees.

2

Applications: duality and variational principles

All existence seemed to be based on duality, on contrast. Either one was a man or one was a woman, either a wanderer or sedentary burgher, either a thinking person or a feeling person-no one could breathe in at the same time as he breathed out, be a man as well as a woman, experience freedom as well as order, combine instinct and mind. One always had to pay for one with the loss of the other, and one thing was always just as important and desirable as the other.

Hermann Hesse, *Narcissus and Goldmund*.

In this chapter we discuss two theoretical applications of the mathematical machinery that we introduced in Ch.1. From the discussion in Sec.1.6 there arises a duality between macroscopic external affinities and currents, the steady and the transient entropy production terms, Kirchhoff's Current Law and Kirchhoff's Loop Law, and the resistance and conductance linear response matrices. In Sec.2.1 we develop a very elementary example where duality seems to interchange the role of the system and that of the environment. In Sec.2.2 we advance some more elements which should support our choice of name for graph duality in the context of NESM. We then derive a version of the Minimum Entropy Production Principle for Schnakenberg-type observables (Sec.2.3), and we discuss its relationship with the Maximum Entropy Production Principle (Sec.2.4).

2.1 System/Environment Duality: example

Let us linger on the simple 3-state example depicted in Fig.2.1, in the attempt to provide an intuitive grasp on the physics of duality. Suppose that the labels ε_i of the example graph are energy levels of an open system, which can emit and absorb energy from the environment. The onset of a NESS might be due to the interaction with two thermal baths [46, 47], whose inverse temperatures β_A and β_B label the states of the dual system, with $\beta_A > \beta_B$. Suppose that transitions 2 and 3 are exclusively due to the interaction with B, while transition 1 is exclusively due to the interaction with A. The ratio of emission and absorption rates is given by $w_{e_1}/w_{-e_1} = \exp \beta_A(\varepsilon_2 - \varepsilon_3)$, and similarly for the others, yielding as macroscopic affinity $A_1 = (\beta_A - \beta_B)(\varepsilon_2 - \varepsilon_3)$. In a nonequilibrium steady state, with current $j_1 = j_2 = j_3 = J_1$, one transition yielding an amount of energy $\varepsilon_2 - \varepsilon_3$ happens on average every $|J_1|^{-1}$ seconds. In the same time two transitions are stimulated by the interaction with reservoir B, which absorbing respectively amounts of energy $\varepsilon_2 - \varepsilon_1$ and $\varepsilon_1 - \varepsilon_3$. It takes shape a picture where to a steady state there corresponds a nonsteady flow of energy from the hotter to the colder bath:

non-Eq. system in a steady state \rightarrow non-steady environment

Whilst purely speculative, this interpretation is consistent with the physical intuition that NESSs are determined by a transient environmental behavior [48]. Vice versa, a detailed-balanced flow arises when there is no temperature gradient, $\beta_A = \beta_B$, in which case we only resolve one reservoir. At

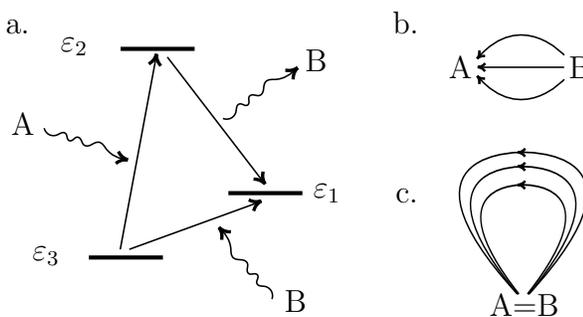


Figure 2.1: (a) Transitions between states due to absorption and emission from two reservoirs. (b) Steady state heat flux between reservoirs. (c) One reservoir with internal fluxes stimulated by the system's nonsteady configuration.

equilibrium, because of steadiness and detailed balancing, as many emitting and absorbing transitions occur. However, fluxes within the system determine a non-null flow of currents in the bath. The reservoir, being a 1-state system, is necessarily in a steady state. Hence the system's state plays the role of external force which causes internal fluxes within the environment:

steady environment \rightarrow equilibrium system out of steady state.

This is nothing but the logical negation of the above proposition, hence its dual under transposition of the material implication symbol (\rightarrow), much in the spirit of a fascinating connection between graph duality and logical duality put forward by McKee [49].

Despite of its simplicity, the example is rather clumsy and only vaguely illustrative: system and environment do not play mirror roles, for which reason we were not able to draw the inverse implications. However, the qualitative principle seems to be robust. It is quite remarkable that graph duality finds a similar interpretation also in mechanical engineering [50], where the statics of structures and machines and their first order kinematics are related to dual properties of their design. Thus there seems to be a vast variety of systems to which duality might apply: it is the author's opinion that the development of a complete statistical model which displays duality between environmental and internal degrees of freedom would be a major advance. The question remains open what is the role of duality for master equation systems.

2.2 System/Environment Duality: discussion

Duality comes in many flavors in physics. Among the first that one encounters: the duality between vectors —velocities— and linear forms —momenta; the Legendre transform which maps the lagrangian into the hamiltonian, pivoting on the bilinear form $\sum_i \dot{q}_i p_i$; the electromagnetic duality, which is the archetypical physical counterpart of Hodge's geometrical theory of differential forms; and, less credited, the electro-technical duality between resistances and condensators, parallel and series reduction, voltage and current laws [32]. The one that we put forward descends from the latter, abstracting and generalizing it to nonlinear regimes, where Ohm's law does not necessarily hold; but it also resonates with each other of the above. While the reference physical situation is that of a thermodynamic system in the framework of the nonequilibrium statistical mechanics of master equation systems, we will

cast our propositions in a very general form. In fact, they can be applied to any lattice theory which bears a couple of conjugate variables. As an example, we treat electromagnetism on a network.

We apply graph duality to the structure of nonequilibrium observables. The mapping $a \leftrightarrow j$ leaves the entropy production σ invariant, but it switches macroscopic observables with those of the dual graph, mapping internal forces to internal currents, external currents to external forces and the steady to the transient entropy production,

$$A^\alpha \leftrightarrow J_*^\mu, \quad A_\mu^* \leftrightarrow J_\alpha, \quad \sigma_{ss} \leftrightarrow \sigma_{db}. \quad (2.1)$$

Since we ascribed A^α to the state of the environment and J_*^μ to that of the system, it is fair to dub this symmetry system-environment duality. Steady states, for which the macroscopic external currents vanish, are dual to detailed-balanced systems, for which the macroscopic external forces vanish: the former are in fact properties of the system under given environmental conditions, while the latter are properties of the environmental influence on the system, independently of the system's state.

Duality is a far-reaching concept, which is not relegated to the symmetric role of currents and forces in the expression for the entropy production. Out of the $a \leftrightarrow j$ special case, we stress that duality is a graph-theoretical property: it tells how well-behaved observables look like from the point of view of the environment and of the system, not which mesoscopic variables enter the construction. For example, a different manifestation of duality is the forthcoming. Let us shift mesoscopic affinities by a weighted cocycle, and mesoscopic currents by a weighted cycle,

$$a \rightarrow a + \sum_\mu H_\mu^* c_*^\mu \quad j \rightarrow j + \sum_\alpha K_\alpha c^\alpha.$$

Due to orthogonality between the cycle and the cocycle spaces, macroscopic external observables are left unmodified after such transformations,

$$\delta A^\alpha = \sum_\mu H_\mu^*(c^\alpha, c_*^\mu) = 0, \quad \delta J_\mu^* = \sum_\alpha K_\alpha(c_*^\mu, c^\alpha) = 0.$$

For this reason we call these symmetry transformations. It is a simple algebraic fact that this kind of transformations are the most general translations of the mesoscopic variables which leave all external observables unaltered.

Notice that the entropy production acquires a new term $\sum_{\alpha} H_{\mu}^{*} J_{*}^{\mu} + \sum_{\alpha} K_{\alpha} A^{\alpha}$ and that the internal variables transform according to

$$\delta A_{\mu}^{*} = H_{\mu}^{*}, \quad \delta J_{\alpha} = K_{\alpha},$$

Without any need for further formalization, we realize that cocycles are the generators of symmetry transformations of cycles, and cycles are the generators of symmetry transformations of cocycles. Observables and symmetries which leave observables invariant are related by duality. So, duality is more than the mere observation that the entropy production is a bilinear form of the forces and currents.

An important notion of duality against which it is interesting to compare ours is the electromagnetic duality. We refer here to C. Timm's work on master equations [51]. Let's think of ρ as a charge density. In order to make the overall network neutral we introduce a supplementary vertex " ∞ ", charged $\rho_{\infty} = -\sum_i \rho_i$. All graph-theoretical notation will refer to this extended graph, which can be further made into a two-dimensional cell complex by introducing a collection $P \supseteq C$ of plaquettes. Plaquettes are analogous to faces as far as their boundary is always an oriented cycle, but they need not to be embedded in the plane, so their number is not constrained by Euler's formula. Choose a conventional clockwise/counterclockwise orientation for each plaquette p and define the boundary (curl) operator

$$(\partial \times)_e^p = \begin{cases} +1, & \text{if } e \downarrow \mathcal{Q} p, e \uparrow \mathcal{Q} p \\ -1, & \text{if } e \uparrow \mathcal{Q} p, e \downarrow \mathcal{Q} p \\ 0, & \text{elsewhere} \end{cases} .$$

Boundaries of plaquettes (columns of $\partial \times$) are cycles. Cycles live in the kernel of the incidence matrix. Therefore $\partial(\partial \times) = 0$, which translates into the well-known fact that the divergence of the curl vanishes.

Introduce an electric field E_e over edges and a magnetic field B_p over plaquettes. The electric field is required to satisfy Gauss's law $\partial E = \rho$. Taking the time derivative of Gauss's law, we have $\partial(\dot{E} + j) = 0$. It follows that $\dot{E} + j$ is a linear combination of cycles. In a basis of fundamental cycles, let \mathcal{B}_{α} be the coefficients of the decomposition:

$$j = -\dot{E} + \mathcal{B}_{\alpha} \dot{c}^{\alpha} =: -\dot{E} + \partial \times B.$$

In the right-hand side we imposed the Ampère-Maxwell Law. This equation establishes a relationship between the magnetic field and the boundary values

\mathcal{B}_α . In fact, since c^α is a complete set of cycles, there exists an $P \times C$ matrix η such that $(\partial \times)^p = \eta_\alpha^p c^\alpha$. Therefore $\mathcal{B}_\alpha = \eta_\alpha^p B_p$. We further impose Faraday's Law $(\partial \times)^T E + \dot{B} = 0$, and apply η :

$$(c^\alpha, E) = -\dot{\mathcal{B}}_\alpha.$$

It follows that any two combinations of plaquettes which share the boundary enclose a volume across whose boundary the magnetic flux is zero (Gauss's Law). Hence only C out of P magnetic field values are independent.

As entropy production it is reasonable to elect the total energy flux

$$\sigma = \frac{d}{dt} [(E, E)_E + (B, B)_P]$$

where $(\cdot, \cdot)_P$ is the scalar product with respect to the plaquettes. Applying Faraday's Law, transposing the curl operator, and using Ampère's Law,

$$\sigma = (E, \dot{E})_E + (B, \dot{B})_P = -(j, E) = (E, \dot{E}) + \mathcal{B}_\alpha \dot{\mathcal{B}}^\alpha.$$

The second identity yields the Integrated Poynting's Theorem. The third displays a simple dependence of the magnetic field on the boundary values. Our result on the general decomposition of the entropy production can now be applied, yielding

$$\sigma = J_\alpha \dot{\mathcal{B}}^\alpha - J_\star^\mu \mathcal{E}_\mu^\star$$

where \mathcal{E}_μ^\star is the electric field along cochorde e_μ^\star . By Eq.(1.37), J_\star^μ is (minus) the time-derivative of the charge in $S(c_\star^\mu)$. Hence under graph duality and $j \leftrightarrow E$ one obtains

$$\mathcal{E}_\mu^\star \leftrightarrow J_\alpha, \quad \mathcal{B}^\alpha \leftrightarrow \rho^\mu + const. \tag{2.2}$$

The electric field is mapped to the source of the magnetic field and vice versa. Thus the example further supports the interpretation of duality as reversing the role of system and environment. Although, notice that the dynamical evolution is not respected: only Kirchhoff's and Faraday's "structure" equations are dual to each other. The lagrangian (see Ref. [51]) turns out not to be self-dual. This is an important difference between system/environment and electromagnetic duality, which is dynamical. Moreover, the former is 2-dimensional, while the latter, restricted to sourceless cases or requiring magnetic charges, involves the Hodge machinery in 3 dimensions. Contrary

to standard electromagnetic duality, in ours divergencelessness of the magnetic field is an essential feature rather than an obstruction to duality.

The electromagnetical example highlights another crucial feature of duality: it only works for kinematical states, viz. instantaneous snapshots of the system. So, for example, by “steady” we mean that Kirchhoff’s law is satisfied, not persistence in time. This is one important limitation that one will have to take care of when considering, for example, markovian evolution: by no means do we claim that duality maps master equations into dual master equations.

Restriction of duality to planar graphs might appear to be a serious limitation. Although, nonequilibrium observables behave “as if” there always existed some dual graph. In a fascinating work [49], McKee attempts a generalization of graph duality, finding a correspondence with logical duality between the universal and existential quantifiers (\forall and \exists) under the involutive action of negation (\neg)¹. In the prologue he comments that “some optimists see them [dualities] as mechanically doubling the number of results of a theory”. We are optimist, claiming that for every proposition that is true of steady states, there exists a dual proposition regarding detailed-balanced systems, regardless of the possibility to draw a dual graph. One explicit example is a dual minimum entropy production principle, discussed in Sec.2.3. From a more formal point of view, notice that property (iii) of graph duality on p.40 is independent of the particular embedding chosen. Indeed, generalizing the concept of a graph to that of an abstract matroid [41, 53], it turns out that matroids always admit a well-defined dual which satisfies property (iii), even though dual matroids might not be visualizable as graphs. In other words, trees and cotrees, cycles and cocycles, chords and cochords always have mutual properties that can be ascribed to an abstract concept of duality, even when there exists no dual graph. This aspect of graph duality arised in the analysis of the linear regime.

As we pointed out at the end of Sec.1.6, embedding graphs in higher-genus surfaces is another possibility for dealing with non-planar graphs. We will not examine this technique in full detail. Still we want to point out a very peculiar behavior: the failure of the one-to-one correspondence between cycles and dual cocycles, and the emergence of topological currents. Fig.2.2 shows four different embeddings of the complete graph on four vertices (K_4)

¹For a work with fascinating points of contact with duality in logic and in probability theory, and its relevance for the definition of entropy see Knuth [52].

in a torus. Let $c = 3$ be the cyclomatic number of K_4 . Depending upon how many cycles wind around the holes of the torus (more precisely: belong to the first homology group of the torus), the number of vertices of the dual graph range from $c + 1 = 4$ to $c + 1 - 2g = 2$, where $g = 1$ is the genus of the torus. In this latter case, which corresponds to the two lower examples, the dual graph has $c - 2g = 1$ independent cocycle, dual to the one cycle which is contractible to a point, and five independent cycles, two more than usual. The two excess cycles are dual of those fundamental cycles of K_4 that are topological. One can then separate topological cycles and contractible cycles in the entropy production

$$\sigma = \sum_{\text{contractible}} A^\alpha J_\alpha + \sum A_\mu^* J_\mu^* + \sum_{\text{topological}} A^\alpha J_\alpha.$$

Dualization is still possible, but one must carefully interpret the physical nature of dual observables. In fact, the last term poses a topological obstruction to the definition of dual external currents. The emergence of topological currents in the study of diffusion theory on manifolds has been widely discussed by the Jiang and the Qians [24], who noticed the possibility to integrate entropy production in terms of topological circulations, in the spirit of Schnakenberg's program. However, this approach, whilst much more concrete than matroids, is doomed to become impracticable when one deals with

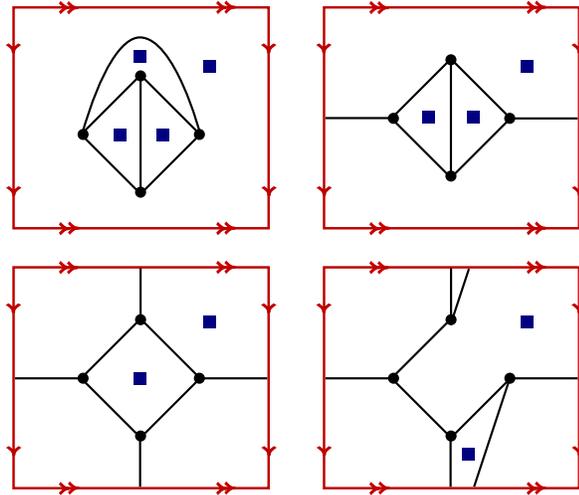


Figure 2.2: Four different embeddings of the complete graph on four vertices K_4 in a torus. Squares denote different faces.

large lattices of more than two dimensions.

Beyond two dimensions, there is a gap between the mathematical realization of duality, which suffers from great limitations (abstractness, in the case of matroids, and excessive complication in the case of surfaces) and the propositional reach of the theory, which seems to be completely independent of the possibility to visualize duals.

2.3 Minimum entropy production

The minimum entropy production principle (MINEP) asserts, using Klein and Meijer’s words [54], that

“the steady state is that state in which the rate of entropy production has the minimum value consistent with the external constraints which prevent the system from reaching equilibrium”.

So worded, it is reminiscent of the inferential method that provides ensembles in equilibrium statistical mechanics, by maximization of the Gibbs-Shannon entropy — a measure of ignorance of the microstate of the system — under suitable constraints. In an information-theoretic framework, constraints are pieces of knowledge the observer gains from the measurement of certain observables of the system, or macroscopic parameters that can be experimentally controlled. In the extremization procedure constraints are introduced through Lagrange multipliers [55, 56].

Not exactly so for MINEP. Its first proof as a closed theorem is attributed to Prigogine [27, Par. VI.2]. In Prigogine’s statement, owing to the applied thermo-chemical setting, knowledge of the nonequilibrium external constraints, such as temperature or chemical potential gradients, is granted from the start. Further generalizations of the principle always entail that constraints can be read off the physical setup of the problem. So, in his extension of the principle to density matrices [57], Callen recalls that

“Prigogine showed that in the steady state which is reached when certain affinities are constrained to have definite values, all unconstrained affinities assume the values which minimize the entropy production function”.

However, the environmental influence on a system might be *a priori* unknown, or difficult to decipher. Here we do not assume previous knowledge

of the nonequilibrium constraints, or affinities. As uninformed observers, we look at the system, measure its fluxes and local constitutive relations, and ask which are the constraints that impede relaxation to equilibrium. More specifically, this work addresses two technical questions: Which Lagrange multipliers should be introduced in the MINEP variational procedure? For systems in the linear regime, the answer is found in Schnakenberg’s macroscopic affinities.

As for most, if not all, constructive variational principles in NESM, the range of validity of the principle is the linear regime. Notice that we assume the linear regime constitutive relations and not derive them from the principle of least dissipation, as is done in classical textbooks on nonequilibrium thermodynamics [58, Ch. 4 and Ch. 5]. In particular, we do not distinguish between the dissipation function and the entropy production.

Let us hint with a simple example why circuitations are good nonequilibrium constraints. Consider the classical problem of heat diffusion in an approximately one-dimensional inhomogenous conductive rod, whose ends are put in contact with thermal reservoirs at slightly different boundary temperatures, $T_b \gtrsim T_a$, while the body of the rod is isolated (see [59, §3.1] and references therein). A temperature profile $T(x)$ establishes. By Fourier’s Law the induced heat current through the rod is

$$j(x) = -k(x)\partial T(x), \quad (2.3)$$

where $k(x)$ is the thermal conductivity at $x \in [a, b]$ and $\partial = \partial/\partial x$. The following identity

$$T_b - T_a + \int_a^b \frac{j(x)}{k(x)} dx \equiv 0 \quad (2.4)$$

is interpreted as a constraint on the currents, where we make use of the equivalence symbol ‘ \equiv ’ to impose constraints. The configuration is steady if $\partial j^{ss}(x) = 0$, which implies $j^{ss}(x) = \text{const}$.

The same result can be obtained by a different route. Let us define the local force as the right incremental ratio

$$a(x) = \lim_{\delta x \rightarrow 0^+} \frac{T^{-1}(x + \delta x) - T^{-1}(x)}{\delta x}, \quad x \in [a, b]. \quad (2.5)$$

We assume that the system satisfies linear regime constitutive equations, that is, that forces and currents are small and linearly related,

$$a(x) = \ell(x)j(x). \quad (2.6)$$

For this assumption to hold it is necessary that the temperature profile is approximately constant and the temperature drop between the extremities of the rod is sufficiently small with respect to its length, in such a way that to first order one can approximate the conjugate force as $a(x) = -T_{av}^{-2}\partial T(x)$, $x \neq b$, where T_{av} is the average value of the temperature [59]. The local linear regime coefficient then reads $\ell(x) = T_{av}^{-2}k(x)^{-1}$. The entropy production

$$\sigma = \int_a^b j(x)a(x)dx,$$

is then a quadratic functional of the currents. We require σ to be stationary, that is $\delta\sigma = 0$, with respect to all possible current profiles that are consistent with constraint (2.4). Introducing one Lagrange multiplier λ , we calculate the variation

$$\frac{\delta}{\delta j(y)} \left[\int_a^b \ell(x)j(x)^2 dx - 2\lambda \int_a^b \frac{j(x)}{k(x)} dx \right] = 0, \quad (2.7)$$

leading to a uniform stationary current $j^{ss} = \lambda T_{av}^2$. The value of the multiplier is fixed by substitution into Eq.(2.4):

$$j^{ss} = T_{av}^2 \lambda = (T_b - T_a) \left[\int_a^b k(x)^{-1} dx \right]^{-1}.$$

The above solution corresponds to a minimum of σ , and it coincides with the steady configuration of currents. We conclude that the steady state is the minimum of the entropy production among nearby current profiles that are compatible with the external constraint. Notice that we prefer to use the “stationary” when referring to the extremal solution of a variational problem, and “steady” for a configuration of currents that satisfies the continuity equation.

The problem of heat-conduction and the minimum entropy production principle in a rod has been widely debated [60], with arguments revolving around the onset of the linear regime. While the exact MINEP solution displays an exponential dependence on the position, it can be shown that under reasonable experimental conditions the deviations between the rigorous MINEP temperature profiles and the steady profiles are small. In this work we are not interested in the careful identification of the range of validity of Eq.(2.6), but rather in the forthcoming geometrical interpretation of the constraint as a circuitation: So we will always assume that our systems admit a well-defined linear regime.

At a steady state as much heat is absorbed by the colder reservoir, as much has to be poured in by the hotter one. If we ideally short-circuitate the rod, bringing the end-points to coincide, the linear system is mapped to a unicyclic system, with a conserved heat flux through the whole ring. Due to the discontinuity of $T(x)$ at $x = a$, the affinity is not a conservative field (i.e., it is not the derivative of some potential in all of its domain). However, we can still integrate it to get the constraint

$$\oint_{\text{ring}} a(x)dx \equiv \frac{1}{T_a} - \frac{1}{T_b},$$

which in the linear regime is equivalent to Eq.(2.4). When the boundary temperatures coincide, that is, at equilibrium, the affinity is indeed an exact form and the circulation vanishes. Thus there exists a correspondence between “topological” circuitations, nonconservative driving forces, and the onset of nonequilibrium behavior. As soon as one abandons the 1-dimensional case, one incurs great difficulties. In particular, steadiness $\partial j^{ss} = 0$ does not imply a uniform current distribution, and one realizes that the problem is of geometrical nature, involving differential forms, topology, etc. However, on a discrete state space this intuition can be efficiently put to work.

According to Schnakenberg’s theory of nonequilibrium observables, the external constraints that force a system into a non-equilibrium steady state are the macroscopic external forces. We will now extremize entropy production with respect to mesoscopic currents in the linear regime, using Schnakenberg’s affinities as constraints,

$$\bar{A}^\alpha \equiv A^\alpha[j] = \sum_e c_e^\alpha \ell_e j_e + O(j^3), \quad (2.8)$$

where \bar{A}^α is a fixed, “observed” value of the affinity. The entropy production is the quadratic form

$$\sigma[j] = \sum_e \ell_e j_e^2 + O(j^4). \quad (2.9)$$

We introduce Lagrange multipliers and vary

$$\frac{\delta}{\delta j_e} \left[\sigma[j] - 2 \sum_\alpha \lambda_\alpha \left(A^\alpha[j] - \bar{A}^\alpha \right) \right] = 0. \quad (2.10)$$

Multipliers λ_α are to be determined by replacement of the stationary solution into (2.8). The calculation is easily carried over, yielding

$$j^{ss} = \sum_\alpha \lambda_\alpha c^\alpha.$$

Stationary currents are linear combinations of a cyclomatic number of boundary terms λ_α . We now prove that the latter are in fact the macroscopic currents conjugate to the constrained values of the affinities. Fixing the Lagrange multipliers we get

$$\bar{A}^\alpha = \sum_\beta \lambda_\beta \sum_e \ell_e c_e^\alpha c_e^\beta = \sum_\beta L^{\alpha\beta} \lambda_\beta,$$

where we recognized the linear response matrix. This relation can be inverted, showing, after Eq.(1.46), that λ_α is the steady current conjugate to the measured value of the affinity \bar{A}^α . The second variation

$$\frac{\delta\sigma}{\delta j_e \delta j_f} - 2 \sum_\alpha c_e^\alpha \frac{\delta\lambda_\alpha}{\delta j_f} = \ell_e \delta_{e,f}.$$

yields a positive Hessian matrix, which guarantees positive concavity.

We thus conclude that the stationary configuration of currents that in the linear regime minimizes the entropy production with constrained macroscopic forces, satisfies Kirchhoff's conservation law. From a dynamical point of view, if under some ergodic hypothesis the steady state is asymptotically reached over the long time (as is the case, for example, for Markovian systems), one can conclude that a nonequilibrium system tends to relax to a state of minimum entropy production, compatibly with the macroscopic external forces that prevent it from reaching equilibrium. This echoes Klein and Meijer's phrasing.

Prigogine's proof of MINEP [27], shaped upon chemical systems, was based on an assumed splitting of the entropy production into a matter flux term and a heat flux term,

$$\sigma = J_{th} A_{th} + J_m A_m. \quad (2.11)$$

Steadiness is equivalent to the requirement that matter currents vanish, $J_m = 0$. Hence entropy production at a steady state consists only of heat flux contributions.

Bridging to our abstract setup, we might interpret heat currents and inverse temperature gradients respectively as Schnakenberg's internal currents and external forces. Pushing this identification out of the steady state, we might also interpret matter currents as external currents and pressure gradients as internal currents, so that Prigogine's splitting corresponds to our splitting of the entropy production in a complete set of observables,

Eq.(1.35). Given this identification, the reasoning follows along the same tracks as Prigogine's. Variation with respect to the mesoscopic observables, at constant external affinities, can be replaced with variation with respect to the external currents, as we did in Eqs.(1.14,1.15). We thus conclude that our approach is completely superimposable on Prigogine's phenomenological derivation, adding to it an abstract and quite general definition of the constraints. Moreover, it generates the following dual principle:

Detailed balanced systems are those systems for which the rate of entropy production has the minimum value that is consistent with the fixed inflowing currents which prevent them from reaching a stationary state.

Finally, to make the link with Prigogine's work even stronger, we recall that in some early reflections [61] he wrote that

“d'une manière un peu obscure mais imagée on pourrait appeler ce principe celui de la moindre vitesse.”

He referred to Gauss's Principle of Least Constraint, which states that the physical trajectories $x_i(t)$ of N particles with masses $m_i, i = 1, \dots, N$ minimize the gaussian curvature $G = \sum_i m_i \|\ddot{x}_i(t)\|^2$, compatibly with whichever constraints on their position and velocities. The method is very powerful as it also deals with non-holonomic constraints, and it is employed in the characterization of the non-equilibrium statistical mechanics of dynamical systems subject to thermostats [62]. Ref. [63] discusses the mathematical solution of the problem. The approach is more interesting when we pose the inverse question: Which are the constraints

$$(k^\alpha, \ell j) = \bar{K}^\alpha$$

to be imposed to the entropy production in the linear regime, in such a way that Kirchoff's Law is satisfied? We find in Ref. [64] that, after we define matrix $K = [k^1, \dots, k^\alpha, \dots]$, minimization of the entropy production yields $j^{min} = \ell^{-1/2} (K \ell^{1/2})^+ \bar{K}$, where M^+ is the Moore-Penrose pseudoinverse of M . When the k^α 's are independent the Moore-Penrose pseudoinverse has an explicit expression, as

$$j^{min} = K^T (K \ell K^T)^{-1} \bar{K}.$$

We want the constrained minimum to solve Kirchhoff's equation:

$$\partial j^{min} = \partial K^T (K \ell K^T)^{-1} \bar{K} = 0.$$

Notice that $K \ell K^T$ is an invertible matrix. Then the columns k^α of K must live in the kernel of ∂ : they are cycles. Notice that $(K \ell K^T)^{-1}$ is indeed the linear response matrix and \bar{K} are values of the affinities. Therefore, in our approach, Prigogine's will is fulfilled, and allows a simple and elegant derivation of MINEP which is well-suited for our algebraic formalism.

A few concluding remarks. Some of the hypothesis upon which we derived the principle can be relaxed. Working in a differential-geometric setting should allow us to extend the principle to continuous systems. In this context, a result similar to Schnakenberg's decomposition has been obtained by Jiang and the Qians [24] for topological currents, such as those that flow along the two fundamental cycles of a torus. The task is then to extend to nontopological currents, through lattice discretizations and limiting procedures. One problem appears at the horizon: As the discretization becomes more and more refined, the number of cycles tends to infinite, becoming non-denumerable in the continuum limit. This clashes with the physical intuition that nonequilibrium constraints should be a few boundary conditions that are experimentally accessible. For physically relevant systems, symmetries might have a role in the reduction of the number of affinities. The condition of locality can also be relaxed, considering the more general mesoscopic phenomenological linear response relation, see Eq.(1.59).

As to the hypothesis of linear regime, in our formulation the assumption seems to be unavoidable if one chooses affinities as nonequilibrium constraints. The possibility is open that better observables might allow for a departure from the linear regime. There exist many instances of variational principles in NESM, most of which can be traced back to Onsager's least dissipation and Prigogine's minimum EP, with their own, and different, inclination. However, notwithstanding high-flown claims, to the author's knowledge none truly departs from the linear regime, at least in an operational sense. So, in this respect our principle is no exception.

Our extremization procedure is based on the identification of the fundamental macroscopic observables which keep a system in a nonequilibrium steady state. The setup is quite general and can in principle be adapted to any system that allows a local conservation law. It can be applied to master equation systems, where its robustness can be tested against well-known

results. It is shown to provide an abstract setup where Prigogine’s original statement sits comfortably, provided that we have a mesoscopic substrate. So, while the principle is no novelty, the procedure and its generality are.

While the hot topic of NESM are, of course, fluctuations, there is a priori no fluctuating character in the principle we have formulated: It is purely geometrical.

Coming to a conclusion, we suggest that the search for an extremal functional is as important as the identification of constraints of physical relevance. This might be a good guiding principle, for example, in the search of a maximum entropy principle (MAXENT): While MAXENT can be constructively employed to derive equilibrium ensembles [55], to our knowledge a similar application to nonequilibrium steady states is still lacking. The possibility is open that giving to Schnakenberg’s affinities the correct weight might allow to derive as useful tools of calculation as are equilibrium ensembles, fulfilling Jaynes’s expectation that “essentially all of the known results of Statistical Mechanics, equilibrium and nonequilibrium, are derivable consequences of this principle” [65].

2.4 Maximum entropy production?

The striving for variational principles in NESM has a long and contrived history. In particular, another, less familiar, variational principle has been proposed that should characterize the behavior of non-equilibrium systems: the maximum entropy production principle (MAXEP). There are at least as many formulations of MAXEP as there are of MINEP. Arguably, the apparent clash between these two instances is due to the fact that they apply to distinct scales and regimes, and employ different notions of “state”. There is a vast literature that tries to sort out the matter [66], and by no means do we mean to be exhaustive. However, we need to put our principle in contact with some instances of MAXEP in order to appreciate their relative significance.

It was Jaynes’s conviction that [67] “there must exist an exact variational principle for steady irreversible processes” and that such principle should capture conservation laws: “we should rather take the conservation laws as exact and given, and seek a principle which gives the correct phenomenological relations”. Jaynes thought that reversing this logic would also reverse the principle: “perhaps the exact phenomenology is the one that has maximum

entropy production for prescribed exact conservation laws”. So, Jaynes’s expectation was that conservation laws and constitutive equations should fit in the same picture, under the aegis of one unifying maximum principle. This supposition informs Gyarmati’s research [58, Par. V.3], as he claims that “the principle of minimum production of entropy is not an independent principle [. . .], but rather is only an alternative reformulation of the Onsager principle valid for stationary cases”.

In this respect, P. Županović, D. Juretić and S. Botrić’s proposition is more closely related to our principle, as it deals with Kirkhoff’s Current Law and Kirkhoff’s Loop Law on networks. It is to this work that we mainly refer in the following.

Suppose we do not know the system’s constitutive equations, but that we do know that entropy (in the form of heat) is dispersed into the environment at a rate

$$\omega = \sum_e \ell_e j_e^2,$$

which is called the dissipation function. This is the case for electrical circuits, where ℓ_e plays the role of a resistance. Entropic balance then requires

$$\sigma - \omega \equiv 0. \tag{2.12}$$

This is particularly reasonable for an electrical circuit, where ω is the electric power and σ the heat flux. Finally we extremize entropy production, varying with respect to the currents, and imposing constraint (2.12),

$$\frac{\delta}{\delta j_e} \left[\sigma + \lambda(\sigma - \omega) \right] = 0. \tag{2.13}$$

We obtain $a_e = 2\lambda/(1 + \lambda) \ell_e j_e$. The value of the multiplier is set by replacing the extremizer in Eq.(2.12), which yields $\lambda = 1$, a stationary value $\sigma^* = \omega$ and the desired mesoscopic phenomenological, $a_e = \ell_e j_e$. Taking the second variation we obtain a negative hessian, hence a concave-down paraboloid, hence we front a maximum entropy production principle.

Variational principle (2.13) is discussed by Martyusheva and Seleznev [66, Eq. 1.16], where it is introduced as Ziegler’s principle, and again by Županović and coworkers [68, Eq. (9)] in a follow-up paper on the relation between MAXEP and the principle of least dissipation: In fact, the procedure is but a restatement of Onsager’s least dissipation principle, which in its original form simply states that $\sigma - \omega$ should be maximum [29].

Embedding Kirchhoff's Current Law into Eq.(2.13),

$$\frac{\delta}{\delta J_\gamma} \left[(1 + \lambda) \sum_\alpha J_\alpha A^\alpha - \lambda \sum_{\alpha, \beta} L^{\alpha\beta} J_\alpha J_\beta \right] = 0,$$

or, equivalently, constraining the solution to the variational problem (2.13) on the $\partial j = 0$ shell, leads to the identification of circuitations $A^\alpha = \sum_\beta L^{\alpha\beta} J_\beta$ as the phenomenological conjugate variables to the currents. This realization of MAXEP does indeed reproduce Jaynes's expectation that the reversed logic should yield the correct phenomenological laws. The MAXEP of Županović et al. is in a sense complementary to our MINEP, reproducing the macroscopic Onsager's relations. With one specification: The MAXEP principle does not imply that "currents in a linear planar network arrange themselves so as to achieve the state of maximum entropy production". That is due to the minimum entropy production principle.

3

Master equation: dynamics

In this brief chapter we give the elements of continuous-time diffusion theory and jump processes on finite state space that are strictly necessary for the development of the forthcoming results. So, we omit a discussion of the Markov property, the derivation of the master equation from the Chapman-Kolmogorov equation, backward and forward equations, and many other interesting topics that are typically found in the dedicated literature [69, 70]. Some more elements about the markovian generators will be found in Ch.7.

3.1 Master equation

On an oriented graph $G = (V, E, \partial)$ with sites $i \in V$ connected by oriented edges $ij \in E$, the time-dependent master equation reads

$$\frac{\partial p}{\partial t}(t) = \frac{dp}{dt}(t) = \sum_{j \in V} [w_{ij}(t)p_j(t) - w_{ji}(t)p_i(t)] \quad (3.1)$$

where $p(t) : V \rightarrow [0, 1]$ is a normalized probability density at time t over the discrete set V and $w_{ij}(t)$ is a positive transition rate from site j to site i at time t . As a simple consequence of the antisymmetry of the summand in the right-hand side, Eq.(3.1) preserves normalization. The equivalence of partial and total time derivative is to signify that there is no further explicit time dependence of the probability density other than the one prescribed by the master equation. We cast it in matrix notation,

$$\dot{p}(t) = W(t)p(t), \quad W(t)_{ij} := \begin{cases} w_{ij}(t), & i \neq j \\ -\sum_k w_{ki}(t), & i = j \end{cases} .$$

Entries along the columns of the generator W add up to zero, hence $(1, 1, \dots, 1)$ is a left-eigenvector of W relative to eigenvalue zero.

The master equation is the diffusion equation associated to continuous-time Markov chains, also known as jump processes. It describes the evolution of an ensemble of trajectories which are sampled with initial probability $p = p(0)$, and which perform jumps from site j to i at rate w_{ij} . The i -th diagonal element of the generator is (minus) the average waiting time at site i before a jump is performed [71]. We write them in short

$$w_i(t) := \sum_k w_{ki}(t).$$

It is usually assumed that G is connected and that rates are strictly positive, hence non-null, along all edges of G , in both directions, at all times. In other words, given any two sites there exists a path connecting them such that the product of the transition rates along the path does not vanish. Furthermore, if the rate of jumps between site i and site j is non-null then also the opposite-direction transition has non-null rate. Unless otherwise stated, the above assumptions are always implicitly understood, and we will say that the master equation is ergodic.

A Markov process is said to be stationary when its transition probabilities are invariant under shift of the time origin. The corresponding master equation turns out to have time-independent rates. For such systems it makes sense to question the existence of steady states. Under the above assumptions, by application of the Perron-Frobenius theorem the master equation can be shown to afford a unique steady (or invariant) state such that

$$Wp^{ss} = 0.$$

We devote Ch.5 to the steady state and its combinatorial properties.

Although we will mainly be interested in the evolution equation for the probability density, for later reference we introduce the adjoint generator. Let $f(t) : V \rightarrow \mathbb{R}$ be a real time-dependent function defined over sites of the graph. The adjoint generator is defined by

$$\langle W^\dagger(t)f(t) \rangle_{p(t)} = \langle f(t) \rangle_{W(t)p(t)}$$

where the average is the ensemble average, $\langle g \rangle_p = \sum_i g_i p_i$. The matrix entries of the adjoint generator are found by transposition of $W(t)$,

$$[W^\dagger(t)f]_i = \sum_j w_{ji}(t)(f_j - f_i). \tag{3.2}$$

The total time derivative of the average of an observable is given by

$$\frac{d}{dt}\langle f(t) \rangle_{p(t)} = \left\langle \frac{\partial f(t)}{\partial t} + W^\dagger(t)f(t) \right\rangle_{p(t)}.$$

3.2 Reduced dynamics

The master equation is a set of V first order differential equations. They are not all independent, as on a connected state space normalization constrains one equation to the others. We now want to recast the dynamics in such a way as to keep track of the normalization constraint. We choose state i_V as a reference state. Let \tilde{p} be a reduced probability vector with entries labelled by index $m = 1, \dots, V-1$ (we do not display the time dependence),

$$\tilde{p} = (p_1, \dots, p_{V-1}),$$

such that $p_V = 1 - \sum_{m=1}^{V-1} \tilde{p}_m$. We have

$$\begin{aligned} \frac{d\tilde{p}_m}{dt} &= (Wp)_m = \sum_{m'} W_{mm'} \tilde{p}_{m'} + W_{mV} \left(1 - \sum_{m'} \tilde{p}_{m'}\right) \\ &= W_{mV} + \sum_{m'} (W_{mm'} - W_{mV}) \tilde{p}_{m'} \\ &=: \mathbf{w}_m + (\tilde{W}\tilde{p})_m, \end{aligned}$$

where in the last identity we defined the vector \mathbf{w} with entries $\mathbf{w}_m = W_{mV}$, and the reduced matrix \tilde{W} , which is invertible. Hence

$$\frac{d}{dt}(\tilde{p} + \tilde{W}^{-1}\mathbf{w}) = \tilde{W}(\tilde{p} + \tilde{W}^{-1}\mathbf{w}). \quad (3.3)$$

The steady state that solves the time-independent equation is

$$\tilde{p}^{ss} = -\tilde{W}^{-1}\mathbf{w}.$$

Equation (3.3) then turns into

$$\frac{d\tilde{p}}{dt} = \frac{d}{dt}(\tilde{p} - \tilde{p}^{ss}) = \tilde{W}(\tilde{p} - \tilde{p}^{ss}). \quad (3.4)$$

The matrix \tilde{W} is obtained from W by subtracting the V -th column from each other column and then by eliminating the V -th row and column. Of

course, the choice of the V -th state is arbitrary, so that all of the above can be recast in terms of any reference state k . For example, for a three-state system with generator

$$W = \begin{pmatrix} -w_{21} - w_{31} & w_{12} & w_{13} \\ w_{21} & -w_{12} - w_{32} & w_{23} \\ w_{31} & w_{32} & -w_{13} - w_{23} \end{pmatrix},$$

choosing $k = 2$, we obtain the reduced generator

$$\tilde{W} = \begin{pmatrix} -w_{21} - w_{31} - w_{12} & w_{13} - w_{12} \\ w_{31} - w_{32} & -w_{13} - w_{23} - w_{32} \end{pmatrix}.$$

The general expression for the reduced generator with reference state k is

$$\tilde{W} = W_{\setminus(k,k)} - \mathbf{w} \cdot (1, 1, \dots, 1), \quad (3.5)$$

where the row vector has $V - 1$ copies of number 1 and, the dot stands for the usual matrix product and \mathbf{w} is the k -th column of W , from which the k -th entry has been removed.

As a trivial application of this approach, we solve the reduced master equation for a two state system. Choosing $k = 2$,

$$\dot{p}_1(t) = w_{12} - (w_{21} + w_{12})p_1(t).$$

The general solution is

$$p_1(t) = \frac{w_{12}}{w_{12} + w_{21}} + e^{-(w_{12} + w_{21})t} \left(p_1(0) - \frac{w_{12}}{w_{12} + w_{21}} \right). \quad (3.6)$$

3.3 Semigroup propagator

The formal solution of the time-dependent master equation is found by the same methods employed for the time-dependent Schrodinger equation, and more generally for defining holonomies of Lie groups [72]. In this section we give an explicit expression for the propagators, which will be employed in the Sec.3.4 to introduce an interaction picture and to derive a path measure for stochastic jump processes. This is standard material, yet the author was not able to find a readily accessible derivation in the literature. It might be handy to have a complete treatment. The quantum-mechanical analogy is

found in the quantum formalism developed by Schütz [73, 74], which turns out to be particularly suggestive for treating many-body particle systems. However, we will not employ the quantum notation.

We first put the master equation in the form of an integral equation, setting the initial probability to $p(t_0) = p$,

$$p(t) = p + \int_{t_0}^t dt_1 W(t_1) p(t_1).$$

By recursive substitution we obtain

$$\begin{aligned} p(t) &= \sum_{n=0}^{\infty} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n W(t_1) W(t_2) \dots W(t_n) p \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{n-1}} dt_n \mathcal{T}_{\leftarrow} \{W(t_1) W(t_2) \dots W(t_n)\} p \\ &= \mathcal{T}_{\leftarrow} \left\{ \exp \int_{t_0}^t dt' W(t') \right\} p, \end{aligned} \quad (3.7)$$

where \mathcal{T}_{\leftarrow} is the time-ordering operator, such that

$$\mathcal{T}_{\leftarrow} \{W(t) W(t')\} = \mathcal{T}_{\leftarrow} \{W(t') W(t)\}, \quad t < t'.$$

The second step in the derivation of Eq.(3.7) follows from the fact that the integral over right hyper-triangles with catheti of length t_1, t_2, \dots, t_n is equal to $1/n!$ the integral over hyper-parallelepipeds with sides t_1, t_2, \dots, t_n .

We can recast the master equation in terms of the propagator as

$$\dot{U}(t, t_0) = W(t) U(t, t_0).$$

Propagators satisfy the semigroup property

$$U(t, t') U(t', t'') = U(t, t''). \quad (3.8)$$

The inverse propagator is given by

$$U(t, t_0)^{-1} = U(t_0, t) = \mathcal{T}_{\rightarrow} \left\{ \exp \int_t^{t_0} dt' W(t') \right\} \quad (3.9)$$

Notice that the time-ordering operator is inverted.

3.4 Jump trajectories and the path measure

In this section we give a representation of the propagator in terms of stochastic jump trajectories, similar to the Feynman path integral representation of a quantum propagator. Unlike the quantum path integral [75, Ch.1], discreteness of the state space makes the path measure well-defined and simple.

We resort to an interaction picture, which is analogous to the Dirac picture in QM. We split the generator in a “free” term that generates permanence at a site and an “interaction” term that generates jumps,

$$W(t) = W_0(t) + W_1(t),$$

with

$$W_0(t)_{ij} = \begin{cases} 0, & i \neq j \\ -\sum_k w_{ki}(t), & i = j \end{cases}, \quad W_1(t)_{ij} = \begin{cases} w_{ij}(t), & i \neq j \\ 0, & i = j \end{cases}.$$

We introduce the free propagator

$$U_0(t, t_0) = \mathcal{T}_\leftarrow \left\{ \int_{t_0}^t dt' W_0(t') \right\}, \quad \frac{d}{dt} U_0(t) = W_0(t) U_0(t).$$

The interaction propagator $\tilde{U}_1(t, t_0)$ is defined by the identity

$$U(t, t_0) =: U_0(t, t_0) \tilde{U}_1(t, t_0). \quad (3.10)$$

The final step is to identify the interaction generator $\tilde{W}_1(t)$ which allows to cast the the interaction propagator as a time-ordered exponential

$$\tilde{U}_1(t) = \mathcal{T}_\leftarrow \left\{ \exp \int_{t_0}^t dt' \tilde{W}_1(t') \right\}, \quad \frac{d}{dt} \tilde{U}_1(t) = \tilde{W}_1(t) \tilde{U}_1(t).$$

To find an explicit expression, we take the time derivative of Eq.(3.10). After some simple manipulations we obtain

$$\tilde{W}_1(t) = U_0(t, t_0)^{-1} W_1(t) U_0(t, t_0). \quad (3.11)$$

We now cast the propagator as a sum over paths, weighted by a suitable probability density. Using the interaction picture Eq.(3.10), the explicit expansion for the propagator Eq.(3.7) and the semigroup property Eq.(3.8),

$$\begin{aligned} p(t) &= U_0(t, t_0) \mathcal{T}_\leftarrow \left\{ \exp \int_{t_0}^t dt' \tilde{W}_1(t') \right\} p \\ &= \sum_{n=0}^{\infty} \int_{t_0}^t dt_n \int_{t_0}^{t_1} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 U_0(t, t_n) W_1(t_n) \dots \\ &\quad \dots U_0(t_3, t_2) W_1(t_2) U_0(t_2, t_1) W_1(t_1) U_0(t_1, t_0) p. \end{aligned} \quad (3.12)$$

In view of the last step, we define the probability $q_i(t', t)$ of staying at site i from time t to time t' as

$$q_i(t', t) = \exp - \int_t^{t'} d\tau w_i(\tau),$$

such that $U_0(t', t)_{ij} = q_i(t', t)\delta_{i,j}$. Making matrix entries explicit, we obtain

$$p_j(t) = \sum_{n=0}^{\infty} \sum_{\substack{i_0, \dots, i_{n-1} \\ i_{m+1} \neq i_m}} \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1 \\ q_j(t, t_n) w_{j i_{n-1}}(t_n) \dots q_{i_1}(t_2, t_1) w_{i_1 i_0}(t_1) q_{i_0}(t_1, t_0) p_{i_0}. \quad (3.13)$$

Notice that since $W_1(t)$ has null diagonal entries, we have to exclude from the summation over sites the occurrence of two consecutive identical sites. Inspection of this formula reveals that there arises a path density and a path measure. Let for simplicity $t_{n+1} = t$ and $i_n = j$. We can formally¹ define a trajectory as $\boldsymbol{\iota} = \{i(t'), t' \in [t_0, t]\}$, with

$$i(t') = \sum_{m=0}^n i_m \chi_{[t_m, t_{m+1})}(t'), \quad (3.14)$$

where χ_I is the step function in the interval I . Inspection of Eq.(3.13) reveals that associated to the trajectory $\boldsymbol{\iota}$ there is a path density

$$\text{Prob}(\boldsymbol{\iota}) = q_{i_n}(t, t_n) \left[\prod_{m=0}^{n-1} w_{i_{m+1} i_m}(t_{m+1}) q_{i_m}(t_{m+1}, t_m) \right] p_{i_0} \\ = \exp \left[\sum_{m=0}^{n-1} \ln w_{i_{m+1}, i_m}(t_{m+1}) - \sum_{m=0}^n \int_{t_m}^{t_{m+1}} w_{i_m}(\tau) d\tau \right] p_{i_0}. \quad (3.15)$$

The latter line can be identified as the Girsanov(-Cameron-Martin) formula for continuous-time Markov chains ???. We can then see Eq.(3.13) as an average over paths,

$$U(t, t_0)_{ji} = \int \mathcal{D}\boldsymbol{\iota} \delta_{i(t), j} \delta_{i(0), i} \text{Prob}(\boldsymbol{\iota}) \quad (3.16)$$

where the path measure is given by

$$\int \mathcal{D}\boldsymbol{\iota} = \sum_{n=0}^{\infty} \sum_{i_0, \dots, i_{n-1}} \int_{t_0}^t dt_n \int_{t_0}^{t_n} dt_{n-1} \dots \int_{t_0}^{t_2} dt_1. \quad (3.17)$$

¹See discussion in Sec.6.6.

In later chapters we will mainly be interested in time-dependent processes; in that case a small simplification is possible by performing the changes of variables $t_{m+1} - t_m = \tau_m$. We obtain

$$\text{Prob}(\boldsymbol{t}) = e^{-\tau_n w_{i_n}} \left(\prod_{m=0}^{n-1} w_{i_{m+1} i_m} e^{-\tau_m w_{i_m}} \right) p_{i_0}, \quad (3.18)$$

$$\int \mathcal{D}\boldsymbol{t} = \sum_{n=0}^{\infty} \sum_{\substack{i_0, \dots, i_{n-1} \\ i_{m+1} \neq i_m}} \int_0^{t-t_0} \prod_{m=0}^n d\tau_m \delta\left(t_0 - t + \sum_{m=0}^n \tau_m\right), \quad (3.19)$$

where we introduced a Dirac delta to impose that the time intervals add to $t - t_0$.

3.5 Appying the path measure

As an example, in this section we use the path measure to perform the direct calculation of the propagator for a two state system. Two state systems are particularly simple because sites have to occur alternatively:

$$i_0 = i_2 = \dots, \quad i_1 = i_3 = \dots$$

We only consider the probability of being at site 1 at time t given that we were at site 1 at time $t_0 = 0$ with certainty. We have

$$U_{11}(t) = \sum_{\substack{n \\ \text{even}}} (w_{12} w_{21})^{n/2} \int_0^t d\tau_1 \dots d\tau_{n+1} \delta(\tau_e + \tau_o - t) e^{-w_{12}\tau_e - w_{21}\tau_o}.$$

where

$$\tau_e = \tau_2 + \tau_4 + \tau_6 \dots, \quad \tau_o = \tau_1 + \tau_3 + \tau_5 \dots$$

To solve the model, we take the Laplace transform

$$\begin{aligned} \tilde{U}_{11}(\omega) &= \int_0^t e^{-t\omega} p_1(t) = \sum_{n \in \mathbb{N}} (w_{12} w_{21})^n \int_0^\infty d\tau_1 \dots d\tau_{2n+1} e^{-(w_{12} + \omega)\tau_e - (w_{21} + \omega)\tau_o} \\ &= \sum_{n \in \mathbb{N}} (w_{12} w_{21})^n \left[\int_0^\infty d\tau e^{-(w_{21} + \omega)\tau} \right]^{n+1} \left[\int_0^\infty d\tau e^{-(w_{12} + \omega)\tau} \right]^n \\ &= \frac{1}{w_{21} + \omega} \sum_{n \in \mathbb{N}} \left[\frac{w_{12} w_{21}}{(w_{21} + \omega)(w_{12} + \omega)} \right]^n. \end{aligned}$$

Using the fact that, for $a < 1$,

$$\sum_{n \in \mathbb{N}} a^n = \frac{1}{1-a}.$$

we obtain

$$\tilde{U}_{11}(\omega) = \frac{w_{12} + \omega}{\omega(w_{12} + w_{21} + \omega)}.$$

Inversion of the Laplace transform yields

$$U_{11}(t) = \frac{w_{12}}{w_{12} + w_{21}} + e^{-(w_{12} + w_{21})t} \left(1 - \frac{w_{12}}{w_{12} + w_{21}} \right),$$

which is consistent with Eq.(3.6).

3.6 Ergodic theorems

We consider two kinds of functions defined along a jump trajectory:

- Vertex functions, which hold values in the waiting times,

$$f^t(t) = \sum_m f_{i_m}(t) \chi_{[t_m, t_{m+1})}(t),$$

- Edge functions, which spike at transitions,

$$g^t(t) = \sum_m g_{i_m i_{m-1}}(t) \delta(t - t_m).$$

Ergodic theorems relating path expectation values and ensemble averages hold for the two kinds of functions:

$$\mathbb{E}^{t'}[f^t(t)] = \sum_i p_i(t) f_i(t), \quad (3.20a)$$

$$\mathbb{E}^{t'}[g^t(t)] = \sum_{i,j} w_{ij} p_j(t) g_{ij}(t). \quad (3.20b)$$

Notice that the path averages run up to time $t' \geq t$, but in fact they turn out to be independent of t' . We prove the first identify. Let θ be the Heaviside step function. Then:

$$\begin{aligned} \mathbb{E}^{t'}[f(t)] &= \sum_n \sum_{k \leq n} \sum_{\{i_m\}} \int_0^{t'} \prod_m dt_m \theta(t_m - t_{m-1}) \dots \\ &\dots w_{i_{k+1} i_k}(\tau_{k+1}) q_{i_k}(t_{k+1}, t) f_{i_k}(t) \chi_{[t_k, t_{k+1})}(t) q_{i_k}(t, t_k) \dots p_{i_0}(0). \end{aligned}$$

We now commute $\sum_n \sum_{k \leq n} = \sum_k \sum_{n \geq k}$ and use the fact that $\chi_{[t_k, t_{k+1})}(t) = \theta(t - t_k)\theta(t_k - t)$,

$$\begin{aligned} \mathbb{E}^{t'}[f(t)] &= \sum_k \sum_{n \geq k} \sum_{\{i_m\}} \int_0^{t'} \left[\prod_{m \neq k} dt_m \theta(t_{m+1} - t_m) \right] \theta(t_{k+1} - t) \int_0^{t'} dt_k \theta(t - t_k) \dots \\ &\quad \dots w_{i_{k+1} i_k}(\tau_{k+1}) q_{i_k}(t_{k+1}, t) f_{i_k}(t) q_{i_k}(t, t_k) \dots p_{i_0}(0), \end{aligned}$$

factorize according to

$$\sum_{\{i_m\}} = \sum_{i_n, i_k} \sum_{\substack{\{i_m\} \\ n > m > k}} \sum_{\substack{\{i_m\} \\ k > m}},$$

and separate contributions before time t and contributions after time t . Notice that we are not constraining the trajectories to end at a given state. Therefore after some work and by comparison with the expression for the propagator, Eq.(3.16), we obtain

$$\mathbb{E}^{t'}[f(t)] = \sum_{k, j, i} U(t', t)_{kj} f_j(t) U(t, 0)_{ji} p_i(0)$$

Since the unit vector is a left eigenvector of the propagator, $\sum_k U(t', t)_{kj} = 1$ and Eq.(3.20a) follows. Eq.(3.20b) is proven by an analogous procedure.

3.7 Path inversion

Let us comment very briefly on an important feature of the path measure in the time-independent case. We define the inverse trajectory ι^* (avoid confusion with the notation for duality),

$$i^*(t') = i(t - t') = \sum_{m=0}^n i_m \chi_{[t-t_{m+1}, t-t_m)}(t'). \quad (3.21)$$

The inverse trajectory is a good trajectory, i.e. it belongs to the space of trajectories over which we integrate in Eq.(3.17), hence it is endowed with a well-defined (forward) path measure. Notice that the inverse trajectory waits at site i_0 the same amount of time as the forward trajectory $(t - t_0) - (t - t_1) = t_1 - t_0 = \tau_0$ as the forward trajectory, while the transitions occur in the inverse

direction. Hence by inspection of the path measure Eq.(3.18) we can guess the correct path measure of the trajectory:

$$\text{Prob}(\boldsymbol{\iota}^*) = e^{-\tau_0 w_{i_0}} \left(\prod_{m=0}^{n-1} w_{i_m i_{m+1}} e^{-\tau_{m+1} w_{i_{m+1}}} \right) p_{i_n}(t). \quad (3.22)$$

This suggests the definition of the inverse probability measure over trajectories as the one satisfying

$$\text{Prob}^*(\boldsymbol{\iota}) = \text{Prob}(\boldsymbol{\iota}^*)$$

Inversion a trajectory is an involutive operation, therefore one has $\text{Prob}^*(\boldsymbol{\iota}^*) = \text{Prob}(\boldsymbol{\iota})$. The inverse path measure can be derived by a more rigorous procedure, analogous to what done above for the forward trajectory, considering the inverse propagator. We will not pursue this result here. Notice that the path measure is invariant under path inversion

$$\mathcal{D}\boldsymbol{\iota} = \mathcal{D}\boldsymbol{\iota}^*. \quad (3.23)$$

We conclude this chapter with a formula which will pave the way for the fluctuation theorems in Ch.4. Notice in fact that when composing the Girsanov-Cameron-Martin formulas of the forward and backward probability densities we obtain

$$\frac{\text{Prob}(\boldsymbol{\iota})}{\text{Prob}^*(\boldsymbol{\iota})} = \left(\prod_{m=0}^{n-1} \frac{w_{i_{m+1} i_m}}{w_{i_m i_{m+1}}} \right) \frac{p_{i_0}(0)}{p_{i_n}(t)}. \quad (3.24)$$

We also refer (somewhat improperly) to Eq.(3.24) as the Girsanov-Cameron-Martin property under time inversion.

4

Master equation: thermodynamics

This chapter is devoted to the stochastic thermodynamics of master equation systems. In the first part of the chapter, we introduce the internal, environmental and total entropy production rates¹ for continuous-time Markov chains in Sec.4.1, and their microscopic counterparts, defined along single jump processes in Sec.4.2. Sec.4.3 gives a survey of Fluctuation Theorems for Schnakenberg-type splittings of the entropy production rate.

The second part delves into the thermodynamical interpretation in the light of the Local Detailed Balance *ansatz*, which is introduced in Sec.4.4 and put to work alongside with our own network analysis of macroscopic observables in Sec.4.5. In this approach, circulations of the mesoscopic forces return Clausius’s expression for the entropy of a cyclic process, affinities of a particular fundamental set are related to temperature differences, and heat fluxes arise as the relevant fluctuating variables. The linear regime constitutive relationships for the heat fluxes are studied in Sec.4.6, while Sec.4.7 exploits the Fluctuation Theorems to prove Green-Kubo type of relationships for the linear response coefficients. We conclude this chapter with a derivation of Local Detailed Balance rates for Open Quantum Systems weakly interacting with the environment.

¹Notice that we restored the specification “rate”.

4.1 Entropy production

The (Gibbs-Shannon) entropy of a probability distribution $p = (p_i)_{i \in V}$ over a finite set is defined as

$$S(p) := - \sum_i p_i \log p_i.$$

Entropy is a state function. It quantifies the amount of ignorance a observer has about the state of the system. It is an internal property of the system. When we deal with continuous-time Markov chains, entropy inherits a time-dependence from the probability distribution,

$$S(t) := S(p(t)) = - \sum_i p_i(t) \log p_i(t). \quad (4.1)$$

Its time derivative describes how the microstate of a jump trajectory becomes more or less predictable in time, according to

$$\begin{aligned} \sigma_{sys}(t) := \dot{S}(t) &= - \sum_i [Wp(t)]_i \log p_i(t) \\ &= \sum_{i < j} [w_{ij} p_j(t) - w_{ji} p_i(t)] \log \frac{p_j(t)}{p_i(t)} \\ &=: \sum_{i < j} j_{ij}(t) \log \frac{p_j(t)}{p_i(t)}, \end{aligned}$$

where we used the fact that $\sum_i [Wp(t)]_i = 0$, and in the third passage we implicitly defined the probability current $j_{ij}(t)$ from state j to state i . The time derivative of the entropy $\sigma_{sys}(t)$ only describes that part of the thermodynamics of an open system which in a way codes the information flow from the system towards an observer. We call this the internal entropy production rate, as it only depends on the state of the system. Along with his network analysis, one major contribution due to Schnakenberg [11] is the identification of a second term σ_{env} to the total entropy production rate of a system, which is due to the entropy flow towards an external environment. He assumed that the total entropy production rate

$$\sigma(t) = \sigma_{env}(t) + \sigma_{sys}(t)$$

should be positive for general nonequilibrium systems and should only vanish at equilibrium steady states, in view of the Second Law of Thermodynamics.

He then observed that the environmental entropy production rate is well described by

$$\sigma_{env}(t) := \sum_{i<j} j_{ij}(t) \log \frac{w_{ij}}{w_{ji}}, \quad (4.2)$$

yielding for the total entropy production rate

$$\sigma(t) = \sum_{i<j} j_{ij}(t) a_{ij}(t), \quad (4.3)$$

where the mesoscopic forces between states are defined as

$$a_{ij}(t) := \log \frac{w_{ij} p_j(t)}{w_{ji} p_i(t)}. \quad (4.4)$$

It is a trivial exercise to prove that a_{ij} is positive if and only if j_{ij} is positive, hence σ is a positive bilinear form. In fact, it can be argued that this identification is unique under reasonable assumptions. In Ch.6 we give a completely different argument for motivating Schnakenberg's choice, based on gauge invariance. Yet another argument comes from information theory [77, §4.2]; we give a survey in Sec.4.2.

The splitting of the entropy production rate in environmental and internal contributions is one of many possible splittings. Esposito and Van den Broeck [78] considered a splitting in terms of the time derivative of the relative entropy with respect to the steady state (adiabatic term) and a jump contribution (non-adiabatic term),

$$\begin{aligned} \sigma_a(t) &:= \sum_{i,j} j_{ij}(t) \log \frac{p_j(t)}{p_j^{ss}} = -\frac{d}{dt} S(p(t) \| p^{ss}) \\ \sigma_{n.a.}(t) &:= \sum_{i<j} j_{ij}(t) \log \frac{w_{ij} p_j^{ss}}{w_{ij} p_i^{ss}}, \end{aligned}$$

where $S(\cdot \| \cdot)$ denotes the relative entropy, or Kullback-Liebler distance. Properties of this splitting are that the adiabatic term vanishes at steady states, and the non-adiabatic term vanishes for systems which satisfy detailed balance, that is when

$$a_{ij}^{ss} = \log \frac{w_{ij} p_j^{ss}}{w_{ij} p_i^{ss}} = 0. \quad (4.5)$$

Notice that this characterization of detailed balance is consistent with the one given in Sec.(1.4), as if Eq.(4.5) holds then there exists a time-dependent vertex potential $u_i(t) = \log p_j(t)/p_j^*$ such that $a_{ij}(t) = u_j(t) - u_i(t)$.

Splittings of the entropy production that are analogous to the adiabatic/nonadiabatic splitting can be given starting from a spanning tree and applying our generalized Schnakenberg decomposition, as in Eq.(1.35). We will discuss in this chapter their thermodynamical characterization. Let us conclude this section with the observation the the external macroscopic forces

$$A(c) = (c, a) = \log \prod_{ij \in c} \frac{w_{ij}}{w_{ji}},$$

turn out to be time-independent (if transition rates are), as they do not depend on the state of the system, but only on the transition rates, which on the other hand can be thought of as properties of the environment. This is another important clue that led Schnakenberg to the identification of these observables as the macroscopic external nonequilibrium constraints.

4.2 Path entropies

In this chapter we introduce microscopic analogues along single paths (stochastic process) whose averages return the various entropy production rates defined above, giving strength to the above definitions.

Consider for the moment a discrete-time stochastic process $(X_\tau)_{\tau=1}^n$. Its (forward) entropy rate is defined as [77]

$$\sigma^+ = -\lim_{n \rightarrow \infty} \frac{1}{n} \sum_{i_1, \dots, i_n} \text{Prob}(X_n = i_n, \dots, X_1 = i_1) \log \text{Prob}(X_n = i_n, \dots, X_1 = i_1),$$

if the limit exists. In the right-hand side there appears the entropy of the joint probability distribution. For example, for independent and identically distributed random variables, sampled with probability μ , the entropy rate turns out to coincide with the entropy $S(\mu)$ of the stationary distribution². In case of stationary ergodic Markov chains having transition matrix $\Pi = (\pi_{ij} \geq 0)_{i,j}$, with $\sum_i \pi_{ij} = 1$, one can prove that

$$\sigma^+ = -\sum_{i,j} \pi_{ij} p_j^{ss} \log \pi_{ij}. \quad (4.6)$$

²Notice that we use both $S(\mu)$ and $S(X)$ to denote the entropy of a process.

The entropy rate Eq.(4.6) is also known as Kolmogorov-Sinai entropy [79]. We now introduce the inverse probability distribution as the probability of the inverse process,

$$\text{Prob}^*(X_n = i_n, \dots, X_1 = i_1) := \text{Prob}(X_n = i_1, \dots, X_1 = i_n) \quad (4.7)$$

and define the entropy production rate at the steady state as

$$\sigma(p^{ss}) := \lim_{n \rightarrow \infty} \frac{1}{n} \sum_{i_1, \dots, i_n} \text{Prob}(X_n = i_n, \dots) \log \frac{\text{Prob}(X_n = i_n, \dots)}{\text{Prob}^*(X_n = i_n, \dots)} \quad (4.8)$$

where in the right-hand side we considered the relative entropy between the forward probability with respect to the inverse probability. It can be shown that the result is

$$\sigma(p^{ss}) = \sum_{i < j} (\pi_{ij} p_j^{ss} - \pi_{ji} p_i^{ss}) \log \frac{\pi_{ij}}{\pi_{ji}}.$$

This approach shows that the definition of the entropy production rate contains information about time-inversion of trajectories, consistently with the spirit of the Second Law, which measures the degree of violation of time-reversal invariance.

We now replicate this approach with continuous-time Markov chains. We claim that the total entropy production satisfies

$$\sigma(t) = \frac{d}{dt} \int \mathcal{D}\boldsymbol{\iota} \text{Prob}^t(\boldsymbol{\iota}) \log \frac{\text{Prob}^t(\boldsymbol{\iota})}{\text{Prob}^t(\boldsymbol{\iota}^*)}, \quad (4.9)$$

where trajectories elapse up time t , and we replaced $\lim_{t \rightarrow \infty} t^{-1}$ with the time-derivative so to generalize to non-steady states. We know from the proof of the ergodic theorem that the time $t' \geq t$ at which we evaluate the expectation value is irrelevant. Then

$$\sigma(t) = \mathbb{E}^{t'} [\sigma^t(t)],$$

where we defined the microscopic analogue of the entropy production along a trajectory as

$$\sigma^t(t) := \frac{d}{dt} \log \frac{\text{Prob}^t(\boldsymbol{\iota})}{\text{Prob}^t(\boldsymbol{\iota}^*)} = \sigma_{env}^t(t) + \sigma_{sys}^t(t).$$

Notice that setting $t' \geq t$ allowed us to commute the time derivative and the path integral in Eq.(4.9). In the right-hand side of the last equation we introduced the environmental and the internal entropy production rates along trajectories,

$$\sigma_{env}^\iota(t) := \sum_m \log \frac{w_{i_{m+1}i_m}}{w_{i_m i_{m+1}}} \delta(t - t_m), \quad (4.10a)$$

$$\sigma_{sys}^\iota(t) := - \sum_m \frac{[Wp(t)]_{i_m}}{p_{i_m}(t)} \chi_{[t_m, t_{m+1})}(t). \quad (4.10b)$$

Integrating over time:

$$\Sigma_{sys}^\iota(t) := \int_0^t \sigma_{sys}^\iota(t') dt' = \log p_{i_0}(0) - \log p_{i_n}(t) \quad (4.11)$$

$$\Sigma_{env}^\iota(t) := \int_0^t \sigma_{env}^\iota(t') dt' = \sum_m \log \frac{w_{i_{m+1}i_m}}{w_{i_m i_{m+1}}},$$

where we defined the (integrated) environmental and internal entropy productions. The internal entropy production is the difference between the so-called self-information of the final state and that of the initial state – a measure of the typicality of the occurrence of a state when sampled from a probability distribution (see Ref. [80]). The total entropy production is

$$\Sigma^\iota(t) := \Sigma_{sys}^\iota(t) + \Sigma_{env}^\iota(t) = \log \frac{\text{Prob}^t(\boldsymbol{\iota})}{\text{Prob}^t(\boldsymbol{\iota}^*)}, \quad (4.12)$$

consistently with the Girsanov-Cameron-Martin property, Eq.(3.24).

Finally, we need to prove that Eq.(4.9) is consistent with Eq.(4.3). We apply both ergodic theorems, Eqs.(3.20a,3.20b), obtaining:

$$\sigma_{env}(t) = \mathbb{E}^t[\sigma_{env}^\iota(t)], \quad \sigma_{sys}(t) = \mathbb{E}^t[\sigma_{sys}^\iota(t)]. \quad (4.13)$$

To resume, we introduced stochastic processes corresponding to the environmental, the internal and the total entropy production rates, such that the mesoscopic expressions are expectation values of the microscopic analogues.

Stochastic thermodynamics was initiated by Sekimoto [81]. A good general review is the one by Seifert [82].

4.3 Fluctuation theorems

Fluctuation Theorems [6–8] prescribe a time-reversal symmetry between extreme fluctuations of non-equilibrium processes. The literature on the argument has literally exploded in the past fifteen years. We do not linger on the physical meaning and mathematical premises, but head on steadfastly to the derivation of Fluctuation Theorems in the context of Schnakenberg’s analysis. Some reference works that might be propaedeutic to this section are the ones by Lebowitz and Spohn [71], by Andrieux and Gaspard [16, 21] and by Faggionato and Di Pietro [19]. In these works Fluctuation Theorems are derived by means of generating functions and Large Deviation Theory. We proceed by a less-elegant, brute-force method which consists in direct application of the path measure, as is done in Refs. [78, 83]. One advantage is that, while Large Deviation Theory by its own nature only deals with the long time behavior, yielding asymptotic-type relations, our approach allows the derivation of more general transient relations. We will be very sketchy and only concentrate on what is strictly necessary for deriving results.

Consider the discrete jump trajectory $\boldsymbol{\iota}$ in Eq.(3.14) and the Girsanov-Cameron-Martin property, which we have rewritten in Eq.(4.12) in terms of the (integrated) entropy production. Given that the entropy production along a trajectory is obviously antisymmetric under path inversion,

$$\Sigma^{\boldsymbol{\iota}^*}(t) = -\Sigma^{\boldsymbol{\iota}}(t),,$$

and that the path measure is invariant, see Eq.(3.23), after some manipulation of Eq.(4.12), and integrating over all trajectories with a given entropy production value $\hat{\Sigma}$ (time-dependence not shown),

$$\begin{aligned} \int \mathcal{D}\boldsymbol{\iota} \delta(\Sigma^{\boldsymbol{\iota}} - \hat{\Sigma}) \text{Prob}(\boldsymbol{\iota}) &= \int \mathcal{D}\boldsymbol{\iota} \delta(\Sigma^{\boldsymbol{\iota}} - \hat{\Sigma}) \text{Prob}(\boldsymbol{\iota}^*) \exp \Sigma^{\boldsymbol{\iota}} \\ &= e^{\hat{\Sigma}} \int \mathcal{D}\boldsymbol{\iota}^* \delta(\Sigma^{\boldsymbol{\iota}^*} + \hat{\Sigma}) \text{Prob}(\boldsymbol{\iota}^*), \end{aligned}$$

we obtain for any value of t the Transient Fluctuation Theorem

$$\frac{\text{Prob}[\Sigma^{\boldsymbol{\iota}} \equiv \hat{\Sigma}]}{\text{Prob}[\Sigma^{\boldsymbol{\iota}} \equiv -\hat{\Sigma}]} = \exp \hat{\Sigma}. \quad (4.14)$$

Given the splitting of the entropy production in Eq.(4.12), considering that the internal entropy production only contributes a boundary term, while the

environmental contribution grows linearly with time, we obtain the Asymptotic Fluctuation Theorem for the environmental entropy production rate

$$\frac{\text{Prob} \left[\frac{1}{t} \int_0^t \sigma_{env}^\nu(t') dt' \equiv \hat{\sigma}_{env} \right]}{\text{Prob} \left[\frac{1}{t} \int_0^t \sigma_{env}^\nu(t') dt' \equiv -\hat{\sigma}_{env} \right]} \underset{t}{\sim} \exp t \hat{\sigma}_{env}, \quad (4.15)$$

where “ $\underset{t}{\sim}$ ” is the symbol for asymptotic tendency at large times. We emphasize again that it is crucial for this to hold that integrating the internal entropy production rate along a trajectory yields a boundary term, Eq.(4.11). This finds correspondence in the fact that its path average is the total time derivative of an ensemble average (namely, the Gibbs-Shannon entropy). The Transient Fluctuation Theorem for the entropy production and the Asymptotic Fluctuation Theorem for the environmental entropy production rate are usually found in the specialized literature [74].

In fact, we can do slightly better than Eq.(4.15). If we integrate over all trajectories with fixed initial and final sites,

$$\begin{aligned} & \int \mathcal{D}\boldsymbol{\nu} \delta_{i_t, j} \delta_{i_0, i} \delta(\Sigma_{env}^\nu - \Sigma_{env}) \text{Prob}^t(\boldsymbol{\nu}) \\ &= \frac{p_i(0)}{p_j(t)} \int \mathcal{D}\boldsymbol{\nu} \delta_{i_t, j} \delta_{i_0, i} \delta(\Sigma_{env}^\nu - \Sigma_{env}) \text{Prob}^t(\boldsymbol{\nu}^*) \exp \Sigma_{env}^\nu, \end{aligned}$$

we obtain the fixed-end points Fluctuation Theorem for the environmental entropy production

$$\frac{\text{Prob} \left[\Sigma_{env}^\nu(t) \equiv \hat{\Sigma}_{env}, i_t = j, i_0 = i \right]}{\text{Prob} \left[\Sigma_{env}^\nu(t) \equiv -\hat{\Sigma}_{env}, i_t = i, i_0 = j \right]} = \frac{p_i(0)}{p_j(t)} \exp \hat{\Sigma}_{env}.$$

Now, we suppose that rates are incommensurable, i.e. that the following ratios are all irrational

$$\frac{w_{ij}}{w_{kl}} \in \mathbb{R} \setminus \mathbb{Q}, \quad \forall kl \neq ij.$$

Find in Sec.5.3 a thorough discussion of this assumption. As a matter of fact, systems with incommensurable rates are the overwhelming majority, as the set of systems with commensurable rates has measure zero in the set of all possible systems. It follows from the discussion in Sec.5.3 that trajectories

which start at site i , with a given environmental entropy production $\hat{\Sigma}_{env}$ (see Eq.(4.12), if there exists any, necessarily end at the same site, and vice versa for the inverse trajectories. Hence for almost all systems we have³

$$\frac{\text{Prob} \left[\Sigma_{env}^\iota(t) \equiv \hat{\Sigma}_{env}, i_0 = i \right]}{\text{Prob} \left[\Sigma_{env}^\iota(t) \equiv -\hat{\Sigma}_{env}, i_0 = j \right]} = \frac{p_i(0)}{p_j(t)} \exp \hat{\Sigma}_{env}. \quad (4.17)$$

Manipulating as usual the above expression, and summing over i and j we obtain the Transient Fluctuation Theorem for the environmental entropy production

$$\frac{\text{Prob} \left[\Sigma_{env}^\iota(t) \equiv \hat{\Sigma}_{env} \right]}{\text{Prob} \left[\Sigma_{env}^\iota(t) \equiv -\hat{\Sigma}_{env} \right]} = \exp \hat{\Sigma}_{env}.$$

Along this line, we move on to prove that similar fluctuation theorems hold for the steady entropy production. We fix a spanning tree T . The key ingredient is that the transient entropy production rate is the total time derivative of an ensemble average

$$\sigma_{db} = \frac{d}{dt} \sum_i p_i(t) \left[-\log p_i(t) + \Gamma_i(t) \right].$$

Let us prove this fact. A cocycle current is the total current which flows out of the source of the cocycle (we remind that a cocycle separates two connected domains of the graph, the source and the target sets of the cocycle). Then the macroscopic current along cocycle c_*^μ is the time derivative of the total probability in the source set of the cocycle, see Eq.(1.37). We split its conjugate internal force according to

$$A_\mu^* = \log \frac{w_{e_\mu^*}}{w_{-e_\mu^*}} + \delta_{e_\mu^*} \log p.$$

where the coboundary operator δ_e is defined by

$$\delta_e \varepsilon = \varepsilon_{t(e)} - \varepsilon_{s(e)}, \quad (4.18)$$

³In other words, with the exception of cycles we have

$$\text{Prob} \left[\Sigma_{env}^\iota(t) \equiv \hat{\Sigma}_{env}, i_t = j, i_0 = i \right] = \text{Prob} \left[\Sigma_{env}^\iota(t) \equiv \hat{\Sigma}_{env} \right] \delta_{i,k} \delta_{j,l} \quad (4.16)$$

where l and k are the unique states which allow a path with environmental entropy production $\hat{\Sigma}_{env}$. Cycles need some further consideration. Summing over i, j, k, l yields Eq.(4.17).

It is easily seen to be the transpose of the incidence matrix, $\delta = \partial^T$. We need the following graph-theoretical result. Let $f = (f_i)_{i \in V}$ be a function on the vertex set. Then

$$\sum_{\mu} J_{*}^{\mu} \delta_{e_{\mu}^{*}} f = (f, \partial j)_V \quad (4.19)$$

From the cycle/cocycle decomposition: $\sum_e j_e g_e = \sum_{\alpha} (c^{\alpha}, g) j_{e_{\alpha}} + \sum_{\mu} (c_{*}^{\mu}, j) g_{e_{\mu}^{*}}$. In this case $g = \delta f$ makes the circulation along cycles vanish, $(c^{\alpha}, \delta f) = 0$, from which we obtain $\sum_{\mu} J_{*}^{\mu} \delta_{e_{\mu}^{*}} f = (j, \delta f)_E = (f, \partial j)_V$. Applying Eq.(4.19), the transient entropy production rate results

$$\sigma_{db} = \frac{d}{dt} \left[S(t) + \sum_{\mu} \log \frac{w_{e_{\mu}^{*}}}{w_{-e_{\mu}^{*}}} \sum_{i \in S(c_{*}^{\mu})} p_i(t) \right].$$

Pulling out the probabilities we obtain the desired result, with

$$\Gamma_i = \sum_{\substack{\mu \\ S(c_{*}^{\mu}) \ni i}} \log \frac{w_{e_{\mu}^{*}}}{w_{-e_{\mu}^{*}}},$$

where the sum over μ is carried over cocycles whose sources contain site i . Let us work out a more intuitive expression for Γ_i . We can always choose an orientation of the edges such that the fundamental spanning tree T is oriented and rooted at some k , i.e. such that there exists a unique oriented path γ_{ik} along T which goes from i to k . Then

$$\Gamma_i = \log \prod_{e \in \gamma_{ik}} \frac{w_e}{w_{-e}}.$$

For equilibrium systems we have

$$\langle \Gamma \rangle_p = \sum_i p_i \Gamma_i = \sum_i p_i \log p_i^{ss} - \log p_k^{ss}$$

which up to an additive constant is the mutual information of state p with respect to the steady state. It is independent of the particular spanning tree chosen: in fact, for equilibrium systems $\sigma_{ss} = 0$ implies that σ_{db} is the same for any choice of a fundamental spanning tree. Therefore $\langle \Gamma \rangle$ can be seen as a measure of the peculiarity of the fundamental set chosen.

Integrating σ_{db} over time yields the transient entropy production

$$\Sigma_{db}(t) = S(t) - S(0) + \langle \Gamma \rangle_{p(t)} - \langle \Gamma \rangle_{p(0)}. \quad (4.20)$$

The second step towards a Fluctuation Theorem is the definition of a well-behaved stochastic process whose mean returns $\Sigma_{db}(t)$. We evaluate $-\log p_i + \Gamma_i$ along a trajectory, yielding as microscopic counterpart

$$\Sigma_{db}^\nu(t) = \log p_{i_0}(0) - \log p_{i_n}(t) + \Gamma_{i_n} - \Gamma_{i_0}.$$

We write its time derivative in this form,

$$\sigma_{db}^\nu(t) = \frac{d}{dt} \Sigma_{db}^\nu(t) = \sum_m \delta(t - t_m) \left[\log \frac{p_{i_{m+1}}(t)}{p_{i_m}(t)} + \Gamma_{i_{m+1}} - \Gamma_{i_m} \right]. \quad (4.21)$$

The validity of this formula can be tested by direct integration (it is seen to be consistent with the one involving step functions, Eq.(4.10b), once one realizes its distributional character and the fact that Dirac deltas are derivatives of Heaviside step functions).

Notice that Γ_i is well-behaved under composition of paths, i.e. $\Gamma_i - \Gamma_j$ is calculated along the unique path in T which goes from j to i ,

$$\Gamma_{i_{m+1}} - \Gamma_{i_m} = \log \prod_{e \in \gamma_{i_{m+1}i_m}} \frac{w_e}{w_{-e}}.$$

Then

$$\sigma_{db}^\nu(t) = \sum_m \delta(t - t_m) \log \left[\frac{p_{i_{m+1}}(t)}{p_{i_m}(t)} \cdot \prod_{e \in \gamma_{i_{m+1}i_m}} \frac{w_e}{w_{-e}} \right].$$

Inserting an edge-delta $\sum_e \delta_{t(e), i_{m+1}} \delta_{s(e), i_m} = 1$ and rearranging logarithms:

$$\sigma_{db}^\nu(t) = \sum_e \overbrace{\sum_m \delta(t - t_m) \delta_{t(e), i_{m+1}} \delta_{s(e), i_m}}^{j_e} \sum_{ij \in \gamma_{t(e)s(e)}} \log \frac{w_{ij} p_j(t)}{w_{ji} p_i(t)}.$$

The over-brace is used to define the fluctuating current along an edge, returning a definition given by Andrieux and Gaspard [21]. The physical picture is clear: microscopic currents spike whenever a jump along e occurs, giving a contribution to the transient entropy production with a suitable weight.

We need another graph-theoretical identity:

$$\sigma_{db} = \sum_\mu (e_\mu^*, a)(c_\mu^*, j) = \sum_e j_e \sum_{e' \in \gamma} a_{e'}, \quad (4.22)$$

where γ is the unique path across the spanning tree T from the source vertex of edge e to its target vertex. In fact, the right-hand side gives

$$\sum_e j_e \left(\sum_{e' \in \gamma} a_{e'} + a_e - a_e \right) = \sigma + \sum_e j_e \left(\sum_{e' \in \gamma} a_{e'} - a_e \right) = \sigma_{db},$$

where we used the fact that the term between parenthesis vanishes when e is a cochord, otherwise it coincides with $-A^\alpha$ when $e = e_\alpha$ is a generating chord.

If we now subtract the transient term from the total microscopic entropy production, applying Eq.(4.22)

$$\sigma_{ss}^\iota(t) = \sigma^\iota(t) - \sigma_{db}^\iota(t) = \sum_\alpha A^\alpha J_\alpha^\iota(t), \quad J_\alpha^\iota(t) := j_{e_\alpha}^\iota(t)$$

which is easily identified as the microscopic steady entropy production rate. Notice that the A^α 's are macroscopic affinities. They are path-independent, and that they do not depend on time. They are non-fluctuating variables.

To resume, so far we managed to find a set of fluctuating microscopic fundamental currents and a state-function such that the entropy production rate along a trajectory can be written as

$$\sigma^\iota(t) = \sum_\alpha J_\alpha^\iota(t) A^\alpha + \frac{d}{dt} [-\log p_{i_t}(t) + \Gamma_{i_t}].$$

Finally, the third and last step is to integrate over trajectories with fixed end-points and given integrated fundamental currents (also known as Helfand moments, [21]), obtaining

$$\frac{\text{Prob} \left[\int_0^t j_\alpha^\iota(t') dt' \equiv \Lambda_\alpha, i_0 \right]}{\text{Prob} \left[\int_0^t j_\alpha^\iota(t') dt' \equiv -\Lambda_\alpha, i_t \right]} = \frac{p_{i_0}(0)}{p_{i_t}(t)} \exp \left(\sum_\alpha A^\alpha \Lambda_\alpha + \Gamma_{i_t} - \Gamma_{i_0} \right), \quad (4.23)$$

from which we derive a Conditional Fluctuation Theorem

$$\frac{\text{Prob} \left[\int_0^t j_\alpha^\iota(t') dt' \equiv \Lambda_\alpha | i_0 \right]}{\text{Prob} \left[\int_0^t j_\alpha^\iota(t') dt' \equiv -\Lambda_\alpha | i_t \right]} = \exp \left(\sum_\alpha A^\alpha \Lambda_\alpha + \Gamma_{i_t} - \Gamma_{i_0} \right).$$

Summing over the initial and final states in Eq.(4.23) we obtain the Transient Fluctuation Theorem for the currents, which is a generalization of the Andrieux-Gaspard theorem:

$$\frac{\text{Prob} \left[\int_0^t j_\alpha^\iota(t') dt' \equiv \Lambda_\alpha \right]}{\text{Prob} \left[\int_0^t j_\alpha^\iota(t') dt' \equiv -\Lambda_\alpha \right]} = \frac{\langle \exp -\Gamma \rangle_{p(0)}}{\langle \exp -\Gamma \rangle_{p(t)}} \exp \sum_\alpha A^\alpha \Lambda_\alpha. \quad (4.24)$$

In the long-time limit the Andrieux-Gaspard theorem is recovered

$$\frac{\text{Prob} \left[\frac{1}{t} \int_0^t j_\alpha^\iota(t') dt' \equiv \lambda_\alpha \right]}{\text{Prob} \left[\frac{1}{t} \int_0^t j_\alpha^\iota(t') dt' \equiv -\lambda_\alpha \right]} \stackrel{t}{\asymp} \exp t \sum_\alpha A^\alpha \lambda_\alpha.$$

Finally, if we integrate over all trajectories with a given steady state entropy production (that is, if we do not resolve single currents) we obtain the Asymptotic Fluctuation Theorem for the steady entropy production rate,

$$\frac{\text{Prob} \left[\frac{1}{t} \int_0^t \sigma_{ss}^\iota(t') dt' \equiv \hat{\sigma}_{ss} \right]}{\text{Prob} \left[\frac{1}{t} \int_0^t \sigma_{ss}^\iota(t') dt' \equiv -\hat{\sigma}_{ss} \right]} \stackrel{t}{\asymp} \exp t \hat{\sigma}_{ss}. \quad (4.25)$$

4.4 Local detailed balance

We discuss in this and later sections the Local Detailed Balance *ansatz*, which allows to give an intuitive physical interpretation of master equation thermodynamics, including macroscopic affinities, which follows the spirit of the Schnakenberg’s original motivation. Schnakenberg considered an auto-catalytic reaction system in which the population of a chemical species X can increase or decrease by one unity according to two independent chemical reactions with molecule reservoirs A and B at fixed density, and stoichiometric coefficients $\nu_A = \nu_B = 1$. While inhibition of one of the reactions yields a detailed balanced open system which relaxes to equilibrium, when both mechanisms concur the system reaches a nonequilibrium steady state, with a net flux of molecules from one reservoir to the other. He commented that

“in our example, these transitions belong to independent chemical reactions and thus have to be treated independently in the mathematical and physical considerations [...] We stress this point because for the purpose of a solution of [the master equation] it is convenient to compress the two transitions formally into one. This is a purely formal trick and must not be misinterpreted as a physical change of the system”.

Let i be the population of X. The total rate at which a molecule is produced or destroyed is resolved into two mechanisms

$$w_{i\pm 1, i} = w_{i\pm 1, i}^{(A)} + w_{i\pm 1, i}^{(B)}.$$

Each set of rates independently satisfies detailed balance

$$w_{i+1,i}^{(A)}/w_{i,i+1}^{(A)} = \exp \beta \mu_A, \quad w_{i+1,i}^{(B)}/w_{i,i+1}^{(B)} = \exp \beta \mu_B, \quad (4.26)$$

where μ_A, μ_B are the chemical potentials. Direct calculation shows that all affinities are integer multiples of the logarithm of

$$\frac{w_{i+1,i}^{(A)} w_{i,i+1}^{(B)}}{w_{i,i+1}^{(A)} w_{i+1,i}^{(B)}} = \frac{\tau_{AB}}{\tau_{BA}} = \exp \beta (\mu_B - \mu_A). \quad (4.27)$$

It can be shown (see Sec.5.3, Refs. [15, 84]) that this quantity is the ratio of the average time τ_{AB} for producing a molecule with mechanism B and annihilating it with mechanism A, with respect to the average time τ_{BA} in which process A produces a molecule which is annihilated through B, at the steady state. This yields a dynamical characterization of Schnakenberg's circulations. On the other hand, there is a thermodynamical characterization as the external forces which determine the nonequilibrium nature of the system: in this case, they are the chemical potential difference, determining a flux of matter. For general chemical reaction networks of dilute systems, Schnakenberg's affinities always have a similar interpretation; the complete treatment can be found in Ref. [16].

We now abandon the chemical setting and only retain the idea that transition rates can be resolved into several mechanisms

$$w_{ij} = \sum_{\nu} w_{ij}^{(\nu)}, \quad (4.28)$$

each independently satisfying detailed balance

$$w_{ij}^{(\nu)}/w_{ji}^{(\nu)} = \exp \beta^{(\nu)} (\varepsilon_j - \varepsilon_i). \quad (4.29)$$

where ε_i is some weight associated to state i . This assumption is known as Local Detailed Balance [46]. In general, we will interpret the state's weight as an energy and the $\beta^{(\nu)}$ as inverse temperatures of several independent reservoirs; this will be the case in Sec.4.8, where we derive Eq.(4.29) for open quantum systems. It's simple however to make a generalization to open systems which exchange both energy and particles, with

$$w_{ij}^{(\nu)}/w_{ji}^{(\nu)} = \exp [\beta^{(\nu)} (\varepsilon_j - \varepsilon_i) + \mu^{(\nu)} (N_j - N_i)], \quad (4.30)$$

and to any other situation where a state function of the system is coupled to a conjugate parameter of the environment. From the graphical point of view, we represent transition mechanisms by means of multiple edges (see Fig.4.1a).

We referred to Local Detailed Balance as an assumption. Is Local Detailed Balance restrictive? At the level of the master equation, it is not: given a set of arbitrary rates, one can always define an energy function and a suitable number of temperatures such that transition rates satisfy local detailed balance. For this reason we prefer to talk about the Local Detailed Balance *ansatz*. In fact, there exists an equivalence class of reservoirs which give rise to the same collection of rates. We say that rates satisfy the condition of minimal coupling: each transition is due to only one mechanism; as we will see, considering more than one mechanisms per rate modifies the thermodynamical description. Choose a spanning tree T . Fixing one ground value ε_k of the energy at k and one reference temperature β , the energy levels of the system are uniquely determined by

$$w_{ij}/w_{ji} = \exp \beta(\varepsilon_j - \varepsilon_i), \quad ij \in T, \quad (4.31)$$

along the links of the spanning tree. Along the remaining $C = E - V + 1$ links we define a cyclomatic number of temperatures $\beta^{(\nu)}$ such that

$$w_{ij}/w_{ji} = \exp \beta^{(\nu)}(\varepsilon_j - \varepsilon_i), \quad ij \in E \setminus T. \quad (4.32)$$

Considering that ε_k and β are arbitrary, it takes $V - 1$ energy levels and $C - 1$ temperatures to realize a minimal coupling reservoir for a given set of transition rates.

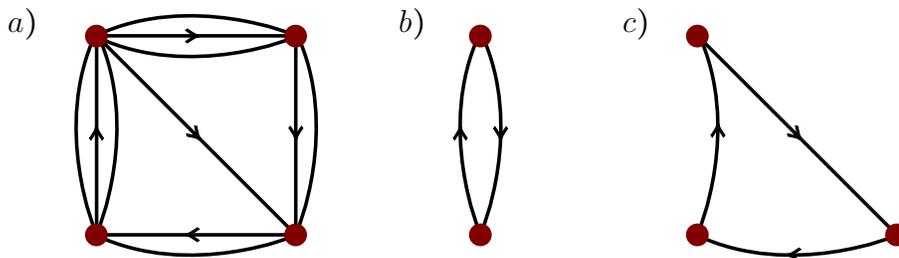


Figure 4.1: a) Multiple transitions for an oriented graph. Convex, concave and straight edges correspond to three different mechanisms. b) A non-topological cycle. c) A topological cycle.

We will talk of “lumping” when we coarse grain, by considering the sum over mechanisms as in Eq.(4.28). Let us define the partial generators

$$[W^{(\nu)}p]_i = \sum_j j_{ij}^{(\nu)} = \sum_j \left(w_{ij}^{(\nu)} p_j - w_{ji}^{(\nu)} p_i \right). \quad (4.33)$$

For example, as Schnakenberg observes, the full dynamics coincides with the dynamics of the lumped system, since $W = \sum_\nu W_\nu$ is the generator of a linear differential equation. In other words, resolution of mechanisms does not affect the dynamics of the system, as the currents add according to a parallel reduction rule

$$j_{ij} = \sum_\nu j_{ij}^{(\nu)}.$$

However, it does affect the thermodynamics, as we move on to discuss.

4.5 Clausius circulations

We briefly describe the master equation thermodynamics in the light of local detailed balance, which was extensively studied by Esposito and Van den Broeck [46]. We momentarily allow for an explicit time dependence of the energy levels, $\varepsilon_i(t)$. All other time-dependencies will not be displayed. The ν -th mesoscopic force along edge ij reads

$$a_{ij}^{(\nu)} = \ln \frac{w_{ij}^{(\nu)} p_j}{w_{ji}^{(\nu)} p_i} = \beta^{(\nu)} [\varepsilon_j(t) - \varepsilon_i(t)] + \ln \frac{p_j}{p_i}. \quad (4.34)$$

We define as local entropy production rate

$$\sigma = \frac{1}{2} \sum_{i,j,\nu} j_{ij}^{(\nu)} a_{ij}^{(\nu)}, \quad (4.35)$$

Notice that it differs from the entropy production rate, Eq.(4.3), which after substitution of the lumped mesoscopic force Eq.(4.28) becomes

$$\tilde{\sigma} = \frac{1}{2} \sum_{i,j,\nu'} j_{ij}^{(\nu')} \ln \frac{\sum_\nu w_{ij}^{(\nu)} p_j}{\sum_\nu w_{ji}^{(\nu)} p_i}.$$

By the log-sum inequality [77], the former is easily shown to never be smaller than the latter

$$\sigma \geq \tilde{\sigma} \geq 0.$$

Hence, if we did not resolve transition mechanisms, we would systematically underestimate the entropy production rate. In particular, it can occur that the lumped transition rates satisfy (global) detailed balance while the system is locally non-equilibrium. Plugging Eq.(4.34) into the entropy production rate Eq.(4.35) we obtain

$$\sigma = \frac{1}{2} \sum_{i,j,\nu} j_{ij}^{(\nu)} \left\{ \beta^{(\nu)} [\varepsilon_j(t) - \varepsilon_i(t)] + \ln \frac{p_j}{p_i} \right\} = - \sum_{\nu} \beta^{(\nu)} q^{(\nu)} + \dot{S}(p), \quad (4.36)$$

where we defined the heat flow from the ν -th reservoir as

$$q^{(\nu)} = - (\varepsilon, W^{(\nu)} p). \quad (4.37)$$

Here (\cdot, \cdot) is the euclidean scalar product over the vertex set. Notice that $q^{(\nu)}$ is not a total time derivative, which ultimately is the reason behind the nonequilibrium character. Defining the work rate $w = \langle \dot{\varepsilon} \rangle_p$ and the average energy $E = \langle \varepsilon \rangle_p$, we are able to give a suggestive detailed version of the First Law of Thermodynamics

$$\dot{E} = w + \sum_{\nu} q^{(\nu)}. \quad (4.38)$$

The forthcoming argument shows that the heat flows introduced in Eq.(4.37) have a natural tendency to flow from the hotter to the colder reservoir, consistently with common intuition. At a steady state the heat flows balance, $\sum_{\nu} q^{(\nu)} = 0$, and the relative entropy term in Eq.(4.36) vanishes. We suppose that $\nu = 0$ corresponds to the reservoir at lowest temperature $\beta = \beta^{(0)}$, and introduce the driving forces conjugate to the heat flows, $\chi^{(\nu)} = \beta - \beta^{(\nu)} \geq 0$. Notice that $\chi^{(\nu)}/\beta$ is the Carnot efficiency of the ν -th reservoir. Then

$$\sigma(p^{ss}) = \sum_{\nu} \chi^{(\nu)} q^{ss(\nu)}. \quad (4.39)$$

Considering a two-reservoir system, we obtain $\sigma_{ss} = \chi^{(1)} q^{(1)}$; since the driving force is positive and the entropy production is positive, the steady heat flux is positive. At a steady state, the system is the intermediary for the heat flow from the hotter to the colder reservoir.

We now consider our Schnakenberg-type decomposition of the entropy production rate. For simplicity, we restrict to systems which satisfy the maximal coupling condition, where all transitions can be due to all mechanisms. Let $N + 1$ be the number of mechanisms (Fig.4.2a). The opposite situation of minimal coupling is also very simple. Actual physical systems in fact lie in the middle, with some transitions due to some baths and some others due to other baths; the following results become more complicated and laborious — and will not be discussed here. From a graph-theoretical point of view, we distinguish between the graph of the system, with multiple edges between states depicting different mechanisms, and its backbone graph, where multiple edges are lumped. There exist two kinds of cycles in a graph with multiple edges. Non-topological cycles are enclosed by two different mechanisms along one edge of the backbone graph (Fig.4.1b). Topological cycles run along cycles of the backbone graph, taking up varied temperatures along the path (see Fig.4.1c). Let for definitiveness cycle c run through states i_m , and let $e_m^{(\nu_m)}$ be the edge connecting i_m to i_{m+1} . The Schnakenberg affinity along c reads

$$A(c) = - \sum_m \beta^{(\nu_m)} (\varepsilon_{i_{m+1}} - \varepsilon_{i_m}) = - \oint_c \frac{\delta \varepsilon}{T},$$

where in the right-hand side we give a suggestive notation, in units where Boltzmann's constant $k_B = 1$. We call these quantities the Clausius circulations.

Spanning trees of a graph with multiple edges can be found by choosing

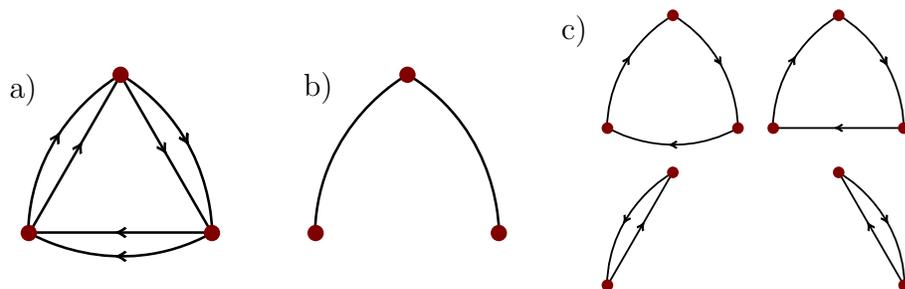


Figure 4.2: *a)* Maximally coupled three-state system with two reservoirs. *b)* The lowest temperature basis. *c)* A basis of fundamental cycles: two topological and two non-topological. The first topological cycle has null affinity.

a spanning tree of the backbone graph and picking an arbitrary temperature for each edge. Our choice falls on an arbitrary topological spanning tree whose fundamental cochords all have lowest temperature (see Fig.4.2b). We now evaluate the steady entropy production rate, Eq.(1.33), in the lowest-temperature basis. Each topological cycle comes in $N + 1$ copies $c^{\alpha(\nu)}$, according to choice of the fundamental chords $e_{\alpha(\nu)}$,

$$A(c^{\alpha(\nu)}) = -\beta \sum_{e \in c^{\alpha} \setminus e_{\alpha}} \delta_e \varepsilon - \beta^{(\nu)} \delta_{e_{\alpha}} \varepsilon = \chi^{(\nu)} \delta_{e_{\alpha}} \varepsilon.$$

The affinity corresponding to $\nu = 0$ vanishes (Fig.4.2c). The topological contribution to the steady entropy production rate then reads

$$\sum_{\nu} \chi^{(\nu)} \sum_{\alpha} j_{e_{\alpha}}^{(\nu)} \delta_{e_{\alpha}} \varepsilon. \quad (4.40)$$

To each backbone cochord e_{μ}^* are associated N non-topological affinities $\chi^{(\nu)} \delta_{e_{\mu}^*} \varepsilon$ (Fig.4.2c). Their conjugate currents $j_{e_{\mu}^*}^{(\nu)}$ flow along the ν -th mechanism of cochord e_{μ}^* . We obtain a contribution to the steady entropy production rate coming from nontopological cycles,

$$\sum_{\nu} \chi^{(\nu)} \sum_{\mu} j_{e_{\mu}^*}^{(\nu)} \delta_{e_{\mu}^*} \varepsilon. \quad (4.41)$$

Since chords and cochords exhaust the edge set, given eqs.(4.40, 4.41) the steady state EP is the sum over all possible edges and all mechanisms

$$\sigma_{ss} = \sum_{\nu} \chi^{(\nu)} q^{(\nu)}, \quad (4.42)$$

which is in the form of the typical Onsager bilinear expression of the forces (temperature differences) and conjugate (heat) fluxes. At the steady state it coincides with Eq.(4.39). Remarkably, Eq.(4.42) does not depend on the backbone spanning tree, while it does depend on the choice of the lowest temperature basis. A different choice will add to this term a total time derivative. Taking Eq.(4.38) into account we obtain

$$\sigma_{ss} = - \sum_{\nu} \beta^{(\nu)} q^{(\nu)} + \beta(\dot{E} - w). \quad (4.43)$$

Finally, using Eq.(4.36) the transient entropy production rate results

$$\sigma_{db} = (\dot{S} - \beta \dot{E}) - w = -\beta \dot{F} - w,$$

where F is the Hemholtz free energy. The splitting of the entropy production rate $\sigma = \sigma_{ss} + \sigma_{db}$ is one of many possible splitting. Esposito and Van den Broeck considered a splitting in an adiabatic term and a non-adiabatic term. Our splitting depends on the choice of basis. Any two splittings are related by a shift of a total time derivative from one term to the other. We will interpret in Ch.6 such shifts as due to gauge transformations. In our case, when the energy levels have no explicit time dependence, we obtain for the transient entropy production rate the time derivative of (minus beta) the Hemholtz free energy.

4.6 Linear regime for the heat fluxes

In this section we expand Local Detailed Balance rates near a set of equilibrium rates and perturb them by varying the reservoirs' temperatures. We then investigate the linear response of the heat fluxes in the case where the state of the system is held fixed, resulting in a quench.

Locally detailed balanced rates can always be written as

$$w_{ij}^{(\nu)} = v_{ij}^{(\nu)} \exp[\beta^{(\nu)}(\varepsilon_j - \varepsilon_i)/2].$$

In fact, $\ln v_{ij}^{(\nu)}$ and $\beta^{(\nu)}(\varepsilon_j - \varepsilon_i)/2$ are respectively the symmetric and the antisymmetric part of the logarithm of the transition rates. When the hotter reservoirs' temperatures are approximately equal to the coldest, we can expand to first order

$$w_{ij}^{(\nu)} = \bar{w}_{ij}^{(\nu)} [1 - \chi^{(\nu)}(\varepsilon_j - \varepsilon_i)/2], \quad (4.44)$$

where

$$\bar{w}_{ij}^{(\nu)} = v_{ij}^{(\nu)} \exp[\beta(\varepsilon_j - \varepsilon_i)/2]$$

are detailed-balanced rates with respect to the canonical distribution, and the temperature differences $\chi^{(\nu)}$ are small. The perturbed partial generator is $W^{(\nu)} = \bar{W}^{(\nu)} + \delta W^{(\nu)}$. We suppose that the (non-steady) state of the system $p = \bar{p}^{ss} + \delta p$ is close to the unperturbed equilibrium steady state. Notice that, being equilibrium, $\bar{L}^{(\nu)}\bar{p}^{ss} = 0, \forall \nu$. Using Eq.(4.37), the heat flows result

$$\begin{aligned} q^{(\nu)} &= -(\varepsilon, [\bar{W}^{(\nu)} + \delta W^{(\nu)}][\bar{p}^{ss} + \delta p]) \\ &= \bar{q}^{(\nu)} + \frac{\chi^{(\nu)}}{2} \sum_{i,j} \varepsilon_i \left[\bar{w}_{ij}^{(\nu)}(\varepsilon_j - \varepsilon_i)\bar{p}_j^{ss} - \bar{w}_{ji}^{(\nu)}(\varepsilon_i - \varepsilon_j)\bar{p}_i^{ss} \right] \end{aligned} \quad (4.45)$$

where

$$\bar{q}^{(\nu)} = -(\varepsilon, \bar{W}^{(\nu)} p)_V$$

is the ν -th heat flux in state p , calculated using the unperturbed generator. Using the fact that the $\bar{w}_{ij}^{(\nu)}$'s satisfy detailed balance, we can work out the last term in Eq.(4.45) to obtain

$$q^{(\nu)} = \bar{q}^{(\nu)} + L^{(\nu)} \chi^{(\nu)}, \quad (4.46)$$

where the linear response coefficient $L^{(\nu)}$ reads

$$L^{(\nu)} = \langle \varepsilon W^{(\nu)\dagger} \varepsilon \rangle_{\bar{p}^{ss}} = \sum_{i,j} \bar{p}_i^{ss} \varepsilon_i \bar{w}_{ji}^{(\nu)} (\varepsilon_j - \varepsilon_i). \quad (4.47)$$

Notice that $q^{(\nu)}$ and $\bar{q}^{(\nu)}$ are calculated in the same close-to-equilibrium state. Therefore $L^{(\nu)} \chi^{(\nu)}$ quantifies the additional heat flux that one obtains from the ν -th reservoir due to a sudden modification of the characteristics of the system, something that might be called a quench. Interestingly, when this occurs there are no off-diagonal Onsager cross-coefficients. This might be a bit surprising, but it has a simple physical interpretation. When one abruptly modifies the temperature of the ν -th reservoir, heat starts flowing into the system, which will eventually heat up and yield some of its heat to lower-temperature reservoirs, until the steady state is reached. At that point, the linear response matrix has developed off-diagonal terms

$$q^{ss(\nu)} = \sum_{\nu'} L^{(\nu\nu')} \chi^{(\nu)'}, \quad L^{(\nu\neq\nu')} = - \frac{\delta}{\delta \chi^{(\nu)'}} \langle \bar{W}^{(\nu)\dagger} \varepsilon \rangle_{p^{ss}} \Big|_{\chi=0},$$

where the dependence on χ comes through the linearly perturbed nonequilibrium steady state $p^{ss} = p^{ss}(\chi)$. Notice that by Eq.(4.37)

$$\sum_{\nu} q^{ss(\nu)} = 0,$$

which implies

$$\sum_{\nu} L^{(\nu\nu')} = 0.$$

Then $L^{(\nu\nu')}$ is a stochastic matrix. Finally, notice that Eq.(4.47) has some similarity with the Kubo representation of linear phenomenological coefficients. We will specify this point in Sec.(4.7).

4.7 Green-Kubo relations for the heat fluxes

Let us define a microscopic stochastic process corresponding to the rate of heat exchange with the ν -the reservoir:

$$q_t^{(\nu)}(t) = \beta^{(\nu)} \sum_m \delta_{\nu_m, \nu} \delta(t - t_m) \delta_{e_m} \varepsilon$$

where ν_m is the mechanism responsible for the m -th transition. Here $\delta_{\nu_m, \nu}$ is the Kroenecker delta, $\delta(t - t_m)$ is the Dirac delta and δ_{e_m} is the coboundary operator, see Eq.(4.18).

Along the same lines as above, the following transient Asymptotic Fluctuation Theorem is proven,

$$\frac{\text{Prob} \left[\frac{1}{t} \int_0^t q_t^{(\nu)}(t') dt' \equiv q^{(\nu)} \right]}{\text{Prob} \left[\frac{1}{t} \int_0^t q_t^{(\nu)}(t') dt' \equiv -q^{(\nu)} \right]} \underset{t}{\sim} \exp \sum_{\nu} \chi^{(\nu)} q^{(\nu)}. \quad (4.48)$$

Following the same line of reasoning as in Ref. [16], we use this to prove that heat fluxes near equilibrium are reciprocal. We will be very sketchy, the interested reader should look at the references for greater detail. Let us introduce the cumulant generating function

$$C[\lambda^{(\nu)}, \chi^{(\nu)}] = \lim_{t \rightarrow \infty} \frac{1}{t} \log \mathbb{E} \left[\exp - \sum_{\nu} \lambda^{(\nu)} \int_0^t q_t^{(\nu)}(t') dt' \right].$$

By virtue of the FT, it is easily shown to satisfy symmetry

$$C[\lambda^{(\nu)}, \chi^{(\nu)}] = C[\chi^{(\nu)} - \lambda^{(\nu)}, \chi^{(\nu)}].$$

We can derive the response coefficients by taking derivatives of the generating function

$$L^{(\nu\nu')} = - \frac{1}{2} \frac{\partial^2 C}{\partial \lambda^{(\nu)} \partial \lambda^{(\nu')}}(0, 0)$$

which is obviously symmetric. This formula also yields $L^{(\nu\nu')}$ in terms of self-correlations of the microscopic heat fluxes:

$$L^{(\nu\nu')} = \frac{1}{2} \int_{-\infty}^{\infty} dt \mathbb{E} \left\{ \left(q_t^{(\nu)}(t) - \mathbb{E} \left[q_t^{(\nu)}(t) \right] \right) \left(q_t^{(\nu')}(0) - \mathbb{E} \left[q_t^{(\nu')}(0) \right] \right) \right\}.$$

4.8 Independent reservoirs in OQS

In this section we derive the Local Detailed Balance condition for open quantum systems weakly interacting with several independent and infinitely large heat baths. We choose to work with quantum, instead of classical, systems in that they allow a simple and general derivation, because it's an area where concepts of nonequilibrium thermodynamics and geometry discussed in this thesis might be fruitfully applied, because it is reasonable to consider the discrete states visited by a master equation as labeled by the discrete energy eigenstates of a quantum systems, and finally because the quantum equation we will derive typically has decoherence times that are much faster than the relaxation times, so that after a transient such systems behave classically. We retrace the microscopic derivation of the Lindblad equation as found in the book by Breuer and Petruccione [85, Part II, §3.3.1] (BP in the following), generalizing it to the case of many heat reservoirs. The reader should constantly rely on the cited reference in order to be able to follow this otherwise rather scholarly exercise. We set $\hbar = 1$.

The setup is as follows. A quantum system (S) interacts with the environment (B). For simplicity, the Hilbert space of the system is supposed to be finite-dimensional. Suppose that the Hilbert space of the environment is further resolved into Hilbert spaces of several heat baths, labeled by ν ,

$$\mathcal{H} = \mathcal{H}_S \otimes \mathcal{H}_B, \quad \mathcal{H}_B = \bigotimes_{\nu} \mathcal{H}_B^{(\nu)}.$$

To the total time-independent hamiltonian,

$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{\text{int}}, \quad \hat{H}_B = \sum_{\nu} \hat{H}_B^{(\nu)}, \quad \hat{H}_{\text{int}} = \sum_{\nu} \hat{H}_{\text{int}}^{(\nu)},$$

there contribute the internal energies of the system and of each bath

$$\hat{H}_S = H_S \otimes I, \quad \hat{H}_B^{(\nu)} = H_B^{(\nu)} \otimes I,$$

where H_S acts on \mathcal{H}_S , $H_B^{(\nu)}$ acts on $\mathcal{H}_B^{(\nu)}$ and the unit operators have suitable dimensionality accounting for the remaining degrees of freedom. As to the interaction hamiltonian, we assume that the reservoirs are independent one of each other, i.e., they do not interact among themselves,

$$\hat{H}_{\text{int}}^{(\nu)} = H_{\text{int}}^{(\nu)} \otimes I,$$

where $H_{\text{int}}^{(\nu)}$ acts on $\mathcal{H}_S \otimes \mathcal{H}_B^{(\nu)}$. Finally, the density matrix of the system is prepared in a completely factorized state at time $t = 0$,

$$\rho(t) = \rho_S(t) \otimes \rho_B, \quad \rho_B = \bigotimes_{\nu} \rho_B^{(\nu)}, \quad t = 0. \quad (4.49)$$

The goal is to find a closed equation for the evolution of the state of the system $\rho_S(t)$, working out the interaction picture von Neumann equation

$$\frac{d}{dt}\rho(t) = -i[\hat{H}_{\text{int}}(t), \rho(t)].$$

The time dependence of $\hat{H}_{\text{int}}(t)$ is not due to an explicit time dependence of the hamiltonian, but only to the interaction picture. There are several assumptions and approximations involved in the derivation. The first is *(i)* the weak coupling assumption, which comes into play after one retains only terms up to second order in the integro-differential equation

$$\frac{d}{dt}\rho(t) = -i[\hat{H}_{\text{int}}(t), \rho(0)] - \int_0^t ds [H_{\text{int}}(t), [H_{\text{int}}(s), \rho(s)]]. \quad (4.50)$$

It is then supposed that *(ii)* the state remains approximately factorized at all later times, and that the state of the environment is not influenced by the system, hence it does not change in time (Born approximation), so that Eq.(4.49) holds at all later times. Taking the trace over the heat bath degrees of freedom in (4.50) we obtain

$$\frac{d}{dt}\rho_S(t) = - \int_0^t ds \text{tr}_B [\hat{H}_{\text{int}}(t), [\hat{H}_{\text{int}}(s), \rho_S(s) \otimes \rho_B]],$$

where we also assumed that

$$\text{tr}_B [\hat{H}_{\text{int}}(t), \rho_S(0) \otimes \rho_B] = 0. \quad (4.51)$$

It is assumed *(iii)* that the future evolution of the system does not explicitly depend on the past history of $\rho_S(s)$ but only on its present value (Markov approximation), yielding the so-called Redfield equation

$$\frac{d}{dt}\rho_S(t) = - \int_0^t ds \text{tr}_B [\hat{H}_{\text{int}}(t), [\hat{H}_{\text{int}}(s), \rho_S(t) \otimes \rho_B]].$$

This equation still depends on the initial preparation at time $t = 0$, thus it is not markovian yet. Markovian dynamics arises at large times, when *(iv)* the

initial instant is set in the far past. We send it to $-\infty$ by making a change of variables $s \mapsto t - s$,

$$\frac{d}{dt}\rho_S(t) = - \int_0^\infty ds \operatorname{tr}_B [\hat{H}_{\text{int}}(t), [\hat{H}_{\text{int}}(t-s), \rho_S(t) \otimes \rho_B]]. \quad (4.52)$$

The pathway to the last approximation is more troubled. We do not reproduce the full discussion here, and refer to [BP], with the following modifications due to the presence of several heat baths. Decomposing the tensor product, the ν -th interaction hamiltonian can be written as

$$\hat{H}_{\text{int}}^{(\nu)} = \sum_\alpha A_\alpha^{(\nu)} \otimes \hat{B}_\alpha^{(\nu)}, \quad \hat{B}_\alpha^{(\nu)} = B_\alpha^{(\nu)} \otimes I$$

where $A_\alpha^{(\nu)}$ acts on \mathcal{H}_S , $B_\alpha^{(\nu)}$ acts on $\mathcal{H}_B^{(\nu)}$ and the identity acts on the remaining bath degrees of freedom. Notice that the span of α in general depends on ν ; we do not keep track of this in the notation. We shall then plug into Eq.(4.52) the interaction hamiltonian

$$\hat{H}_{\text{int}}(t) = \sum_\nu \sum_\alpha A_\alpha^{(\nu)}(t) \otimes \hat{B}_\alpha^{(\nu)}(t), \quad (4.53)$$

after we solve its Schroedinger picture evolution. This is achieved by expressing the $A_\alpha^{(\nu)}$ in a basis of eigenoperators, a sort of operatorial Fourier expansion in terms of the discrete energy gaps ω in the spectrum of the system's hamiltonian. The microscopic derivation follows unmodified up to [BP, eqs.(3.132, 3.133)]. The Schroedinger picture bath interaction term reads

$$\hat{B}_\alpha^{(\nu)}(t) = \exp[i\hat{H}_B^{(\nu)}t] \hat{B}_\alpha^{(\nu)} \exp[-i\hat{H}_B^{(\nu)}t].$$

Eq.(4.52) turns into

$$\begin{aligned} \frac{d}{dt}\rho_S(t) = & \sum_{\nu,\nu'} \sum_{\omega,\omega'} \sum_{\alpha,\beta} e^{i(\omega'-\omega)t} \Gamma_{\alpha\beta}^{(\nu\nu')}(\omega) \\ & \left[A_\beta^{(\nu)'}(\omega) \rho_S(t) A_\alpha^{(\nu)}(\omega')^\dagger - A_\alpha^{(\nu)}(\omega')^\dagger A_\beta^{(\nu)'}(\omega) \rho_S(t) \right] + h.c. \end{aligned} \quad (4.54)$$

(*h.c.* = hermitian conjugate), where we introduced the half-Fourier transforms of the self-correlation functions

$$\Gamma_{\alpha\beta}^{(\nu\nu')}(\omega) = \int_0^{+\infty} ds e^{i\omega s} \left\langle \hat{B}_\alpha^{(\nu)}(s)^\dagger \hat{B}_\beta^{(\nu)'}(0) \right\rangle_{\rho_B},$$

each cross-term $\Gamma_{\alpha\beta}^{(\nu\neq\nu')}(\omega)$ measuring correlations between different baths. We remind that the average is taken with respect to the state of the environment, which factorizes at all times, and that we are working in the interaction picture. Eq.(4.51) becomes

$$\sum_{\nu} \sum_{\alpha} \text{tr}_{\nu} \left\{ B_{\alpha}^{(\nu)} \rho_B^{(\nu)} \right\} [A_{\alpha}^{(\nu)}, \rho_S(0)] = 0$$

which holds independently of the initial state of the system, implying

$$\langle B_{\alpha}^{(\nu)}(t) \rangle = \text{tr}_{\nu} \left\{ \rho_B^{(\nu)} B_{\alpha}^{(\nu)}(t) \right\} = 0,$$

where we trace over the ν -th bath degrees of freedom. It follows that cross-bath correlations and their half-Fourier transforms vanish. Finally, (v) the rotating-wave approximation consists in approximating the exponential term $e^{i(\omega' - \omega)t}$ with $\delta_{\omega\omega'}$. This is justified when the bath correlation functions decay sufficiently fast with respect to the typical relaxation times. One then decomposes $\Gamma_{\alpha\beta}^{(\nu\nu)}(\omega)$ in its real and imaginary parts [BP,(Eq.3.127)], and defines the effective hamiltonian H_{eff} and, more importantly, the Lindbladian dissipator $\mathcal{L} = \sum_{\nu} \mathcal{L}^{(\nu)}$, with

$$\mathcal{L}^{(\nu)} \rho_S = \sum_{\omega, \alpha, \beta} \gamma_{\alpha\beta}^{(\nu)}(\omega) \left[A_{\beta}^{(\nu)}(\omega) \rho_S A_{\alpha}^{(\nu)}(\omega)^{\dagger} - 1/2 \left\{ A_{\alpha}^{(\nu)}(\omega)^{\dagger} A_{\beta}^{(\nu)}(\omega), \rho_S \right\} \right],$$

where the γ 's are Fourier transforms of the baths' correlation functions,

$$\gamma_{\alpha\beta}^{(\nu)}(\omega) = \int_{-\infty}^{+\infty} ds e^{i\omega s} \text{tr}_{\nu} \left\{ \rho_B^{(\nu)} \hat{B}_{\alpha}^{(\nu)}(s)^{\dagger} \hat{B}_{\beta}^{(\nu)}(0) \right\}.$$

The Lindblad equation reads

$$\frac{d}{dt} \rho_S = -i[H_{\text{eff}}, \rho_S] + \mathcal{L} \rho_S. \quad (4.55)$$

We do not give the explicit expression for the effective hamiltonian term, which does not contribute to the evolution of populations. An important property is that it commutes with the system's hamiltonian, $[H_{\text{eff}}, H_S] = 0$.

We can now formulate the Local Detailed Balance assumption: each bath is prepared in a thermal state with canonical ensemble

$$\rho_B^{(\nu)} = \frac{\exp -\beta^{(\nu)} H_B^{(\nu)}}{\text{tr}_{\nu} \exp -\beta^{(\nu)} H_B^{(\nu)}}.$$

By the Kubo-Martin-Schwinger condition on the correlation functions,

$$\mathrm{tr}_\nu \left\{ \rho_B^{(\nu)} B_\alpha^{(\nu)}(s)^\dagger B_\beta^{(\nu)}(0) \right\} = \mathrm{tr}_\nu \left\{ \rho_B^{(\nu)} B_\beta^{(\nu)}(0) B_\alpha^{(\nu)}(s + i\beta^{(\nu)})^\dagger \right\},$$

we obtain the fluctuation relations [BP, Eq.(3.149)]

$$\gamma_{\alpha\beta}^{(\nu)}(\omega) = \gamma_{\beta\alpha}^{(\nu)}(-\omega) \exp \beta^{(\nu)} \omega. \quad (4.56)$$

When all temperatures coincide, the thermal state $\exp -\beta H_S$ can be shown to be the steady state of the Lindblad equation (if ergodic).

The last steps for connecting the theory of the quantum master equation and the classical master equation is choosing a basis and projecting the Lindblad equation on it. Among the many possibilities, the following two choices are meaningful. The first is the time-dependent basis where the density operator is diagonal at all times, which is attained via a time-dependent unitary transformation $U(t)$,

$$\rho_S(t) = \sum_i |i(t)\rangle p_i(t) \langle i(t)|.$$

The diagonalized master equation reads

$$\dot{p}_i(t) = \sum_\nu \sum_j \left[w_{ij}^{(\nu)}(t) p_j(t) - w_{ji}^{(\nu)}(t) p_i(t) \right] \quad (4.57)$$

with time-dependent transition rates

$$w_{ij}^{(\nu)}(t) = \sum_\omega \sum_{\alpha,\beta} \gamma_{\alpha\beta}^{(\nu)}(\omega) \langle i(t) | A_\beta^{(\nu)}(\omega) | j(t) \rangle \langle j(t) | A_\alpha^{(\nu)}(\omega) | i(t) \rangle.$$

In this basis the Lindblad equation has the form of a classical-looking time-dependent master equation, and in principle it allows to define the thermodynamics, fluctuation theorems etc. [86]. However, there is an important *caveat*. To obtain the transition rates, one should know the diagonalizing unitary basis, and this is only possible if one first solves the Lindblad equation itself. So we have a conceptual loophole.

To be precise, this microscopic derivation identifies a class of Lindblad equations. *The* Lindblad equation, in all its generality, is obtained as the time derivative of a generic dynamical map $\rho_S \rightarrow \mathcal{V}(t)\rho_S$ which is trace-preserving, convex linear, completely positive and which satisfies the semigroup property.

While the latter basis can be defined for any Lindbladian semigroup generator, systems which correspond to the above microscopic derivation enjoy the existence of the energy basis

$$H_S = \sum_i \varepsilon_i |i\rangle\langle i|.$$

It can be shown that in this basis the equations for the populations and for the coherences decouple, the first yielding the so-called Pauli master equation with time-independent rates

$$w_{ij}^{(\nu)} = \sum_{\alpha,\beta} \gamma_{\alpha\beta}^{(\nu)} (\varepsilon_j - \varepsilon_i) \langle j|A_\alpha^{(\nu)}|i\rangle \langle i|A_\beta^{(\nu)}|j\rangle.$$

Finally, using Eq.(4.56), and after a simple manipulation of the indices, we derive the Local Detailed Balance condition

$$w_{ji}^{(\nu)} = w_{ij}^{(\nu)} \exp \beta^{(\nu)} (\varepsilon_j - \varepsilon_i). \quad (4.58)$$

Local detailed balance will play an important role for the interpretation of our geometrical theory of gauge transformations in thermodynamical terms. We gave a quantum-mechanical derivation; it would be (more than) an interesting exercise to provide for a classical stochastic derivation through the brownian motion of mesoscopic particles subject to several independent baths of microscopic particles. On the other hand, the quantum-mechanical derivation poses many interesting questions on its own. Given an arbitrary state of the environment, under what conditions can we represent it as a collection of locally detailed balanced reservoirs? Keeping track of the interaction between baths seems to be a very hard task, but it's interesting to inquire how to account for initial-time coherences between noninteracting baths. While we can study the classical thermodynamics of the Pauli master equation, one would expect that quantum nonequilibrium thermodynamics should be based on the Von Neumann entropy, accounting for the (independent) behavior of the coherences. It would be a major result to define a consistent nonequilibrium thermodynamics for a generic Markovian semigroup generator, for example by giving conditions on the Lindblad operators that satisfy detailed balance analogous to the Kolmogorov criterion. More specifically, the definition of entropy production rate is still elusive even for microscopically-derived Lindblad equations. In this respect, Local Detailed Balance might serve the purpose as Eq.(4.36) can be extended to quantum systems

$$\sigma = - \sum_{\nu} \text{tr}_S \{ \mathcal{L}^{(\nu)} \rho_S (\ln \rho_S - \ln \mu^{(\nu)}) \} \quad (4.59)$$

where

$$\mu^{(\nu)} = \frac{\exp -\beta^{(\nu)} H_S}{\text{tr}_S \exp -\beta^{(\nu)} H_S} \quad (4.60)$$

is the canonical quantum measure with respect to temperature $\beta^{(\nu)}$. This formula generalizes [BP,(Eq.3.99)] including a non-vanishing term at a nonequilibrium steady state. A quantum term due to coherences is only included in the time derivative of the Von Neumann entropy term $\text{tr}_S \{\mathcal{L}\rho_S \ln \rho_S\}$, while the additional term is analogous to its classical counterpart. Difficult to say whether this is fully satisfactory. A test-bed for the formula would be its positivity. Furthermore, as we briefly discussed in Sec.(4.4), Local Detailed Balance is not restrictive for classical master equations, as for a given set of rates one can always find a set of temperatures and of energy levels for which Local Detailed Balance holds, reproducing correctly the thermodynamics of the system. If this procedure could be replied for a generic Lindblad generator or for a microscopically derived generator whose bath's state is not canonical, this would make Eq.(4.59) of much wider applicability.

The nonequilibrium thermodynamics of Lindblad-type systems is discussed in [86, 87]. A tentative definition of entropy production rate for open quantum systems is given in [88]. On the definition of detailed balance for quantum markovian semigroups [89–91]. A recent article [92] discusses a fluctuation theorem for quantum markovian systems.

5

Steady states

There exists a well-known graph theoretical expression for the steady state of a master equation in terms of rooted oriented spanning trees. In Sec.5.1 we introduce the expression and discuss the so-called matrix-tree theorems associated to it. In Sec.5.2 we give a simple proof, and in Sec.5.3 we further linger on certain combinatorial aspects associated to the cycle fluxes of a Markov process, re-deriving a result by Hill [15] by means of the Fluctuation Theorem. We then briefly discuss the relationship between the canonical equilibrium partition function and a nonequilibrium analogous expression, finding that the nonequilibrium partition function also retains some information on the linear regime.

5.1 Matrix-tree theorems

A spanning tree is a subset T of the edge set of a graph which satisfies the following properties:

- Contains no cycles;
- Has $V - 1$ edges;
- Connects all vertices.

Any two of the above suffice to characterize a spanning tree. It follows that in a spanning tree there exists only one path between any two vertices. We can choose one particular vertex i as the root and orient all edges of the

spanning tree so that there is a unique oriented path from any other vertex to the root. In this case we talk of an oriented rooted spanning tree T_i .

Let $\pi(A)$ be the evaluation function, which takes the product of all transition rates along edges of an oriented subgraph A ,

$$\pi(A) = \prod_{e \in A} w_e.$$

The Kirchhoff state associated to the set of transition rates $\mathbf{w} = (w_{ij})_{i,j}$ is

$$z_i = \frac{Z_i(\mathbf{w})}{Z(\mathbf{w})} = \frac{\sum_{T_i} \pi(T_i)}{\sum_j \sum_{T_j} \pi(T_j)}, \quad (5.1)$$

where \sum_{T_i} ranges over all rooted oriented trees, and we defined the homogeneous polynomials of degree $V - 1$ in the transition rates

$$Z_i(\mathbf{w}) := \sum_{T_i} \pi(T_i), \quad Z(\mathbf{w}) = \sum_j Z_j(\mathbf{w}).$$

The Kirchhoff's state coincides with the steady state of the master equation, $p_i^{ss} = z_i$. We give a purely graph-theoretical of this fact in Sec.5.2. On the other hand, it's simple to derive an algebraic formula for the steady state [94]. Since W has only one eigenvector relative to eigenvalue zero, it has null determinant but non-null minors. Choosing row i and expanding the determinant through Laplace's formula,

$$\det W = \sum_j W_{ij} (-1)^{i+j} \det W_{\setminus(i,j)} = 0,$$

we read off that the i -th vector of cofactors $((-1)^{i+j} \det W_{\setminus(i,j)})_{j \in V}$ is a null eigenvector of L . Remember that eigenvalue zero has multiplicity one, hence all such vectors, for different i , are collinear. By comparison with the steady master equation, we obtain

$$p_j^{ss} \propto (-1)^{i+j} \det W_{\setminus(i,j)}, \quad \forall i.$$

Since $\det W_{\setminus(i,j)}$ is homogeneous of degree $V - 1$ in the transition rates, it is necessarily true that

$$Z_j(\mathbf{w}) = \sum_{T_j} \prod_{e \in T_j} w_e = (-1)^{i+j} \det W_{\setminus(i,j)}, \quad (5.2)$$

independently of the i -th row which is eliminated from L ; notice instead that it is crucial that the j -th column be fixed. This is known as the matrix-tree theorem for weighted oriented graphs. It is the important result of this section. From now on we linger on further inessential algebraic and graph-theoretical considerations. We first consider the reduced dynamics introduced in Sec.(3.2). The normalized reduced steady state reads

$$\tilde{p}_i^{ss} = (\tilde{W}^{-1}\mathbf{w})_i = \sum_j \frac{(-1)^{i+j} \det \tilde{W}_{\setminus(j,i)}}{\det \tilde{W}} \mathbf{w}_j,$$

where the inverse of \tilde{W} has been expressed in terms of the transposed matrix of cofactors. We remind that \tilde{p}^{ss} is obtained from p by removing the k -th entry, that \tilde{W} is the reduced laplacian Eq.(3.5) and that \mathbf{w} is the k -th column of W , with the k -th entry removed. Since \tilde{p}_i^{ss} is the ratio of two homogeneous polynomials, we are allowed to identify

$$Z_i(\mathbf{w}) = \sum_j (-1)^{i+j} \det \tilde{W}_{\setminus(j,i)} \mathbf{w}_j, \quad Z(\mathbf{w}) = \det \tilde{W},$$

yielding a simple expression for the normalization polynomial $Z(\mathbf{w})$ as the determinant of the reduced density matrix. Consider now the characteristic polynomial of the generator

$$\xi(\lambda) = \det(\lambda \mathbf{1} - W) = \sum_{v=0}^V C_v(\mathbf{w}) \lambda^v,$$

where coefficient $C_v(\mathbf{w})$ is a polynomial of degree $V - v$ in the transition rates. A theorem in linear algebra states that the v -th coefficient of the characteristic polynomial is $(-1)^{V-v}$ the sum over all principal minors of W with $V - v$ rows and columns, where a principal minor is the determinant of the submatrix obtained by removing rows i_1, \dots, i_v and the corresponding columns [95, Sec.1.2]. It is understood that when $V = v$, whereupon we should be removing all rows and columns of W , we set $C_V = 1$. On the opposite side, when $v = 0$, the only minor is $\det W = 0$, hence $C_0 = 0$. When $v = V - 1$, we obtain the diagonal elements of W ,

$$C_{V-1}(\mathbf{w}) = -\text{tr } W = \sum_{i,j} w_{ij}. \quad (5.3)$$

The above examples, C_0 , C_{V-1} and C_V , are somewhat trivial. We are mostly interested in C_1 , which by the above discussion coincides with $(-1)^{V-1}$ the

sum over all principal minors obtained by removing one row and column. By Eq.(5.2), we obtain

$$C_1(\mathbf{w}) = (-1)^{V-1} \sum_i Z_i(\mathbf{w}) = (-1)^{V-1} Z(\mathbf{w}). \quad (5.4)$$

On the other hand, we can express $\xi(\lambda)$ in terms of its roots, the eigenvalues λ_α . Besides eigenvalue zero, there are real eigenvalues, labeled by ι , and possibly couples of complex conjugate eigenvalues $\lambda_\kappa \pm i\omega_\kappa$, so that

$$\xi(\lambda) = \lambda \prod_\alpha (\lambda - \lambda_\alpha) = \lambda \prod_\iota (\lambda - \lambda_\iota) \prod_\kappa [(\lambda - \lambda_\kappa)^2 + \omega_\kappa^2].$$

Expansion in powers of λ is a dull exercise, and it leads to an expression for the coefficients of the characteristic polynomial as a sum of products of eigenvalues and as a sum over principal minors [95, Theorem 1.2.12]. As an example, coefficient C_0 is obviously zero and $C_V = 1$ by construction. As to C_{V-1} , we have

$$C_{V-1}(\mathbf{w}) = - \sum_\alpha \lambda_\alpha = - \text{tr } W, \quad (5.5)$$

consistently with Eq.(5.3). Finally,

$$(-1)^{V-1} C_1(\mathbf{w}) = \prod_\alpha \lambda_\alpha = \prod_\iota \lambda_\iota \prod_\kappa (\lambda_\kappa + \omega_\kappa)^2 = Z(\mathbf{w}). \quad (5.6)$$

To resume, the coefficient of the characteristic polynomial relative to λ is the sum over all roots and all rooted spanning trees of the graph. In fact, this result generalizes to the other coefficients of the characteristic polynomial [31, Theorem 7.5], and it is a consequence of the all-minors matrix-tree theorem [96]. The generalization of a spanning tree is a forest F , which is a subgraph of G with no cycles. A forest with $E(F) = E - 2$ edges can be obtained from a spanning tree by removing one edge; the vertex set is then necessarily disconnected in two components V_1 and V_2 (one can eventually be an isolated vertex). Each component can be assigned a root i_1, i_2 , and edges can be oriented so that there exists a unique path from any other vertex to either one of the roots. This defines a rooted oriented forest F_{i_1, i_2} with $E - 2$ edges, and we can proceed similarly for more sparse forests. The v -th coefficient of the characteristic polynomial then reads

$$C_v(\mathbf{w}) = (-1)^{V-v} \sum_{\substack{i_1, \dots, i_v \\ i_1 \neq \dots \neq i_v}} \sum_{F_{i_1, \dots, i_v}} \pi(F_{i_1, \dots, i_v})$$

where F_{i_1, \dots, i_v} spans over all forests on $E - v$ edges with given roots.

Let us briefly state a few specializations of the matrix-tree theorem. When W is symmetric, by simple inspection of the steady master equation the steady state is seen to be uniform, $p^{ss} = (1/V, \dots, 1/V)$. Then all cofactors of W are equal to each other and equal to the spanning tree polynomial, which in turn is the product of the non-null eigenvalues of the laplacian

$$Z(\mathbf{w}) = V Z_i(\mathbf{w}) = \prod_{\alpha} \lambda_{\alpha}.$$

To conclude, when W is the laplacian matrix of a graph, with all $w_{ij} = w_{ji} = 1$, any minor of W counts the number of spanning trees of the graph

$$\#(\text{spanning trees}) = \frac{1}{V} \prod_{\alpha} \lambda_{\alpha} = \det W_{\setminus(i,j)}, \quad \forall(i,j).$$

5.2 Proof of steady state formula

We give a simple graph-theoretical proof of Kirkkhoff's formula (5.1). The method takes inspiration from Hill's diagrammatic method for the determination of cycle fluxes [15, Sec.7] [93].

Let g be a connected subgraph of G . The contraction G/g is the graph obtained by identifying g with a unique vertex, which we also call g . Upon contraction, edges of g disappear, edges which have only one endpoint in g are redirected to vertex g and vertices which have both endpoints in g but do not belong to its edge set become loops; since loops are irrelevant for spanning tree combinatorics, they are eliminated. Contraction is also well-defined for oriented graphs. Notice that the orientation of the edges of g is irrelevant for contraction. In general, contracting a graph with respect to an arbitrary connected subgraph will produce loops and multiple edges. However, it is an intuitive fact that every contraction of a tree yields a tree, and that every contraction of a spanning tree spans the contracted graph. Examples of contractions are given in fig.5.2.c,d,e,f.

A self-avoiding walk is a path with no cycles. We denote with γ a self-avoiding walk from vertex i to vertex j . Spanning trees are in a sense self-similar upon contraction, as the following formula holds

$$Z_j[G] = \sum_{\gamma} \pi(\gamma) Z_{\gamma}[G/\gamma]. \quad (5.7)$$

Here, the sum is taken with respect to all self-avoiding walks from vertex i to vertex j , and $Z_\gamma[G/\gamma]$ is the Kirchhoff weight of the contracted graph with root in the contracted vertex γ . If t is a spanning tree of G/γ , then T , consisting of the edges of t and of γ over the vertex set V , is a spanning tree of G . Notice that since there is a unique path from j to i in T , the contracted tree t is uniquely identified. Then the correspondence is one-to-one and Eq.(5.7) holds.

The contraction formula is the central tool for this paragraph. As a corollary, it implies that Kirchhoff's formula for the steady state is correct. Suppose edge ij exists. Then $c = \gamma \cup ij$ is an oriented cycle. Since all vertices in c are identified upon contraction and loops disappear,

$$T_j/c = T_j/\gamma.$$

Every self-avoiding walk identifies a unique cycle which passes through ij , and vice versa. Therefore, multiplying Eq.(5.7) by w_{ij} and replacing the sum over self-avoiding walks with the sum over simple cycles through ij ,

$$w_{ij}z_j = \sum_c f(c)\pi(c), \quad w_{ji}z_i = \sum_c f(c)\pi(-c), \quad (5.8)$$

where

$$f(c) = f(-c) = \frac{Z_c(G/c)}{Z(G)}.$$

Finally, the Kirchhoff current along edge ij is

$$j_{ij}^z := w_{ij}z_j - w_{ji}z_i = \sum_{c \ni ij} f(c) [\pi(c) - \pi(-c)]. \quad (5.9)$$

This result was recently re-derived derived by Zia and Schmittmann [98, Sec.2], who noticed the factorization of the terms $\pi(c) - \pi(-c)$ but did not exhibit an explicit formula for its factor. The steady current is expressed as a combination of cycles. We know from Sec.1.3 that cycles and cuts are orthogonal and that the rows of the incidence matrix are cuts. Then, the currents in Eq.(5.9) satisfy Kirchhoff's conservation law:

$$\partial j^z = 0.$$

This proves that $(z_i)_{i \in V}$, as given by Kirchhoff's formula, is the unique normalized steady state of the master equation.

Detailed balance occurs when all macroscopic external affinities vanish, as we saw in Eq.(1.4), implying

$$\pi(c) = \pi(-c)$$

Given Eq.(5.9), we have

$$w_{ij}p_j^{eq} = w_{ji}p_i^{eq}, \quad (5.10)$$

where we called p^{eq} the equilibrium steady state.

5.3 Cycle fluxes

We append to the last section a proof of Hill's remarkable formula for average rotation times [15, Eq.(7.8)] based on the transient fluctuation theorem, and we discuss the problem of determining the algebraic relations between cycle fluxes. We call the quantities

$$J^+(c) = f(c)\pi(c), \quad J^-(c) = f(c)\pi(-c).$$

the cycle fluxes and $J(c) = J^+(c) - J^-(c)$ the net cycle flux. Let

$$\Omega = \sum_{i,j} w_{ij}z_j = \sum_i w_i z_i \quad (5.11)$$

be the average frequency of jumps. Then $w_{ij}z_j/\Omega$ is the average fraction of jumps from j to i . Since at a steady state jumps are due to all possible cyclic trajectories which pass through ij , then the directional cycle flux $J^+(c)$ might be intuitively interpreted as the number of cycles c completed per unit time, or in other words as the average frequency it takes to perform cycle c . Similarly for $J^-(c)$ along the inverse cycle $-c$. Then we have

$$\frac{J^+(c)}{J^-(c)} = \exp A(c). \quad (5.12)$$

This is a very remarkable result of Hill, which has received little attention. Seifert [84] used this result to discuss constraints on the efficiency at maximum power of certain nano-machines. Notice that the entropy production at the steady state admits a simple form in terms of the cycle fluxes as

$$\sigma^{ss} = \sum_c J^+(c) \ln \frac{J^+(c)}{J^-(c)},$$

where the sum runs over all simple oriented cycles of the graph (including both orientations).

We now give a heuristic proof based of Eq.(5.12) on the Transient Fluctuation Theorem. We suppose for simplicity that rates are incommensurable, i.e. that their ratio is irrational

$$\frac{w_{ij}}{w_{kl}} \in \mathbb{R} \setminus \mathbb{Q}, \quad \forall kl \neq ij.$$

This excludes equilibrium systems, but we might regard commensurable rates as approximations of incommensurable rates with an arbitrarily small error. We say that two trajectories γ and γ' are thermodynamical-equivalent if their entropy production is the same. Consider the two different cyclic paths c_1 and c_2 depicted in Fig.5.1.b. The entropy production $\Sigma(c_1)$ of all trajectories along c_1 that elapse from time 0 to time t , sampled from the steady state, whatever the waiting times happen to be, and the entropy production along c_2 necessarily differ, because rates are incommensurable. Therefore, thermodynamical-equivalent trajectories run along the same paths, up to the engraftation of non-topological cycles, that is, of edges which are walked in both directions (see Fig.reffig:cyclefluxes.c). Such grafts do not contribute to the total entropy production.

Let c be a fixed cycle. The fluctuation theorem states that, in path space, in a given time interval t , the probability that a trajectory with initial vertex sampled from the steady state, produces entropy $\Sigma(c) = (c, a)$, and the probability that a trajectory with initial vertex sampled from the steady

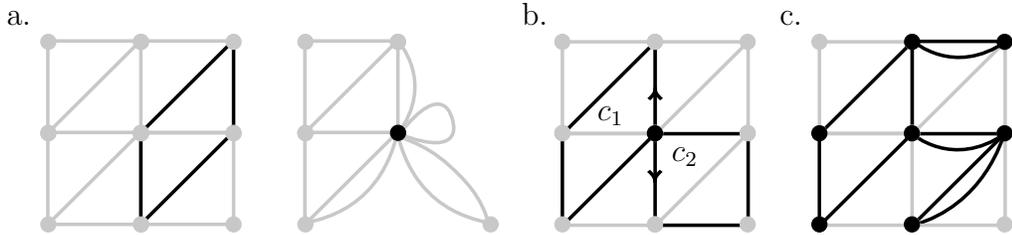


Figure 5.1: a) Contraction of a cycle into a vertex (both in black). b) Two thermodynamically inequivalent cycles. c) A cycle with grafts.

state produces entropy $\Sigma(-c) = -\Sigma(c)$ are related by

$$\frac{\text{Prob}[\Sigma^\iota \equiv \Sigma(c)]}{\text{Prob}[\Sigma^\iota \equiv -\Sigma(c)]} = \exp \Sigma(c),$$

By the above discussion, the set of trajectories which have exactly a given value of the total entropy production, if there exists any, coincides with a set of thermodynamical equivalent trajectories. Therefore, the fraction of trajectories that realize a cycle c at the steady state is

$$J^+(c) \propto \text{Prob}[\Sigma^\iota \equiv \Sigma(c)].$$

We do not calculate the proportionality constant. Eq.(5.12) follows.

One last issue that we would like to address is the inter-dependence of the cycle fluxes. We propose a conjectural result, discussing the specific example in fig.5.2. Let c_1 and c_2 be two oriented cycles, as in Fig.5.2.a, where we also introduce a (de)composition of cycles. We do not further specify this definition, which requires some care when one composes disconnected cycles and cycles which only have one vertex in common. Fig.5.2.b shows how to contract the graph in grey with respect to the several cycles, and which spanning trees contribute to the respective coefficients $f(c)$, after being suitably oriented. For this special simple case, the following result holds

$$f(c_1)f(c_2) = f(c_1 \cup c_2)f(c_1 \cap c_2).$$

Since it is a simple fact that $\pi(c_1)\pi(c_2) = \pi(c_1 \cup c_2)\pi(c_1 \cap c_2)$, we obtain

$$J^+(c_1)J^+(c_2) = J^+(c_1 \cup c_2)J^+(c_1 \cap c_2).$$

The generalization of these formulas to general graphs is a work in progress.

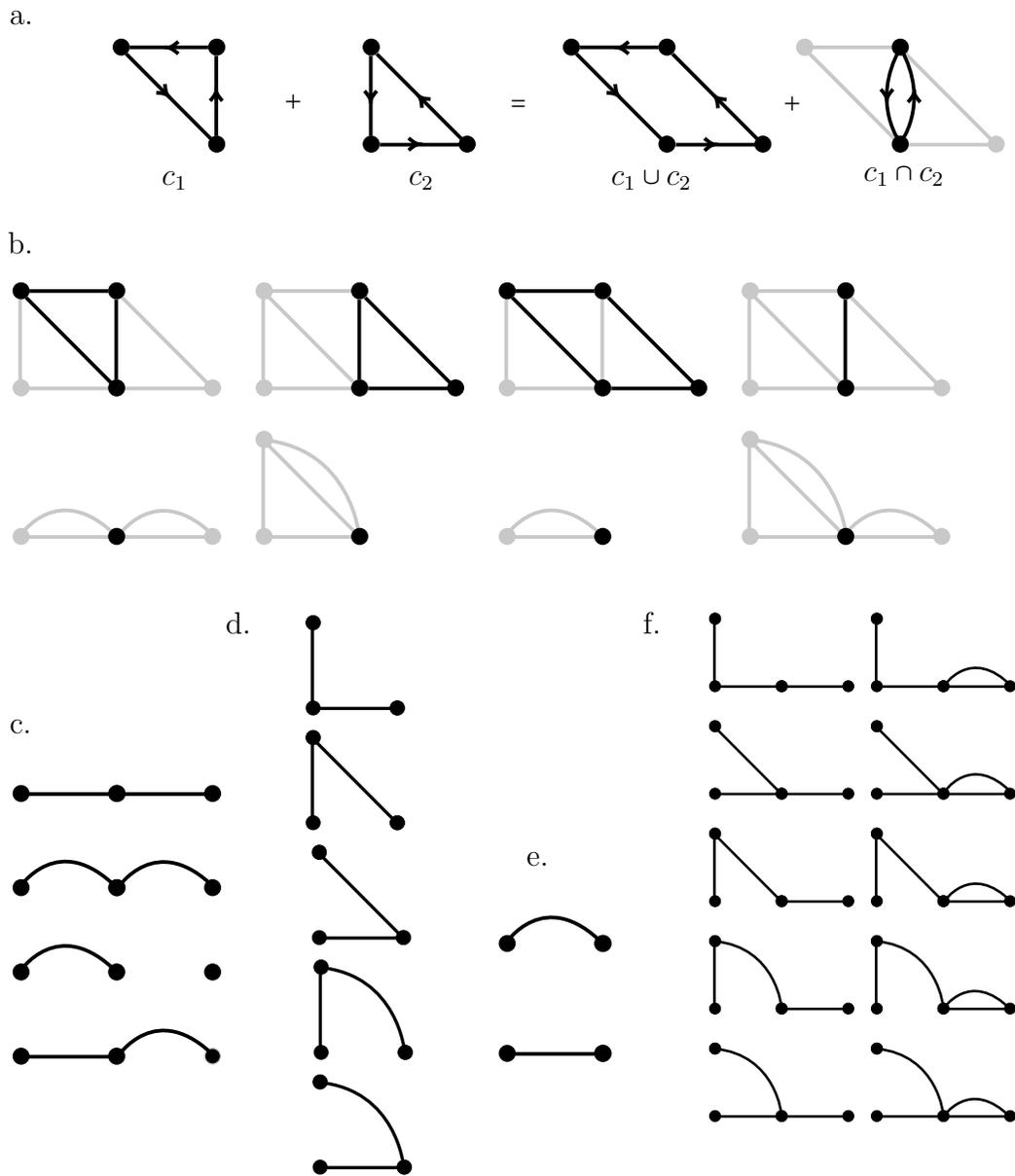


Figure 5.2: a) Composition of cycle c_1 with cycle c_2 , yielding cycle $c_1 \cup c_2$ and cycle $c_1 \cap c_2$. b) Contraction of a graph with respect to: cycle c_1 , cycle c_2 , cycle $c_1 \cup c_2$ and the edge $c_1 \cap c_2$ shared by c_1 and c_2 . c) Combinatorial contributions to $f(c_1)$. d) e) f) Idem for $f(c_1)$, $f(c_1 \cup c_2)$, $f(c_1 \cap c_2)$.

5.4 Recovering eq. partition functions

It is a commonplace that there is no such thing as a partition function in nonequilibrium statistical mechanics. Using Arndt’s words, “In thermal equilibrium the probability measures can in principle be expressed through an appropriate ensemble. For driven systems an equally powerful concept is missing” [99]. However, as Zia and Schmittmann foreshadow [26], the normalization factor Z “may play the role of a (super-)partition function”. It is a tempting hypothesis that is currently taken into account. A piece of evidence in this direction has been advanced by Arndt himself and by Blythe and Evans [100, 101], who proved for certain driven lattice systems that a non-equilibrium phase transition is accompanied with the accumulation of zeros of Z towards the real axis. We will hark back to this and similar results in Ch.?, where we discuss a class of non-equilibrium phase transitions.

Blythe and Evans also claimed that Z reduces to the equilibrium partition function when transition rates satisfy detailed balance. We pinpoint this assertion. Usually the equilibrium steady state is denoted

$$p_i^{eq} = \frac{e^{-\beta u_i}}{Q(\beta)}, \quad (5.13)$$

where $Q(\beta) = \sum_j e^{-\beta u_j}$ is the canonical partition function. The most general class of transition rates compatible with Eq.(5.13) satisfying detailed balance, Eq.(5.10), is

$$w_{ij}^{(\lambda)} = v_{ij} \exp \frac{\beta}{2} [(2 - \lambda)u_j - \lambda u_i],$$

where $\lambda \in \mathbb{R}$ is a parameter and $v_{ij} = v_{ji}$ is a symmetric edge weight, which we assume to be independent of the temperature. Notice that different sets of transition rates yield the same steady state but different stochastic dynamics – this is the case for example for the Glauber [102] and the Kawasaki dynamics for the Ising model.

Let’s first consider $\lambda = 0$. This is the case for transition rates that are derived from Arrhenius’s law [103]. The idea is that transitions are due to thermal fluctuations that allow the crossing of a potential hill, whose depth only depends on the energy of the starting state and not on that of the arrival state. Since in a rooted spanning tree each vertex, but the root, is the source of exactly one edge, we can factorize according to

$$Z^0(\mathbf{v}, \beta) = \left(\sum_T \prod_{e \in T} v_e \right) \cdot \sum_i \exp \left(\beta \sum_{j \neq i} u_j \right) = T(\mathbf{v}) Q(\beta) e^{\beta U},$$

where $U = \sum_{j \in V} u_j$ is the total energy of the system and $T(\mathbf{v})$ is the spanning tree polynomial. As a generating function, Z^0 coincides with the canonical partition function, but for a meaningless shift of the thermodynamic potentials and of the average energy,

$$-\frac{\partial}{\partial \beta} \ln Z^0 = \langle u \rangle + U. \quad (5.14)$$

The situation is more interesting when $\lambda \neq 0$. We prove in the rest of this paragraph that

$$-\frac{\partial}{\partial \beta} \ln Z^\lambda = \langle u \rangle + U + \frac{\lambda}{2} \sum_{i < j} \left[\bar{\ell}_{ij} / \ell_{ij} (u_i + u_j) \right], \quad (5.15)$$

where ℓ_{ij} is the resistance along edge ij and $\bar{\ell}_{ij}$ is the effective resistance, to be introduced below. Resistances emerge in the analysis of first order departure from the stationary state, so that Z^λ also encodes information about the out-of-equilibrium linear regime (see Sec.1.7). Defining

$$v_{ij}^\lambda = v_{ij} \exp -\frac{\beta \lambda}{2} (u_i + u_j) \quad (5.16)$$

we obtain

$$Z^\lambda(\mathbf{v}, \beta) = T(\mathbf{v}^\lambda) Q(\beta) e^{\beta U}.$$

In this case the spanning-tree term does depend on the temperature. Relation (5.14) updates to

$$-\frac{\partial}{\partial \beta} \ln Z^\lambda - \frac{\lambda}{2} \sum_{i < j} \left[(u_i + u_j) \frac{\partial \ln Z^\lambda}{\partial \ln v_{ij}^\lambda} \right] = \langle u \rangle + U. \quad (5.17)$$

We now perturb the system $p_i^{eq} \rightarrow p_i^{eq}(1 + \eta_i)$, keeping the transition rates fixed. The perturbed affinity reads $a_{ij} \simeq \eta_j - \eta_i$ and the current is $j_{ij} = \ell_{ij}^{-1}(\eta_j - \eta_i)$, where the conductance (inverse resistance) is given by $\ell_{ij}^{-1} = Q^{-1} v_{ij}^\lambda$. At each node i there is an external inflowing current $J_i = \sum_j j_{ij}$, such that

$$J_i = \sum_{j \sim i} \ell_{ij}^{-1} (\eta_i - \eta_j) = \sum_j L_{ij} \eta_j, \quad (5.18)$$

where $L_{ij} = \delta_{ij} \sum_{i'} \ell_{ii'}^{-1} - \ell_{ij}^{-1}$ is a weighted laplacian matrix. We now assume that all incoming currents but those at nodes k and l are null, so that there

is a net flow of current from vertex k towards vertex l , such that $J_k = -J_l = J$ ¹. We define the effective conductance between vertex k and l as

$$\bar{\ell}_{kl}^{-1} = \frac{\eta_k - \eta_l}{J_k - J_l} = \frac{\eta_k - \eta_l}{2J}. \quad (5.19)$$

To solve Eq.(5.18) for the potential, we eliminate the l -th equation and invert the matrix $L_{(l)}$ obtained by removing the l -th row and column:

$$\eta_{i \neq l} = \sum_{j \neq l} [L_{(l)}^{-1}]_{ij} J_j = J \sum_{j \neq l} [L_{(l)}^{-1}]_{ik} \quad (5.20)$$

so that $\eta_k = J[L_{(l)}^{-1}]_{kk}$, and vice versa by the same argument $\eta_l = -J[L_{(k)}^{-1}]_{ll}$. The (k, k) -th entry of the inverse of $L_{(l)}$ is the ratio of the (k, k) -th cofactor of $L_{(l)}$ and of its determinant,

$$\eta_k - \eta_l = J \left(\frac{\det L_{(k,l)}}{\det L_{(k)}} + \frac{\det L_{(l,k)}}{\det L_{(l)}} \right) \quad (5.21)$$

where $L_{(k,l)}$ is the matrix obtained by removing both the k -th and the l -th row and column. It is well known that the diagonal cofactors of L are identical and coincide with the spanning tree polynomial

$$\det L_{(k)} = \det T(\ell). \quad (5.22)$$

We then obtain

$$\bar{\ell}_{kl}^{-1} = \frac{\det L_{(k,l)}}{\det L_{(k)}} = \left(\frac{\partial \ln L_{(k)}}{\partial \ell_{kl}^{-1}} \right)^{-1} = \left(\frac{1}{\ell_{kl}^{-1}} \frac{\partial \ln L_{(k)}}{\partial \ln \ell_{kl}^{-1}} \right)^{-1} \quad (5.23)$$

where the second identity follows from the fact that by definition of determinant ℓ_{kl}^{-1} multiplies the (k, l) minor $\det L_{(k,l)}$ in $\det L_{(k)}$. Eq.(5.15) follows.

¹Our definition of J differs from that of Wu [45, Eq.(4.32)] by a factor 2. Since the conclusion is the same for both, either the author or Wu made an error.

6

Nonequilibrium Geometry

Open systems subject to dissipation are usually modeled through markovian dynamics and further characterized by nonequilibrium thermodynamics. The link between dynamics and thermodynamics is the concept of thermodynamic force. In this chapter we assume that markovian dynamics on a finite graph enjoys a gauge symmetry under local scalings of the probability density, derive the transformation law for the transition rates and interpret the thermodynamic force as a gauge potential. A widely accepted expression for the total entropy production of a system arises as the simplest gauge-invariant completion of the time derivative of Gibbs's entropy. We show that transition rates can be given a simple physical characterization in terms of locally-detailed-balanced heat reservoirs. It follows that Clausius's measure of irreversibility along a cyclic transformation is a geometric phase. In this picture, the gauge symmetry arises as the arbitrariness in the choice of a prior probability. Thermostatics depends on the information that is disposable to an observer; thermodynamics does not.

In Secs.6.1,6.2 we discuss the foundational questions which purport gauge invariance, starting with a personal episode and interpreting gauge transformations as changes of prior probabilities. In Sec.6.3 we put the principle to work, in Sec.6.4 we discuss Wilson loops. Finally, we generalize to time-dependent gauge transformations in Sec.6.5, and attack the problem of gauge invariance using generating functions in Sec.6.6.

6.1 On information and entropy

This chapter starts with a personal anecdote. During the 15th National Convention on Statistical Physics and Complex Systems held in Parma, June 2011, Angelo Vulpiani and the author had a cordial but vigorous corridor quarrel about the physical nature of entropy. Vulpiani's foregoing talk [104], *The role of chaos for the foundation of statistical mechanics*, was devoted to the ontology of chaos, grossly dividing the community among those who believe that chaos should be welcomed as a fundamental ingredient in a second-law-dominated world (a line of thought which has Prigogine as its popularizing champion, and which has been variously criticized and even mocked through the years [105]), and those who believe that irreversibility is compatible with determinism. Unwilling to take a stand on this issue, in the question time the author pointed out, with amused but slightly polemical tone, that there exists at least a third viewpoint, which might be called the "informationist" to which, needless to say, he subscribes.

Vulpiani was prepared to the question and promptly projected slides to respond. In the informationist approach to statistical mechanics, which dates back to Jaynes's cornerstone article *Information Theory and Statistical Mechanics* [55], the Gibbs-Shannon (or differential) entropy

$$S(p) = - \int_X dx p(x) \log p(x), \quad x = (x_1, \dots, x_n) \in X, \quad (6.1)$$

plays a crucial role as the measure of the unbiased plausibility of a probability, given certain observational constraints (see [106] for a thorough discussion on the relationship between statistical mechanics and information theory). Vulpiani's confutation of the informationist viewpoint, in his judgement, prised on the non-invariance of $S(p)$ under changes of integration variable. In fact, consider an invertible map $y \mapsto x = f(y)$ with jacobian

$$J(y) = \det \left(\frac{\partial f}{\partial y} \right).$$

The volume element transforms according to

$$dx = J(y) dy.$$

The probability measure is reasonably assumed to be invariant,

$$\text{Prob}(dx) = p(x) dx = p'(y) dy = \text{Prob}'(dy). \quad (6.2)$$

Therefore, the probability density transforms according to

$$p'(y) = J(y)p(f(y)). \quad (6.3)$$

Let the inverse image of the domain X be $Y = f^{-1}(X)$. Performing a change of variables in Eq.(6.1) we obtain

$$S(p) = - \int_Y dy p'(y) \left[\log p'(y) - \log J(y) \right] = S(p') + \langle J \rangle_{p'},$$

where $\langle \cdot \rangle_{p'}$ is the expectation value. It satisfies

$$\langle J \rangle_{p'} = \langle J \circ f^{-1} \rangle_p. \quad (6.4)$$

From a geometrical point of view, the above transformation laws, Eqs. (6.2), (6.3) and (6.4) can be so stated: under coordinate changes, the probability density transforms like a scalar density, the probability measure is a volume form, the expectation value transforms like a scalar.

Later in the conference aisle, the question triggered further discussion, with Vulpiani holding that coordinate-dependence of the Gibbs-Shannon entropy is nonsensical, since the thermodynamics of bodies does not care for the coordinates that we use to describe systems. This point of view is very common among physicists. Hnizdo and Gilson [107] write: “Whereas the thermodynamic entropy is not expected to depend upon the choice of variables, the differential entropy can be changed by a transformation of variables”. They Gilson solve the problem by only considering symplectic transformations, which are volume-preserving. However, this limitation is not fully satisfactory, and the problem remain open.

As Vulpiani was making his point, he was beating with his hand on a metal banister to convey that the reality of any thermodynamical object is given, with or without information. We point out that, from an informationist’s perspective, Vulpiani’s beating on the banister is a measurement process that an observer — Vulpiani — performs with an instrument with finite resolution — his hand — in order to acquire information — for example, the temperature of the banister, its stiffness etc. Temperature is defined as a heat exchange between the system and a small thermometer; the latter is supposed to influence the system’s state in an unmeasurably small manner. Thermometers interact with certain degrees of freedom of the system: for example, the electromagnetical forces of the outer, non-shielded electrons of a molecule. Every-day thermometers do not interact strongly with the nucleus,

electro-weakly with the electrons, they do not exchange gluons, massive vector bosons, gravitons, strings, quanta of space-time and whatever is beyond our knowledge. A thermometer has a finite resolution, just like Vulpiani's hand. So what is *the* temperature? It depends on the coarse graining of "reality" that physical apparatuses always entail. Along this line of thought, of the two questions

how much entropy is within a body?

how much entropy does an observer measure in a body?

only the second has the status of a physical question. The entropy amount does depend on the measuring apparatus. As we will explain later, the choice of an apparatus is related to the choice of integration variables in Eq.(6.1). In other words, the *thermostatistics* of an object is subjective.

However, the author agrees with Vulpiani in one respect. If we put a body in contact with an environment, with the observer now sitting outside and looking at the complex "system + environment", the *thermodynamics* should be independent of the chosen variables: a physical evolution involving heat flows from the system to the environment, or viceversa, will occur in the same manner, whichever the observer-dependent quantification of the flowing heat and of the system's entropy. Dynamics, not statics, is physical.

6.2 Priors

A gauge theory has an internal symmetry whose action leaves all physical observables invariant [72]. Strictly speaking, any symmetry leaves observables invariant, there comprising the choice of units and reference frames [108]. However, conventionally one refers to gauge symmetries as to supplementary redundancies of the variables, which are not related to space-time symmetries: hence "internal". In this section we provide a physical and slightly philosophical motivation for the gauge invariance, identifying the gauge symmetry of Non-Equilibrium Statistical Mechanics as the arbitrariness in the choice prior probabilities [109].

In the "informationist" approach to statistical mechanics, whose forefather is Jaynes [55, 56], the Gibbs-Shannon entropy is a measure of the ignorance that an observer has about the state of the system. Maximization of the entropy, subject to constraints according to whatever pieces of

information the observer gains from measurement, produces the most plausible distribution given that the sites' occurrences are a priori equally likely, according to Laplace's principle of insufficient reason. There is a source of subjectivity, which Jaynes accepted as physical, related to the choice of the observables one sets up to measure. However, there is a second one which is in-built and which made Jaynes uneasy in his earlier writings. From [56]:

“Laplace’s “Principle of Insufficient Reason” was an attempt to supply a criterion of choice [. . .] However, except in cases where there is an evident element of symmetry that clearly renders the events “equally possible”, this assumption may appear just as arbitrary as any other that might be made. Furthermore, it has been very fertile in generating paradoxes in the case of continuously variable random quantities, since intuitive notions of “equally possible” are altered by a change of variables.”

He then advised to replace Laplace's with the maximum entropy principle. So doing, he swept the dirt under the carpet, as the Shannon-Khinchin's set of axioms for the entropy include equiprobability [110], and Shannon's monotonicity axiom [111] [56, p. 630] makes reference to it.

Moreover, as we saw in the previous section alleged paradoxes are found in the continuous variables case, where the differential entropy [77, Ch.9], Eq.(6.1), has been a source of dismay [107,112], for it is not invariant under a change of variables. Related to this is the following riddle (from [113, Ch.8]): if we pick a number x between 1 and 10 at random, the probability that it is smaller than 5 is $1/2$; but if we pick x' at random between 1 and 100, the probability that it is smaller than 25 is $1/4$. How is it possible that picking either a number or its square aren't equally likely? The solution to this puzzle is to recognize that the choice of an arbitrary prior is congenital. It hides in that “at random” which is the continuous counterpart of Laplace's principle: in the first case we assume x is uniform, so that the prior is $1/10 dx$; in the second we assume that $x' = x^2$ is uniform, with prior $1/100 dx' = 1/50 x dx$. Formally, in order to make Eq.(6.1) mathematically sound, one will interpret $p(x)$ as the Radon- Nikodym derivative of the probability measure $p(x)dx$ with respect to the arbitrary prior dx . A change of variables corresponds to a change of prior.

This is not, as Jaynes thought, an artifact of continuous variables. Think for example of a dice. Basing on visual impressions — which, by the way, are the result of a measure process — we might be tempted to assign equal

probabilities $1/6$ to each face. However, if we knew that an incredibly huge mass was hidden near one of its corners, due to friction with air and the inelastic impact with the gaming table, we would have sufficient reason to believe that the three faces which are adjacent to the loaded corner will have probability approximately $1/3$, and the others near zero. Our gambling strategy will depend on this prior knowledge. As a way out, in spite of invoking measure theory, up to additive constants we might just regard (neg)entropy as a special case of relative entropy

$$S(p||p^{(\text{pr})}) = \sum_i p_i \log p_i/p_i^{(\text{pr})}, \quad (6.5)$$

with respect to a uniform prior $p_i^{(\text{pr})} = V^{-1}$. We refer the reader to Banavar and Maritan’s work [114] for some nice physical implications of working with relative entropy.

The physical rationale is that the quantification of the entropy of a system depends on the choice of the underlying degrees of freedom. If we assume that all configurations of positions and momenta of a number of classical particles are equiprobable, we implicitly coarse-grain the atomic and subatomic structure. The question “how much entropy is within a body” makes no sense on its own, since we can always go deeper into the inner structure of matter, according to the resolution of our “gedanken-apparatus”. *Thermostatics* depends on the prior. However — and here comes the key point — if we put a gas in contact with heat reservoirs, the process will occur in exactly the same manner, irregardless of our quantification of the system’s entropy. *Thermodynamics* is independent of the prior.

This is the gauge principle we assume. A gauge transformation is a change of priors. Gauge fixing means to choose a prior; it is analogous to the choice of a position with respect to which we measure displacements, with the important difference that in Newtonian mechanics the choice of a reference frame is absolute, in gauge theories the choice of a “reference frame” varies point by point.

6.3 Implementing gauge invariance

In this section we prove that Schnakenberg's definition for the thermodynamic force is the most natural candidate if we assume that thermodynamics is gauge-invariant. More precisely, we postulate that

$$p'_i = e^{-\phi_i} p_i \quad (6.6)$$

is a symmetry of the theory, with $\phi_i \in \mathbb{R}$. For sake of consistency, we need to prescribe transformation laws for all of the objects which participate to the master equation. First, consider transition rates. We assume an edgewise and linear transformation law $w'_{ij} = v_{ij} w_{ij} e^{\phi_j}$, where we singled out e^{ϕ_j} , without loss of generality. Notice that the special case with all $v_{ij} = 1$, namely

$$w'_{ij} = w_{ij} e^{\phi_j} \quad (6.7)$$

leaves the currents invariant,

$$j'_{ij} = j_{ij}. \quad (6.8)$$

The following graph-theoretical analysis proves that Eq.(6.7) is the most general edgewise linear transformation law compatible with Eq.(6.6). In fact, under the assumptions of connectedness and of nonvanishing rates, there exists a unique steady state p^{ss} of the master equation; let's consider its explicit expression, given in terms of spanning trees. By construction, each site of the graph, but the root i , is the starting point of exactly one edge of T_i , so that we can factorize

$$Z'_i = e^{\Phi - \phi_i} \sum_{T_i} \pi_v(T_i) \pi_w(T_i), \quad (6.9)$$

where $\Phi = \sum_{j \in V} \phi_j$. By Eq.(6.6), Z'_i must be proportional to the analogous expression for $e^{-\phi_i} Z_i$. We obtain

$$\sum_{T_i} \pi_w(T_i) = c^{1-V} \sum_{T_i} \pi_v(T_i) \pi_w(T_i) \quad (6.10)$$

where c is a proportionality constant. Since all transition rates are positive and the equality must hold for all sets of transition rates, it follows that $\pi_v(T_i) = c^{V-1}$ independently of the spanning tree. Furthermore, the transformation law should be universal, i.e. it should not depend on the

specific graph. As graphs become larger, typically the number of spanning trees grows exponentially in the number of edges of the graph — whereby “typically” loosely means “for most graphs” [115, 116]. For example, for a complete graph on V vertices, by Cailey’s law there are 2^{V-2} spanning trees and $V(V-1)/2$ edges. This entails that the number of equations specified by $\pi_v(T_i) = c^{V-1}$ becomes enormously larger than the number of the unknowns. The only universal solution is $v_{ij} = c, \forall ij$; the constant can then be scaled to unity with a redefinition of the time unit $t \rightarrow t/c$.

We now face a seeming paradox. In fact, considering the transformed master equation $\dot{p}'_i = \sum_j j'_{ij}$ and keeping into account Eq.(6.6) and Eq.(6.8), we obtain an equation which is *not* equivalent to the starting master equation, Eq.(3.1)! The solution delves into the geometrical interpretation of summation symbols. We consider again the incidence matrix

$$(\partial_1)_i^{jk} = \begin{cases} +1, & \text{if } j < k, k = i \\ -1, & \text{if } j < k, j = i \\ 0, & \text{elsewhere} \end{cases}, \quad (6.11)$$

and the expression of the master equation as a continuity equation

$$\dot{p} + \partial_1 j = 0. \quad (6.12)$$

Technically speaking, the incidence matrix is a boundary operator which maps edges into their boundary sites. Normalization of the probability can be written as

$$\sum_{i \in V} p_i = \partial_0 p = 1 \quad (6.13)$$

where we introduced one further boundary operator ${}^0\partial = (1, 1, \dots, 1)$, which maps sites to the connected component of the graph they belong to. Although this latter definition is rather trite, it gets more pertinent when the graph has several disconnected components. Notice that $\partial_0 \partial_1 = 0$, from which conservation of probability follows. Therefore “summation over i ” has different geometrical meanings according to the context.

Strictly speaking, p_i should not be considered as a number, but rather as a one-component vector which lives in the internal vector space $\Psi_i \cong \mathbb{R}$ which is attached to site i . The gauge transformation Eq.(6.6) is interpreted as a linear change of basis in Ψ_i . It follows that we should consider the boundary operator’s entries as linear maps on Ψ_i , which transform according to

$$(\partial'_1)_i = e^{-\phi_i} (\partial_1)_i, \quad (\partial'_0)_i = e^{\phi_i} (\partial_0)_i. \quad (6.14)$$

With this prescription, Eq.s (6.12) and (6.13) are covariant. To simplify the notation a bit, we introduce a modified sum symbol \sum' such that

$$\sum'_i = \sum_i e^{\phi_i}. \quad (6.15)$$

This modified symbol is crucial for the up-coming result, so let us further linger on it. Consider the average of a gauge-invariant site function $f' = f$ (a scalar field),

$$\langle f \rangle_p = \sum_i p_i f_i = \sum'_i p'_i f_i. \quad (6.16)$$

Requiring gauge invariance $\forall f$ yields the transformation law for the summation symbol. In other words, while the probability measure $\langle \cdot \rangle_p$ is gauge invariant, the probability density p_i is not, in analogy with the continuous variables case, see Eq.(6.2).

Finally, the Gibbs-Shannon entropy transforms according to

$$\delta S = S'[p'(\tau)] - S[p(\tau)] = \langle \phi \rangle_p = -S(p' || p) \quad (6.17)$$

where S' is calculated using \sum' . On the right-hand side, the transformation law is succinctly expressed in terms of relative entropy. Remarkably, while relative entropy is not a difference of entropies, in this context it is naturally interpreted as (minus) the entropy change after a gauge transformation. The rate at which the entropy of the system changes is subject to

$$\delta \dot{S} = \sum_{i < j} j_{ij} (\phi_i - \phi_j). \quad (6.18)$$

In gauge theories, non-gauge invariant terms are adjusted with the introduction of a connection, which is an antisymmetric edge variable $a_{ij} = -a_{ji}$ such that

$$\delta a_{ij} = \phi_j - \phi_i. \quad (6.19)$$

Once a connection is given, the term¹

$$\sigma = \sum_{i < j} j_{ij} a_{ij} \quad (6.20)$$

¹In this case, the sum has meaning of a bilinear form from the space of edges to real numbers, so no gauge transformation is needed.

has a transformation law which balances Eq.(6.18), making $\dot{S} + \sigma$ invariant. In principle, connections can be constructed as convex linear combinations of terms such as

$$\log \frac{p_i^{ss}}{p_j^{ss}}, \quad \log \frac{\omega_j}{\omega_i}, \quad \dots \quad (6.21)$$

where $\omega_i = \sum_k w_{ki}$ is the average frequency of a jump out of site i . So, for example, adding $\sum_{i<j} j_{ij} \log p_i^{ss}/p_j^{ss}$ yields the relative entropy with respect to the steady state. The latter plays an important role in the theory of Markov processes as a Lyapunov functional (see Sec.7.5 and [11, Sec.V]); fitly, it is gauge invariant, while entropy per se is not. However, the options listed above are, technically speaking, exact: they are differences of site functions, so that their circuitations vanish, thus making the graph's geometry rather dull. As a further consequence, gauge invariant terms obtained this way vanish at the steady state.

A good candidate as a “truly edge” connection variable is given by the driving force, defined in Eq.(4.4). Although it is not the only antisymmetric edge variable that one could engineer which transforms according to Eq.(6.19), it is certainly the simplest. Then $\dot{S} + \sigma$ coincides with Schnakenberg's total entropy production [11, Eq.(7.6)],

$$\sigma_{tot} = \dot{S} + \sigma = \sum_{i<j} j_{ij} \log \frac{w_{ij} p_j}{w_{ji} p_i}, \quad (6.22)$$

which is widely accepted as the entropy production rate of a Markov process. In this setting σ arises as the simplest term which completes \dot{S} into a gauge invariant quantity and which does not vanish at the steady state.

A gauge transformation will result in a shift of a total time derivative from σ to \dot{S} , with a consequent redefinition of the internal entropy and of the entropy flow towards the environment. For example, letting $\phi_i = \log p_i^{ss}$, we obtain

$$S' = -S(p || p^{ss}), \quad \sigma' = \sum_{i<j} j_{ij} \log \frac{w_{ij} p_j^{ss}}{w_{ji} p_j^{ss}}, \quad (6.23)$$

whose microscopic analogues along single stochastic trajectories have been interpreted by Esposito and Van den Broeck as non-adiabatic and adiabatic terms, obeying detailed fluctuation theorems [78]. In fact, regarding fluctuation theorems gauge transformations have the only effect of changing the boundary terms.

To our knowledge, until very recently the geometric nature of the thermodynamic force was confined to the mathematical literature [24] and to work by Graham [117], with no explicit reference to gauge invariance. In the year of writing, for continuous diffusive processes the interpretation of the force as a gauge potential has been put forward by Feng and Wang [118]. Sagawa and Hayakawa [119] made a proposal for a gauge potential connecting nonequilibrium steady states along slowly driven protocols; differently from Feng and Wang’s, their connection has null curvature. They also observe that “the gauge symmetry does not seem to play any important role”. We fill the gap, taking an orthogonal approach: we do not assume the connection to be given, and derive it as the most natural candidate which guarantees covariance of the master equation; the appearance of a gauge potential is a byproduct of the symmetry, a conclusion which in a way parallels Abe and Kaneko’s analysis of driven quantum equilibrium states [120].

6.4 Parallel transport and Wilson loops

From a geometrical viewpoint (see Refs. [36, 37]), not only a provides a connection over the manifold, but it also constitutes a measure of the oriented length of paths along chains of edges $\gamma = (i_n i_{n-1}, \dots, i_1 i_0)$,

$$\Sigma(\gamma) = \sum_{\kappa=1}^n a_{i_\kappa i_{\kappa-1}} = \int_{\gamma} a. \quad (6.24)$$

Since the length is additive upon composition of paths, the real positive numbers obtained by exponentiating $\Sigma(\gamma)$ can be thought of as elements in the multiplicative group of real positive numbers (\mathbb{R}^+, \times) , which is the gauge group of the theory. In the representation theory of groups, group elements are not seen as “static” objects, but rather as “active” linear maps; they act on vectors ψ_i which live in the internal vector spaces Ψ_i . Such vectors acquire phases as they are parallel transported along paths, thus connecting far-apart sites,

$$\underline{\psi}_{i_n} = \exp \Sigma(\gamma) \psi_{i_0}, \quad (6.25)$$

where $\underline{\psi}_{i_n}$ represents the result of parallel transport along path γ . In our case, due to the very simple gauge group, the displaced vector is just a real number and parallel transport produces a scaling factor. The interpretation of group

elements as linear maps further entails that new equivalent representations can be obtained by performing basis transformations in Ψ_i , one per each site: this yields a gauge transformation. In the case at hand, such a basis change amounts to an orientation-preserving rescaling $\psi'_i = e^{-\phi_i}\psi_i$. Transformed vectors are parallel transported according to $\underline{\psi}'_{i_n} = \exp \Sigma'_\gamma \psi'_{i_0}$, where Σ' is a new representation of the group element, defined in terms of a transformed connection a' . Requiring equivalence with Eq.(6.25) for any possible path γ yields the transformation law for the vector potential, Eq.(6.19). Grossly, this introduces the geometrical framework for gauge theories.

Gauge transformations define an equivalence relation “ \sim ” between gauge potentials; so, for example, the adiabatic force $\log(w_{ij}p_j^{ss}/w_{ji}p_i^{ss})$, see Ref. [78], is gauge-equivalent to ours, Eq.(4.4). The connection is said to be exact when it is equivalent to $a'_{ij} = 0$. It is well known [24, 117, 118, 121] that equilibrium systems are characterized by an exact potential. In fact, when $a_{ij} = \phi_i - \phi_j$, the steady solution of the master equation is $p_i^{ss} \propto e^{-\phi_i}$, as direct substitution into Eq.(3.1) shows. Detailed balance follows, $w_{ij}/w_{ji} = p_i^{ss}/p_j^{ss}$.

Along closed cycles c , with $i_0 = i_n$, the exponentiated length is a Wilson loop. When Wilson loops are all unity the connection is exact and the oriented length of an open path only depends on the extremal sites, and not on the particular path which connects them, for which reason the connection is said to be flat. As a remarkable consequence, Kolmogorov’s criterion [26, 30] is equivalent to all Wilson loops being equal to unity. Hence detailed balanced systems can be seen as the special class of models with a flat connection, with zero curvature; they all belong to the same equivalence class.

On a discrete state space, knowledge of a finite number of Wilson loops suffices to characterize the connection. The so-called Mandelstam identity

$$W(c_1 \circ c_2) = W(c_1)W(c_2) \tag{6.26}$$

allows to compose loops. A basis of loops can be found this way. Consider an arbitrary spanning tree T of the graph — this time with no preferred root and orientation. Let $i_\alpha j_\alpha$ be one of the edges which do not belong to T . By definition, adding $i_\alpha j_\alpha$ to the spanning tree generates a cycle c_α , which can be oriented according to the orientation of $i_\alpha j_\alpha$. By Euler’s formula, there are $E - V + 1$ such cycles. We proved in the first chapter that any loop can be decomposed in terms of the c_α ’s. Let e_{ij}^α be +1 if $ij = i_\alpha j_\alpha$, -1 if $ji = i_\alpha j_\alpha$, otherwise it is zero. It can be shown that

$$\log \prod_\alpha W(c_\alpha)^{e_{ij}^\alpha} \sim a_{ij}. \tag{6.27}$$

Wilson loops allow to reconstruct the gauge potential, up to gauge transformations [122]. By Eq.(6.27), the choice of a spanning tree fixes the gauge by selecting one particular representative in the equivalence class of a_{ij} .

Spanning trees also allow to give a physical interpretation of the connection, using the Local Detailed Balance *ansatz*. Any graph which coincides with a spanning tree, $E = T$, has no cycles, hence it can only accomodate equilibrium systems. Then there exists a site function $\phi_i = \beta u_i$ such that

$$w_{ij}/w_{ji} = e^{\beta(u_j - u_i)}, \quad ij \in T, \quad (6.28)$$

where we introduced an inverse temperature β , in units of Boltzmann's constant. The inverse temperature and the energy u_i are determined up to an energy shift and a rescaling of units, $u_i \rightarrow k(u_i + v)$, $\beta \rightarrow k^{-1}\beta$. In general, adding further edges $i_\alpha j_\alpha$ to the graph will not result in a detailed balanced system, unless we fine-tune their rates. We then define a new set of temperatures β^α , such that

$$w_{i_\alpha j_\alpha}/w_{j_\alpha i_\alpha} = e^{\beta^\alpha(u_{j_\alpha} - u_{i_\alpha})}, \quad i_\alpha j_\alpha \in E \setminus T. \quad (6.29)$$

We just proved that the thermodynamics of any collection of transition rates can be described in terms of at most $E - V$ reservoirs, each at its own temperature, satisfying the condition of local detailed balance (see Sec.4.4). In this “minimal” case each transition is due to the interaction with exactly one reservoir. This *ansatz* allows to recast the basis Wilson loops in this form

$$W(c_\alpha) = \exp [(\beta - \beta_\alpha)(u_{i_\alpha} - u_{j_\alpha})]. \quad (6.30)$$

Therefore, temperature differences are the fundamental thermodynamic forces of nonequilibrium systems, as one could expect. Since there is no external time-dependent driving, which would result in time-dependent transition rates, no work is performed by an external agent along one single realization of the process, and by the first law of stochastic thermodynamics [82], along a transition the energy gap δu coincides with the heat exchanged δq . It is then illuminating to rewrite the geometric phase as

$$\log W(c) = \oint_c \frac{\delta q}{T}, \quad (6.31)$$

yielding Clausius's measure of irreversibility along one realization of a cyclic irreversible process. The length $\Sigma(\gamma)$ is the entropy exchanged with the environment along any trajectory which performs a sequence of jumps, whichever

the jumping times might be. This notion is completely independent of the time parametrization of the trajectory: it is purely geometrical.

The above construction can be easily generalized to Markov processes with time-dependent transition rates (see Sec.6.5) and to time-dependent gauge transformations. In this respect, our formalism has evident points of contact with stochastic pumping along cyclic protocols, whose geometrical nature has been recently studied [123] [124]. It would be a conceptual advance to give a unified description of both aspects of NESM. We notice in passing that Sinitsyn [125, §6] makes a remark on gauge transformations applied to the current generating function, arguing that they follow from the modification of the “prior” currents which have flown before a given initial time.

Regarding the nature of gauge transformations, for continuous variables they have been shown to follow from coordinate changes. Thus the gauge group could be seen as (a subgroup of) the group of diffeomorphisms. It has been a matter of disagreement [126] [127, §2.1.3] whether diffeomorphisms and gauge transformations should be considered by the same standards; the diatribe mainly revolves around gravity and its formulation as a local affine theory [128]. The identification of ours as a gauge transformations is justified by the usage of the gauge machinery, which is analogous to well-established practice for the formalization of geometric phases in QM and of electromagnetism as a $U(1)$ gauge theory. Employing analogies with the latter, C. Timm [51] discussed a slightly different gauge-theoretic structure for master equations.

To conclude, while we are conscious that the very simple gauge group makes the geometrization of irreversible thermodynamics unnecessary for all practical purposes, it allows to better appreciate the importance of macroscopic affinities as fundamental observables, and it might serve as a good starting ground for later generalizations. We point out that a Schnakenberg-type analysis is still lacking for quantum nonequilibrium systems, either described by a Lindblad-type equation or a by a more general interaction of a system with reservoirs of quantum degrees of freedom. It is tenable that excursions to the quantum world might require more interesting gauge groups and a more pertinent application of gauge theory.

6.5 Time-dependent gauge transformations

The extension of time-dependent gauge transformations is straightforward,

$$p(t) \rightarrow p^\Phi(t) = \exp[-\Phi(t)]p(t),$$

where $\Phi(t) = \text{diag}[\phi_1(t), \dots, \phi_V(t)]$. The ME reads

$$\dot{p}^\Phi(t) = L^\Phi(t)p^\Phi(t), \quad (6.32)$$

where we defined the transformed generator

$$L^\Phi(t) = e^{-\Phi(t)}L(t)e^{\Phi(t)} - \dot{\Phi}(t).$$

Consider the splitting of the generator in a free and an interaction part, taking into account that $L_0(t)$ and $\Phi(t)$, being diagonal, commute:

$$L^\Phi(t) = e^{-\Phi(t)}L_1(t)e^{\Phi(t)} + L_0(t) - \dot{\Phi}(t) = L_1^\Phi(t) + L_0^\Phi(t).$$

where in the last identity we defined the transformed free generator $L_0^\Phi := L_0 - \dot{\Phi}$ and the transformed jump generator $L_1^\Phi := \exp -\Phi L_1 \exp \Phi$. Interaction picture propagators are then easily calculated

$$U_0^\Phi(t) = e^{-\Phi(t)}U_0(t)e^{\Phi(t)}, \quad L_1^\Phi(t) = e^{-\Phi(t)}L_1(t)e^{\Phi(t)},$$

respectfully of the path measure Eq.(3.12).

6.6 Microscopic analysis

When we introduced the stochastic trajectory Eq.(3.14), we blandly observed that it was a formal expression. Strictly speaking, it's inappropriate to multiply graph elements by a step function. In practical situations, graph vertices are always associated to a weight ϕ_i , which can eventually be a time-dependent function. We then prefer to represent a trajectory $i(t')$ from time 0 to t , given the initial state i_0 , by a real-valued process

$$R^\nu(t') = \sum_{m=0}^n \chi_{[t_m, t_{m+1})}(t') \phi_{i_m}(t') - \phi_{i_0}(0), \quad t' \in [0, t]$$

where the subtraction accounts for the initial datum, so to conventionally make all such processes null at the initial time, $R^\nu(0) = 0$. This is a very physical standpoint: even when we consider the deterministic motion of a body, we never deal with its absolute position, but we rather associate a real number (actually, a rational number) given by comparison of its distance from a fixed arbitrary origin with a conventional unit length. The motion of the object is independent of the choice of unit length and of the origin. Ultimately, what *is* the trajectory? Since it is impossible to make physical claims on its objective nature, we might regard the trajectory as the equivalence class of all possible descriptions that we can give of it. We assert this principle for stochastic trajectories. Rather than a sequence of vertices of a graph, a trajectory ν is an equivalence class of real-valued processes $R^\nu(t')$. For practical purposes, we already set the origin, thus spending part of the gauge, by choosing $R^\nu(0) = 0$.

It is well-known that the moment generating function of a stochastic process contains all useful information about the process. In this section we derive a diffusion equation for the moment generating function of $R^\nu(t)$, showing that it coincides with the time-dependent gauge-transformed master equation, Eq.(6.32). So, after giving a macroscopic thermodynamic characterization of gauge invariance in terms of Schnakenberg's observables, we are able to interpret gauge invariance at the microscopic level.

The first step is to rewrite

$$\begin{aligned} R^\nu(t) &= \sum_{m=0}^n [\phi_{i_m}(t_{m+1}) - \phi_{i_m}(t_m)] + \sum_{m=0}^{n-1} [\phi_{i_{m+1}}(t_{m+1}) - \phi_{i_m}(t_{m+1})] \\ &= \int_0^t dt' \left\{ \sum_{m=0}^n \chi_{[t_m, t_{m+1})}(t') \phi_{i_m}(t') + \sum_{m=0}^{n-1} \delta(t' - t_m) [\phi_{i_{m+1}}(t') - \phi_{i_m}(t')] \right\}. \end{aligned}$$

where we defined

$$\varphi_i(t') = \frac{d\phi_i}{dt'}(t'), \quad (6.33)$$

and we remind that $\chi_{[t_m, t_{m+1})}$ is the step function in the interval $(t_{m+1}, t_m]$, $t_0 = 0$ and $t_{n+1} := t$. This overly complicated rewriting of $\phi_{i_n}(t) - \phi_{i_0}(0)$ is worth the identification of contributions of two different kinds. An integrating counter is thought to be attached at each vertex, and one spiking counter is attached along edges. The value of the integrating counter is increased by an amount

$$\int_{t_m}^{t_{m+1}} dt' \varphi_{i_m}(t')$$

when the trajectory delays at i_m between time t_m and time t_{m+1} . The value of the spiking counter is increased by an amount

$$\phi_{i_{m+1}}(t_{m+1}) - \phi_{i_m}(t_{m+1})$$

when the trajectory performs a stochastic jump at time t_{m+1} from site i_m to site i_{m+1} . We concentrate on stochastic processes associated to these counters, respectively defined as

$$Q_i^t(t) = \int_0^t dt' \sum_{m=0}^n \delta_{i, i_m} \chi_{[t_m, t_{m+1})}(t') \varphi_i(t'),$$

$$P_{ij}^t(t) = \int_0^t dt' \sum_{m=0}^{n-1} \delta_{i, i_{m+1}} \delta_{j, i_m} \delta(t' - t_{m+1}) [\phi_i(t') - \phi_j(t')],$$

The respective moment generating functions are defined as

$$\zeta_k^Q(\lambda, t) = \mathbb{E}_k \left[\exp - \sum_i \lambda_i Q_i(t) \right],$$

$$\zeta_k^P(\Lambda, t) = \mathbb{E}_k \left[\exp - \sum_{i,j} \lambda_{ij} P_{ij}(t) \right],$$

where the average is taken with respect to all paths with fixed end point k at time t , while $\lambda = (\lambda_i)_i$ and $\Lambda = (\lambda_{ij})_{i,j}$ are respectively a vector and a matrix of conjugate parameters. Derivatives with respect to the λ 's generate moments and correlation functions,

$$\left(-\frac{\partial}{\partial \lambda_1} \right)^{N_1} \dots \left(-\frac{\partial}{\partial \lambda_V} \right)^{N_V} \zeta_k^Q(\lambda, t) \Big|_{\lambda=0} = \mathbb{E}_k [Q_1(t)^{N_1} \dots Q_V(t)^{N_V}],$$

and similarly for the P -processes. Notice that the processes Q_i are not independent of all other Q_j 's, nor are they independent of the P -processes.

We now want to derive evolution equations for ζ_j^Q and ζ_j^P . We work explicitly with the path measure. Let's first concentrate on the Q -process. We consider Eq.(3.17) at time $t + dt$ and split it as follows

$$\begin{aligned} \int^{t+dt} \mathcal{D}\mathbf{u} &= \sum_{n=0}^{\infty} \sum_{i_0, \dots, i_{n-1}} \left[\overbrace{\int_t^{t+dt} dt_n \int_t^{t_n} dt_{n-1} \dots \int_0^{t_1} dt_0}^{1st} \right. \\ &+ \left. \overbrace{\int_t^{t+dt} dt_n \int_0^t dt_{n-1} \dots \int_0^{t_1} dt_0}^{2nd} + \overbrace{\int_0^t dt_n \int_0^{t_n} dt_{n-1} \dots \int_0^{t_1} dt_0}^{3rd} \right]. \end{aligned}$$

The first contribution gives terms of order dt^2 . As to the third, using

$$\exp - \sum_i \lambda_i Q_i(t + dt) = \prod_{m=0}^n \exp \left[-\lambda_{i_m} \int_{t_m}^{t_{m+1}} dt' \varphi_{i_m}(t') \right]$$

with $t_{n+1} = t + dt$, and given Eq.(3.13), we obtain the integrand

$$\begin{aligned} q_k(t + dt, t) e^{-\lambda_k \int_t^{t+dt} dt' \varphi_k(t')} &\left\{ q_k(t, t_n) e^{-\lambda_k \int_{t_n}^t dt' \varphi_k(t')} \right. \\ &\times \left. \left[\prod_{m=0}^{n-1} w_{i_{m+1} i_m} q_{i_m}(t_{m+1}, t_m) e^{-\lambda_{i_m} \int_{t_m}^{t_{m+1}} dt' \varphi_{i_m}(t')} \right] p_{i_0} \right\}, \end{aligned}$$

where we collected all terms up to time t between braces, and $i_n = k$. Integrating with respect to the third contribution to the path measure we obtain

$$\begin{aligned} q_k(t + dt, t) e^{-\lambda_k \int_t^{t+dt} dt' \varphi_k(t')} \zeta_k^Q(\lambda, t) \\ = [1 - w_k dt - \lambda_k \varphi_k(t) dt] \zeta_k^Q(\lambda, t). \end{aligned} \quad (6.34)$$

The second contribution requires more care. Since $t_n \geq t$ in this range of integration, we rearrange the integrand as

$$\begin{aligned} q_k(t + dt, t_n) e^{\lambda_k \int_{t_n}^{t+dt} dt' \varphi_k(t')} w_{k, i_{n-1}} q_{i_{n-1}}(t_n, t) e^{-\lambda_{i_{n-1}} \int_t^{t_n} dt' \varphi_{i_{n-1}}(t')} \\ q_{i_{n-1}}(t, t_{n-1}) e^{-\lambda_{i_{n-1}} \int_{t_{n-1}}^t dt' \varphi_{i_{n-1}}(t')} \left[\prod_{m=0}^{n-2} w_{i_{m+1} i_m} \dots \right]. \end{aligned}$$

Singling out \sum_j , with $j = i_{n-1}$, upon path-averaging:

$$\begin{aligned} \sum_j \int_t^{t+dt} dt'' q_k(t+dt, t'') e^{-\lambda_k \int_t^{t''} dt' \varphi_k(t')} w_{kj} q_j(t'', t) e^{-\lambda_j \int_t^{t''} dt' \varphi_j(t')} \zeta_j^Q(t) \\ = \sum_j w_{kj} \zeta_j^Q(t) dt + O(dt^2). \end{aligned} \quad (6.35)$$

Putting Eqs. (6.34) and (6.35) together we obtain

$$\frac{d}{dt} \zeta_k^Q(\lambda, t) = \sum_j w_{kj} \zeta_j^Q(\lambda, t) - [w_k + \lambda_k \varphi_k(t)] \zeta_k^Q(\lambda, t). \quad (6.36)$$

Derivatives with respect to the λ 's yield a hierarchy of coupled evolution equations for the moments. When $\lambda = 0$, given that

$$\zeta_k^Q(0, t) = p_k(t),$$

we obtain the master equation for the probabilities, as expected. In general, the equation for the M -th moment depends on all lower moments. For example, the equation for the first moment reads

$$\frac{d}{dt} \mathbb{E}_i [Q^u(t)] = \sum_j \left\{ w_{ij} \mathbb{E}_j [Q^u(t)] - w_{ji} \mathbb{E}_i [Q^u(t)] \right\} + \varphi_i(t) p_i(t).$$

We can proceed in a similar way for ζ^P . The derivation is simpler and will not be carried over explicitly. We obtain:

$$\frac{d}{dt} \zeta_i^P(\Lambda, t) = \sum_j w_{ij} e^{-\lambda_{ij} [\phi_i(t) - \phi_j(t)]} \zeta_j^P(\Lambda, t) - w_i \zeta_i^P(\Lambda, t). \quad (6.37)$$

Eqs. (6.36) and (6.37) reproduce two different traits of the behavior of the gauge-transformed equation, Eq.(6.32). Now, we set all λ_i, λ_{ij} 's equal to λ and choose $\varphi(t)$ as the time derivative of $\phi(t)$, as is done in Eq.(6.33). The R -process defined above is given by

$$R^u(t) = \sum_i Q_i(t) + \sum_{i,j} P_{ij}(t), \quad (6.38)$$

with moment generating function given by

$$\zeta_k^R(\lambda, t) = \mathbb{E}_k [\exp -\lambda R(t)].$$

As we said above, the P and Q -processes are not independent, even though they do not depend directly on the value of all other counters, since they depend on the same underlying microscopic dynamics. Hence expectation values do not factor. The time evolution equation for $\zeta^R = (\zeta_1^R, \dots, \zeta_V^R)$ has to be found from direct calculation. We finally obtain

$$\frac{d}{dt}\zeta_i^R(\lambda, t) = \sum_j w_{ij} e^{-\lambda[\phi_i(t) - \phi_j(t)]} \zeta_j^R(\lambda, t) - \left[w_i + \lambda \frac{d\phi_i}{dt}(t) \right] \zeta_i^R(\lambda, t). \quad (6.39)$$

This is the central result of this section. Absorbing λ in the definition of ϕ_i , or equivalently choosing $\lambda = 1$, Eq.(6.39) comes to coincide with Eq.(6.32), with $\zeta^R(1, t)$ playing the role of $p^\Phi(t)$. As a special case, we have the time-independent processes, with

$$\varphi_i(t') = 0, \quad \phi_i(t) = \phi_i(0) := \phi_i.$$

In conclusion, the time-dependent gauge-transformed master equation is seen to be equivalent to the moment generating function of a stochastic process. The stochastic process associates weights to the states visited by a trajectory, thus giving physical consistency to what is otherwise just a formal expression. We interpret this procedure as a choice of gauge.

7

Decay modes

In this chapter we give a detailed survey of the properties of real and complex decay modes of a master equation generator. We introduce the time-reversal generator and a special class of normal systems, including reversible ones, which are particularly well-behaved under time-reversal. Decay modes of normal systems obey certain orthogonality relations with respect to a suitable scalar product, affecting the late time-behavior of the relative entropy with respect to the steady state: Normal systems do not display superposition of modes. We introduce the Fisher matrix associated to a generator and prove that the time-reversal generator has inverse Fisher matrix. In the vicinity of the steady state, this formalism allows to recast propositions about monotonicity and convexity of the relative entropy as problems in linear algebra. While monotonicity is well-known to hold, convexity is a tempting possibility, as it would make for a nice new principle of thermodynamics. We are able to spot a clear-cut condition for the violation of convexity and we generate a class of counterexamples with initial probability distribution picked arbitrarily close to the steady state, thus rejecting the conjecture in all possible regimes.

In the last section we put forward a geometrical interpretation of several results of this chapter in terms of the Fisher-Rao metric on the space of statistical states. More precisely, we argue that (i) the choice of a nonequilibrium generator picks out one preferred basis for the Fisher-Rao metric near the invariant state, in such a way that (ii) a diagonal Fisher matrix occurs for systems which commute with their time reversal, while (iii) degeneracies are accompanied with the sort of critical behavior which is typical of nonequilibrium phase transitions — but with no cogent need for a thermodynamic

limit on the number of states. We finally linger on the geometric meaning of the results, showing that (iv) decay modes can be seen as local reference frames for the Fisher-Rao metric, so that p -normal systems correspond to coordinate patches which make it euclidean at one point of the manifold, thus realizing a sort of statistical equivalence principle.

7.1 Eigenvalues and decay modes

The generator W of an ergodic master equation has one eigenvector relative to the null eigenvalue, the steady state. Besides that, it is well-known that by application of the Perron-Frobenius theorem all other eigenvalues are shown to have negative real part, and they might come in complex conjugate couples. We call their conjugate eigenvectors the decay modes. The real part of the eigenvalues determines the exponential decay of modes towards the invariant state, while the complex part yields an oscillating character. Generic eigenvalues/eigenvectors of W will be labelled by α, β ; among them, real eigenvalues will be labelled by ι, ι' and complex eigenvalues by κ, κ' .

Unless otherwise specified, we assume that W is diagonalizable, i.e. that it affords a complete set of eigenvectors. Later we will relax this assumption and inspect properties of defective generators.

7.2 The time-reversal generator

The time-reversal generator is what comes closest to reverting the direction of time. Whilst it is not capable of inverting the full dynamics, it properly inverts the path measure and certain steady-state thermodynamic properties of the master equation. Here we will only deal with the linear algebra of the decay modes. Time-reversal is a standard construction for markovian dynamics [69, p.47] [70, Sec. 3.7]. It has been considered by various authors in relation to fluctuation theorems [78, 83, 129]. Some contents of this and later sections have been anticipated by the author in Ref. [5].

Although we will mostly work with the master equation, the definition of time-reversal is particularly intuitive in the adjoint formalism. Let two scalar functions take values $f = (f_i)_i$ and $g = (g_i)_i$ at time $t = 0$. We consider their steady state correlation $\langle fg \rangle := \sum_i p_i^{ss} f_i g_i$. The observable f is made to evolve with the adjoint generator, $f(\delta t) = f + \delta t W^\dagger f$. We ask which generator

should be employed to evolve $g \rightarrow \bar{g}(\delta t)$ in such a way that

$$\langle f(\delta t)g(0) \rangle = \langle f(0)\bar{g}(\delta t) \rangle.$$

We then define \bar{W}^\dagger through

$$\langle (W^\dagger f)g \rangle = \langle f(\bar{W}^\dagger g) \rangle.$$

An explicit calculation shows that the time-reversal generator enjoys the following properties. Off-diagonal and diagonal elements read respectively

$$\bar{w}_{ij} = w_{ji} p_i^{ss} / p_j^{ss}, \quad \bar{w}_i := - \sum_{k \neq i} w_{ki}.$$

In particular exit frequencies are preserved, $\bar{w}_i = w_i$. The time-reversal generator \bar{W} is indeed a markovian generator, as its off-diagonal entries are positive and its columns add up to zero,

$$\sum_{k \neq i} w_{kj} + \sum_{i \neq j} w_{ji} p_i^{ss} / p_j^{ss} = 0,$$

where we used $\sum_j w_{ij} p_j^{ss} = \sum_j w_{ji} p_i^{ss} = 0$. Introducing the diagonal matrix

$$P := \text{diag}\{p_1^{ss}, \dots, p_V^{ss}\}$$

the time-reversal generator can be written as

$$\bar{W} := P W^T P^{-1}, \tag{7.1}$$

where T denotes matrix transposition. Hence time-reversal is involutive:

$$\bar{\bar{W}} = P \bar{W}^T P^{-1} = P P^{-1} W P P^{-1} = W.$$

The steady state of the time-reversal generator is the same as that of W ,

$$\bar{W} p^{ss} = P W^T P p^{ss} = 0,$$

since $P p^{ss} = (1, 1, \dots, 1)^T$ is the left-eigenvector of W relative to zero.

As to the other eigenvalues, since Eq.(7.1) is a similarity of matrices, \bar{W} has the same spectrum as W^T , which in turn has the same spectrum as W . Then W and its time-reversal \bar{W} have the same spectrum. Not so for the eigenvectors. Let $\bar{q}^{\alpha,R}$ be a right eigenvector of \bar{W} , relative to λ_α ,

$$\bar{W} \bar{q}^{\alpha,R} = \lambda_\alpha \bar{q}^{\alpha,R}.$$

Then

$$W^T P^{-1} \bar{q}^{\alpha,R} = \lambda_\alpha P^{-1} \bar{q}^{\alpha,R},$$

which means that $P^{-1} \bar{q}^{\alpha,R}$ is a left eigenvector of W relative to eigenvalue λ_α . Then P sends left eigenvectors of W to right eigenvectors of \bar{W} , and P^{-1} sends right eigenvectors of W to left eigenvectors of \bar{W} , relative to the same eigenvalue. The bi-orthonormality principle [95, p. 59] states that the left and right eigenvectors of a real matrix are orthogonal

$$(q^{\alpha,W}, q_i^{\beta,R})_{\mathbb{C}} = (q^{\alpha,W^*}, q_i^{\beta,R}) = 0, \quad \alpha \neq \beta,$$

where $*$ denotes complex conjugation, (\cdot, \cdot) is the euclidean scalar product and $(\cdot, \cdot)_{\mathbb{C}}$ is its hermitian counterpart. Here α and β label both real eigenvalues and couples of complex conjugate eigenvalues. Let us reserve index ι to real eigenvalues. Then the real eigenvectors $q^{\iota,L}$ and $q^{\iota',R}$ can be scaled so to satisfy

$$(q^{\iota,L^*}, q_i^{\iota',R}) = \delta^{\iota\nu}. \quad (7.2)$$

Let κ label couples of complex conjugate eigenvalues, and let the real and imaginary parts of the left and right complex eigenvectors be determined by $q^{\kappa,L} = 1/\sqrt{2}(q_1^{\kappa,L} + iq_2^{\kappa,L})$ and $q^{\kappa,R} = 1/\sqrt{2}(q_1^{\kappa,R} + iq_2^{\kappa,R})$. We have

$$(q_1^{\kappa,L} + iq_2^{\kappa,L}, q_1^{\kappa,R} + iq_2^{\kappa,R}) = 0, \quad (q_1^{\kappa,L} - iq_2^{\kappa,L}, q_1^{\kappa,R} + iq_2^{\kappa,R}) = ic^\kappa.$$

With little work c^κ is seen to be real and can be scaled to unity. Bi-orthonormality relations hold for the real and imaginary parts of the eigenvectors as in Eq.(7.2).

7.3 Normal generators

Among all possible generators, an important role is played by those which commute with their time reversal

$$[W, \bar{W}] = W\bar{W} - \bar{W}W = 0. \quad (7.3)$$

which we dub p^{ss} -normal. Systems with a p^{ss} -normal generator will be called simply “normal”. Let us compare the evolution of a system initially in state

p , which is first run for a short time δt with W and then for a short time δt with \bar{W} , with respect to the situation where the system is first run with \bar{W} and then afterwards with W :

$$\bar{U}(\delta t)U(\delta t)p - U(\delta t)\bar{U}(\delta t)p = \delta t \delta t [\bar{W}, L]p + O(\delta t^3).$$

Thus the operator $[W, \bar{W}]$ retains a slightly geometrical flavor as a “curvature”, as it measures how circuitation along an infinitesimal parallelogram of sides δt and δt fails to reproduce the initial state. In the forward picture, normality occurs when

$$\langle (Wf)(Wg) \rangle = \langle (\bar{W}f)(\bar{W}g) \rangle. \quad (7.4)$$

Among p^{ss} -normal there are reversible generators, such that $\bar{W} = W$,

$$\bar{w}_{ij} = w_{ji} p_i^* / p_j^* = w_{ij}.$$

Their rates satisfy detailed balance, and vice versa, balanced rates define a reversible generator. Hence reversible and equilibrium generators coincide.

The class of p^{ss} -normal generators is broader than just equilibrium systems. To appreciate this, we need to turn to systems with complex spectrum. Suppose that the spectrum of W is nondegenerate (no multiple eigenvalues). Let q^t be a real eigenvector of W relative to the real eigenvalue λ^t , and q^κ be a complex eigenvector relative to the complex eigenvalue λ_κ . Since W is real then also $q^{\kappa*}$ is an eigenvector, relative to the complex conjugate eigenvalue λ_κ^* . We have

$$\begin{aligned} L\bar{W}q^\kappa &= \bar{W}Wq^\kappa = \lambda^\kappa \bar{W}q^\kappa, \\ L\bar{W}q^t &= \bar{W}Wq^t = \lambda^t \bar{W}q^t. \end{aligned}$$

Then $\bar{W}q^\kappa$ and $\bar{W}q^t$ are eigenvectors of W relative respectively to λ^κ and λ^t . Since we supposed the spectrum to be nondegenerate, we conclude that q^κ, q^t are also eigenvectors of \bar{W} ,

$$\bar{W}q^\kappa = \eta_\kappa q^\kappa, \quad (7.5a)$$

$$\bar{W}q^t = \eta_t q^t. \quad (7.5b)$$

Consider the matrix $P^{-1/2}W\bar{W}P^{1/2}$. It is easily seen to be symmetric, hence its spectrum is real. Since it is obtained from $W\bar{W}$ by a similarity transformation, the spectrum of $W\bar{W}$ is real. Applying W to Eq.(7.5a) we obtain

$$W\bar{W}q^\kappa = \lambda_\kappa \eta_\kappa q^\kappa,$$

whence q^κ is an eigenvectors of $L\bar{W}$ relative to eigenvalue $\lambda_\kappa\eta_\kappa$, which must be real. It follows that

$$\eta_\kappa = \lambda_\kappa^*. \quad (7.6)$$

Finally, using the bi-orthonormality condition (7.2) one finds that $\eta_l = \lambda_l$. Hence we conclude that when W is normal, it has the same spectrum and the same eigenvectors as those of \bar{W} , but eigenvectors relative to positive and negative frequency eigenvalues are interchanged. When the spectrum is real, the two operators exactly coincide, returning reversible systems.

The significance of all this is better appreciated by scrutinizing the time-evolution of an initial probability density

$$p = p^{ss} + \sum_l b_l q^l + \sum_\kappa (c_\kappa q^\kappa + c_\kappa^* q^{\kappa*}). \quad (7.7)$$

We remind that eigenvalues of W have negative real part

$$\lambda^\kappa = -1/\tau_\kappa \pm i\omega_\kappa.$$

Let us propagate (7.7) to time t with L and with \bar{W} :

$$e^{tL}p = p^{ss} + \sum_l b_l e^{-t/\tau^l} q^l + \sum_\kappa e^{-t/\tau_\kappa} (c_\kappa e^{i\omega_\kappa t} q^\kappa + c_\kappa^* e^{-i\omega_\kappa t} q^{\kappa*}), \quad (7.8a)$$

$$e^{t\bar{W}}p = p^{ss} + \sum_l b_l e^{-t/\tau^l} q^l + \sum_\kappa e^{-t/\tau_\kappa} (c_\kappa e^{-i\omega_\kappa t} q^{\kappa*} + c_\kappa^* e^{i\omega_\kappa t} q^{\kappa*}). \quad (7.8b)$$

The reversal propagator inverts all of the frequencies: while the dissipative exponential decay is exactly the same for W and \bar{W} , the oscillatory modes are inverted. In a way, the unitary character of the evolution is time-reversed, while the non-unitary dissipative behavior is left unchanged.

7.4 The Fisher matrix

We introduce the matrix

$$H := P^{-1/2} W P^{1/2}. \quad (7.9)$$

A crucial property of H is that its transpose is obtained after the same transformation of the time-reversal generator,

$$H^T = P^{-1/2} \bar{W} P^{1/2}. \quad (7.10)$$

In particular it follows that equilibrium systems are those for which H is symmetrical and normal systems are those for which H is a normal matrix

$$\begin{aligned} W \text{ reversible :} & \quad H = H^T, \\ W \text{ } p^{ss}\text{-normal :} & \quad HH^T = H^T H. \end{aligned}$$

Since Eq.(7.9) is a similarity of matrices, H and W have the same spectrum, with left and right eigenvalues of H related to those of W by

$$\begin{aligned} e^{\alpha,L} &= P^{1/2} q^{\alpha,L}, & e^{0,L} &= P^{1/2} (1, 1, \dots, 1)^T, \\ e^{\alpha,R} &= P^{-1/2} q^{\alpha,R}, & e^{0,R} &= P^{-1/2} p^{ss}. \end{aligned}$$

Where unnecessary we will omit the superscript for “right”. Explicitly, we have $e_i^\alpha = q_i^\alpha / \sqrt{p_i^{ss}}$ and $e_i^{0,L} = e_i^{0,R} = \sqrt{p_i^{ss}}$. We will let index a range from 0 through the span of α in the following, so that $e^a = e^0, e^\alpha$.

Let us momentarily restrict to generators whose spectrum is contained in the field of real numbers. We further introduce more matrices $G' = (g_{ab})_{a,b}$ and $G = (g_{\alpha\beta})_{\alpha,\beta}$, with entries

$$g^{ab} = (e^a, e^b), \quad g^{\alpha\beta} = (e^\alpha, e^\beta) = \sum_i q_i^\alpha \cdot q_i^\beta / p_i^{ss}.$$

where (\cdot, \cdot) is the euclidean scalar product. Matrix G will be referred to as the Fisher matrix. We leave to a later chapter a thorough discussion of the choice of this name and its geometrical and statistical significance. We find

$$g^{00} = \sum_i p_i^{ss} = 1, \quad g^{0\alpha} = \sum_i q_i^\alpha = 0.$$

Hence

$$G' = \begin{pmatrix} 1 & 0 \\ 0 & G \end{pmatrix}.$$

On the field of reals, the spectral theorem asserts that a matrix is symmetric if and only if it admits a basis of orthogonal eigenvectors, which therefore can be chosen to be orthonormal:

$$g^{\alpha\beta} = \delta^{\alpha\beta}, \quad G = \mathbf{1}_{V-1}, \quad G' = \mathbf{1}_V.$$

Hence, if we restrict to generators with real spectrum, the Fisher matrix is diagonal if and only if the generator is of equilibrium, in which case its modes

can be scaled so to make G the unit matrix. This result was known to Van Kampen [130, Sec. 5.7.].

Over the complex field, the spectral theorem generalizes to normal matrices [95, p.59, p.123]: it suffices (and is necessary) that $HH^\dagger = H^\dagger H$ to make H unitarily diagonalizable, *i.e.* with a complete set orthonormal eigenvectors with respect to the hermitian scalar product

$$(e^\alpha, e^\beta)_\mathbb{C} = \sum_i e^{\alpha*} e^\beta = \delta^{\alpha\beta}.$$

Let the eigenvalues come in $k \leq V/2$ complex conjugate couples and $V-1-2k$ real eigenvalues, with corresponding eigenvectors labelled by $(\kappa, -)$, $(\kappa, +)$ and ι respectively, that is, e_+^κ is the eigenvector of H relative to eigenvalue λ_κ while $e_-^\kappa = e_+^{\kappa*}$ is relative to eigenvalue λ_κ^* . Then according to the spectral theorem the following orthonormality relations are satisfied:

$$(e_+^\kappa, e_+^{\kappa'})_\mathbb{C} = (e_-^\kappa, e_-^{\kappa'})_\mathbb{C} = \delta^{\kappa, \kappa'} \quad (7.11a)$$

$$(e_-^\kappa, e_+^{\kappa'})_\mathbb{C} = (e^\iota, e_+^\kappa)_\mathbb{C} = 0 \quad (7.11b)$$

$$(e^\iota, e_+^{\iota'})_\mathbb{C} = \delta^{\iota, \iota'}. \quad (7.11c)$$

Notice however that in general, for non-normal matrices, the hermitian scalar product of two complex modes will not be a real number, so that if we were to define the Fisher matrix as above we would obtain a complex matrix. For reasons that will soon become clear, it is recommendable that the Fisher matrix is a real positive-definite symmetric matrix. Then it is necessary to switch to the real and imaginary parts of the eigenvectors,

$$e_1^\kappa = \frac{1}{\sqrt{2}} (e_+^\kappa + e_-^\kappa), \quad e_2^\kappa = \frac{1}{i\sqrt{2}} (e_+^\kappa - e_-^\kappa).$$

Plugging into Eqs.(7.11a,7.11b) we obtain

$$(e_1^\kappa, e_1^{\kappa'}) + (e_2^\kappa, e_2^{\kappa'}) + i(e_1^\kappa, e_2^{\kappa'}) - i(e_2^\kappa, e_1^{\kappa'}) = 2\delta^{\kappa, \kappa'},$$

$$(e_1^\kappa, e_1^{\kappa'}) - (e_2^\kappa, e_2^{\kappa'}) + i(e_1^\kappa, e_2^{\kappa'}) + i(e_2^\kappa, e_1^{\kappa'}) = 0.$$

Notice that in these formulas the scalar product is the euclidean one. Considering separately the real and imaginary parts of these expressions together with Eqs.(7.11b,7.11c), the full set of orthonormality relations is found:

$$(e_1^\kappa, e_1^{\kappa'}) = \delta^{\kappa\kappa'} = (e_2^\kappa, e_2^{\kappa'}),$$

$$(e_2^\kappa, e_1^{\kappa'}) = 0 = (e_1^\kappa, e_2^{\kappa'}),$$

$$(e_2^\kappa, e^\iota) = 0 = (e_1^\kappa, e^\iota),$$

$$(e^\iota, e_2^{\iota'}) = \delta^{\iota\iota'}.$$

At this point it is clear that how we should construct the Fisher matrix in the complex case. We introduce the basis of real vectors

$$\tilde{e}^\alpha = \begin{cases} e_1^\alpha, & \alpha = 1, \dots, k \\ e_2^{\alpha-k}, & \alpha = k+1, \dots, 2k \\ e^{\alpha-2k}, & \alpha = 2k+1, \dots, V-1 \end{cases} \quad (7.12)$$

We further introduce the matrix \mathbf{e} with vectors \tilde{e}^α as its columns. Finally we define the Fisher matrix as

$$G = \mathbf{e}^T \mathbf{e} = ((\tilde{e}^\alpha, \tilde{e}^\beta))_{\alpha,\beta} = \begin{pmatrix} (e_1^\kappa, e_1^{\kappa'}) & (e_1^\kappa, e_2^{\kappa'}) & (e_1^\kappa, e^{\iota'}) \\ (e_2^\kappa, e_1^{\kappa'}) & (e_2^\kappa, e_2^{\kappa'}) & (e_2^\kappa, e^{\iota'}) \\ (e^\iota, e_1^{\kappa'}) & (e^\iota, e_2^{\kappa'}) & (e^\iota, e^{\iota'}) \end{pmatrix}_{\kappa,\kappa',\iota,\iota'}$$

Notice that since G is the Gram matrix of a collection of linearly independent real vectors, it is by construction a positive definite symmetric matrix.

We can now state the central result of this chapter, so far. The Fisher matrix G is diagonal if and only if the generator W is normal, in which case the eigenvectors of the generator W can be chosen so to make G the unit matrix. For generators with real spectrum, the Fisher matrix G is diagonal if and only if W satisfies detailed balance.

The Fisher matrix has been constructed by means of the right eigenvectors of H . Since by Eq.(7.10) left eigenvectors of H play a symmetric role as right eigenvectors of the time-reversal generator, the Fisher matrix of the time-reversal is easily constructed as

$$\bar{G} = \begin{pmatrix} (e_1^{\kappa,L}, e_1^{\kappa',L}) & (e_1^{\kappa,L}, e_2^{\kappa',L}) & (e_1^{\kappa,L}, e^{\iota',L}) \\ (e_2^{\kappa,L}, e_1^{\kappa',L}) & (e_2^{\kappa,L}, e_2^{\kappa',L}) & (e_2^{\kappa,L}, e^{\iota',L}) \\ (e^{\iota,L}, e_1^{\kappa',L}) & (e^{\iota,L}, e_2^{\kappa',L}) & (e^{\iota,L}, e^{\iota',L}) \end{pmatrix}_{\kappa,\kappa',\iota,\iota'}$$

Is there any relationship between the Fisher matrix of a generator and the Fisher matrix of its time-reversal? According to the following claim, the answer is in the affirmative.

Eigenvectors of H can be scaled so that the Fisher matrix \bar{G} of the time-reversal generator \bar{W} is the inverse of that of generator W :

$$G\bar{G} = \bar{G}G = \mathbf{1}. \quad (7.13)$$

An indirect proof of this fact will follow from considerations to come. For later reference, we report a table of the span of the several indices that have

been employed in this section:

$$\begin{aligned}
a, b &= 0, \dots, V-1, \\
\alpha, \beta &= 1, \dots, V-1, \\
\kappa, \kappa' &= 1, \dots, k, \\
\iota, \iota' &= 1, \dots, V-2k-1,
\end{aligned}$$

where we remind that V is the finite number of discrete states of the system and k is the number of complex conjugate couples of eigenvalues of W .

7.5 Relative entropy and monotonicity

We consider the relative entropy with respect to the steady state:

$$S := S(p \| p^{ss}) = \sum_i p_i \ln(p_i/p_i^{ss}). \quad (7.14)$$

It is easily seen to be a monotonically decreasing function along solutions of the master equation $p = p(t), t \in [0, \infty)$. The following proof is taken from Schnakenberg [11]; a similar simple proof can be found in Van Kampen [130]:

$$\begin{aligned}
S' &:= \frac{dS}{dt} = \sum_i (Wp)_i \ln(p_i/p_i^{ss}) \\
&= \sum_{i,j} w_{ij} p_j [\ln(p_i p_j^{ss}) - \ln(p_j p_i^{ss})] \\
&\leq \sum_{i,j} w_{ij} p_j [p_i p_j^{ss} / (p_j p_i^{ss}) - 1] \\
&\leq \sum_{i,j} (\bar{w}_{ji} - w_{ji}) p_i \\
&\leq 0,
\end{aligned}$$

where we used concavity of the logarithm and the last equality is due to $\sum_j w_{ji} = \sum_j \bar{w}_{ji}$. Unfortunately, the same procedure cannot be reproduced for the second time derivative.

We prosecute this paragraph with a discussion of the close-to-steady-state regime, showing that monotonicity implies a certain algebraic relationship between eigenvalues and scalar overlaps between eigenvectors. There are two acceptations of vicinity to the steady state: We can either look at the long time limit of a solution of the master equation; Or else we can prepare the

system in a state which is close enough to the steady state. The second acceptation is more general. They are not in principle equivalent, as in the long time limit only one real mode or one couple of complex conjugate modes govern the tendency to the steady state. We will always refer to the second situation unless otherwise specified. Let then

$$p = p^{ss} + \sum_l \varepsilon_l q^l + \sum_\kappa (\varepsilon_\kappa^- q_+^\kappa + \varepsilon_\kappa^+ q_-^\kappa),$$

where $\varepsilon_\kappa^+ = \varepsilon_\kappa^{-*}$, and all ε -terms are comparably small. We define

$$\varepsilon_\kappa^+ = \frac{1}{\sqrt{2}}(\varepsilon_\kappa^1 + i\varepsilon_\kappa^2), \quad \varepsilon_\kappa^- = \frac{1}{\sqrt{2}}(\varepsilon_\kappa^1 - i\varepsilon_\kappa^2),$$

and collect these terms in a unique vector $\boldsymbol{\varepsilon} = (\varepsilon_\alpha)_\alpha$ whose vector's components ε^α are defined in exactly the same manner as \tilde{e}^α was defined in Eq.(7.12). We then obtain

$$\begin{aligned} p &= P^{1/2} \left\{ e^0 + \sum_l \varepsilon_l e^l + \frac{1}{2} \sum_\kappa [(\varepsilon_\kappa^1 - i\varepsilon_\kappa^2)(e_1^\kappa + ie_2^\kappa) + (\varepsilon_\kappa^1 + i\varepsilon_\kappa^2)(e_1^\kappa - ie_2^\kappa)] \right\} \\ &= P^{1/2} \left[e^0 + \sum_l \varepsilon_l e^l + \sum_\kappa (\varepsilon_\kappa^1 e_1^\kappa + \varepsilon_\kappa^2 e_2^\kappa) \right] \\ &= P^{1/2} (e^0 + \boldsymbol{e} \cdot \boldsymbol{\varepsilon}), \end{aligned}$$

where $\boldsymbol{e} \cdot \boldsymbol{\varepsilon} = \sum_\alpha \varepsilon_\alpha \tilde{e}^\alpha$. The first time derivative of p reads

$$Wp = P^{1/2} H \boldsymbol{e} \cdot \boldsymbol{\varepsilon}$$

It's a simple exercise to compute the action of H on the real and imaginary parts of the eigenvectors:

$$H e_1^\kappa = -\frac{1}{\tau_\kappa} e_1^\kappa - \omega_\kappa e_2^\kappa, \quad H e_2^\kappa = -\frac{1}{\tau_\kappa} e_2^\kappa + \omega_\kappa e_1^\kappa.$$

It follows that

$$H \boldsymbol{e} = -(\Upsilon + i\Omega) \boldsymbol{e} = - \begin{pmatrix} \ddots & & & & & \\ & \tau_\kappa^{-1} & \omega_\kappa & & & \\ & -\omega_\kappa & \tau_\kappa^{-1} & & & \\ & & & \ddots & & \\ & & & & \tau_l^{-1} & \\ & & & & & \ddots \end{pmatrix} \begin{pmatrix} \vdots \\ e_1^\kappa \\ e_2^\kappa \\ \vdots \\ e^l \\ \vdots \end{pmatrix}$$

where we introduced

$$\begin{aligned}\Upsilon &= \text{diag}\{\dots, \tau_\kappa^{-1}, \tau_\kappa^{-1}, \dots, \tau_l^{-1} \dots\} \\ \Omega &= \bigotimes_\kappa \begin{pmatrix} 0 & -i\omega_\kappa \\ i\omega_\kappa & 0 \end{pmatrix} \bigotimes \mathbf{0}_{V-2k}.\end{aligned}$$

Properties of these matrices are: Self-adjointness, $\Upsilon^\dagger = \Upsilon$, $\Omega^\dagger = \Omega$; Skew-symmetry of $\Omega = -\Omega^T$; They commute, $[\Upsilon, \Omega] = 0$; The square of Ω is

$$\Omega^2 = \text{diag}\{\dots, \omega_\kappa^2, \omega_\kappa^2, \dots\},$$

which a posteriori motivates the introduction of a factor i in its definition.

We now expand relative entropy (7.14) to second order in ε (repeated indices in the following expression are implicitly summed over):

$$\begin{aligned}S &= \sum_i \left(p_i^{ss} + \varepsilon_\iota q_i^\iota + \varepsilon_\kappa^+ q_{+,i}^\kappa + \varepsilon_\kappa^- q_{-,i}^\kappa \right) \ln \left(1 + \varepsilon_\iota q_i^\iota / p_i^{ss} + \varepsilon_\kappa^+ q_{+,i}^\kappa / p_i^{ss} + \varepsilon_\kappa^- q_{-,i}^\kappa / p_i^{ss} \right) \\ &= \sum_i \left(p_i^{ss} + \varepsilon_\iota q_i^\iota + \varepsilon_\kappa^+ q_{+,i}^\kappa + \varepsilon_\kappa^- q_{-,i}^\kappa \right) \left[\varepsilon_\iota q_i^\iota / p_i^{ss} + \varepsilon_\kappa^+ q_{+,i}^\kappa / p_i^{ss} + \varepsilon_\kappa^- q_{-,i}^\kappa / p_i^{ss} + \right. \\ &\quad \left. - \frac{1}{2} \left(\varepsilon_\iota q_i^\iota / p_i^{ss} + \varepsilon_\kappa^+ q_{+,i}^\kappa / p_i^{ss} + \varepsilon_\kappa^- q_{-,i}^\kappa / p_i^{ss} \right)^2 \right] + \mathcal{O}(\varepsilon^3).\end{aligned}$$

The linear term vanishes while the second order term has to be carefully worked out. We obtain

$$S = \frac{1}{2} \sum_i p_i^2 / p_i^{ss} = \frac{1}{2} (\boldsymbol{\varepsilon}, G \boldsymbol{\varepsilon}) + \mathcal{O}(\varepsilon^3).$$

Finally using the above equations we find that (up to order ε^2)

$$S' = \sum_i p_i (Lp)_i / p_i^{ss} = \boldsymbol{\varepsilon}^T \mathbf{e}^T H \mathbf{e} \cdot \boldsymbol{\varepsilon} = -\boldsymbol{\varepsilon}^T (\Upsilon + i\Omega) G \boldsymbol{\varepsilon}.$$

For sake of clarity, notice that H acts on the internal index i while the matrix $(\Upsilon + i\Omega)$ acts on the eigenvector labels α , for which reason we were able to commute it with \mathbf{e}^T . Symmetrizing, we obtain

$$S' = -\frac{1}{2} \boldsymbol{\varepsilon}^T [(\Upsilon - i\Omega)G + G(\Upsilon + i\Omega)] \boldsymbol{\varepsilon} =: \boldsymbol{\varepsilon}^T S' \boldsymbol{\varepsilon}$$

where the last equality defines S' . We have the following result: The symmetric form defined by the matrix S' is positive, whence

$$\{\Upsilon, G\} - i[\Omega, G] > 0, \tag{7.15}$$

where $\{\cdot, \cdot\}$ and $[\cdot, \cdot]$ are respectively the anticommutator and the commutator of two matrices.

This result follows from the fact that the relative entropy is monotone along a solution of the master equation. Intuitively, since monotonicity holds arbitrarily far from the steady state, in particular it holds for any solution which passes by p at some time t . A complete mathematically satisfactory proof is out of the reach of this work.

Inequality (7.15) is far from obvious, and a direct proof seems to be elusive. For normal systems, we have $\mathbf{G} = \mathbf{1}$ so that it reduces to $\Upsilon > 0$, which is obvious. For non-normal systems this inequality entails a detailed relationship between the length and superpositions of the eigenvectors and the eigenvalues.

7.6 Convexity: an overview

In this paragraph we question whether the second derivative of the relative entropy is strictly positive

$$S'' := \frac{d^2 S}{dt^2} \stackrel{?}{>} 0, \quad (7.16)$$

or in other words whether the relative entropy is convex. This would make for a nice principle of thermodynamics. We know that the entropy production is not a strictly decreasing function of time but for equilibrium systems, for which it reduces to (minus) the time derivative of relative entropy with respect to the steady state, which in turn for equilibrium systems is easily shown to be monotone. Is relative entropy monotone also for nonequilibrium systems, irregardless of the behavior of the entropy production?

Making (7.16) explicit:

$$S'' = S''_{irr} + S''_{rev} = \sum_i (W^2 p)_i \ln(p_i/p_i^{ss}) + \sum_i (W p)_i (W p)_i / p_i^{ss}. \quad (7.17)$$

Here the reversible and the irreversible contributions to the second derivative of the relative entropy are defined. It is evident that

$$S''_{rev} \geq 0. \quad (7.18)$$

For (7.16) to hold it is sufficient (but not necessary) that

$$S''_{irr} \stackrel{?}{>} 0. \quad (7.19)$$

Positivity of the irreversible term has been conjectured by Esposito [?]. Both problems, (C1) convexity of S and (C2) positivity of S''_{irr} , turn out to be difficult, so it is fundamental to circumstantiate them. First, we will consider the situation where we are close enough to the steady state.

We now introduce some basic facts and incidentally prove that conjecture (C1) holds for normal systems and that (C2) holds for normal systems if a condition on the spectrum is satisfied. Introducing the scalar product

$$\langle a, b \rangle := \sum_i \frac{a_i b_i}{p_i^{ss}}, \quad (7.20)$$

the two contributions in the near the steady state can be written as

$$\begin{aligned} S''_{rev} &= \langle Wp, Wp \rangle, \\ S''_{irr} &= \langle \bar{W}p, Wp \rangle + O(\varepsilon^3). \end{aligned}$$

Notice that the first is general and it is just a rewriting of the corresponding term in (7.17). The second only holds near the steady state; its proof is straightforward:

$$\begin{aligned} S''_{irr} &= \sum_{i,j,k} W_{ij} W_{jk} p_k (p_i/p_i^s - 1) + O(\varepsilon^3) \\ &= \sum_j \frac{1}{p_j^s} \left(\sum_i \bar{W}_{ji} p_i \right) \left(\sum_k W_{jk} p_k \right) + O(\varepsilon^3). \end{aligned}$$

In fact, the above proof shows that \bar{W} and W are one the adjoint of the other with respect to the scalar product, so we have

$$\begin{aligned} S''_{rev} &= \langle p, \bar{W}Wp \rangle, \\ S''_{irr} &= \langle W^2 p, p \rangle + O(\varepsilon^3). \end{aligned}$$

Let \bar{S}''_{rev} and \bar{S}''_{irr} be the correspondent time-reversed quantities, calculated by replacing \bar{W} with W . Since the scalar product is symmetric, the irreversible contribution is left unchanged, $S''_{irr} = \bar{S}''_{irr}$, while in general \bar{S}''_{rev} differs from S''_{rev} . Normal systems are exceptional in this respect,

$$\bar{S}''_{rev} = \langle p, \bar{W}Wp \rangle = \langle p, W\bar{W}p \rangle = S''_{rev}.$$

In this case we have (to order ε^2)

$$S'' = \frac{1}{2} (S''_{rev} + \bar{S}''_{rev} + 2S''_{irr}) = \frac{1}{2} \|(W + \bar{W})p\|^2 > 0$$

where the norm is defined by the scalar product $\langle \cdot, \cdot \rangle$. Conjecture (C1) is then proven for normal systems close to the steady state. Notice in particular that for equilibrium systems we have $S''_{rev} = S''_{irr} > 0$ in the so-called linear regime.

We now apply the above formalism of the Fisher matrix to the problem of convexity. It is a straightforward calculation that

$$S'' = \boldsymbol{\varepsilon}^T S'' \boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^T (S''_{rev} + S''_{irr}) \boldsymbol{\varepsilon},$$

where we introduced the symmetric matrices

$$\begin{aligned} S''_{rev} &= (\Upsilon - i\Omega)G(\Upsilon + i\Omega), \\ S''_{irr} &= \frac{1}{2} [(\Upsilon - i\Omega)^2 G + G(\Upsilon + i\Omega)^2]. \end{aligned}$$

For normal systems, $G = \mathbf{1}$, we obtain

$$S''_{rev} = \Upsilon^2 + \Omega^2, \quad S''_{irr} = \Upsilon^2 - \Omega^2, \quad S'' = 2\Upsilon^2.$$

The first and third matrices are obviously positive definite, as they should be. The second is positive if and only if the real part of the eigenvalues is strictly greater in modulus than the imaginary part. We condense these results in the following result: Convexity of the relative entropy near the steady state holds for normal systems. The irreversible contribution to the second derivative of the entropy production is positive for normal systems if and only if the real part of each eigenvalue is bigger in modulus than the imaginary part. Similar results have been advanced by Maes and coworkers [131].

7.7 Finding counterexamples to convexity

The counterexample to both conjectures (C1) and (C2) is given in terms of the following generator

$$W = \frac{1}{4} \begin{pmatrix} -401 & 1 & 1 \\ 400 & -2 & 1 \\ 1 & 1 & -2 \end{pmatrix}, \quad (7.22)$$

with steady state

$$p^{ss} = (3, 801, 402)/1205. \quad (7.23)$$

Notice that the system is strongly unbalanced, as one rate dominates over all others. As a consequence, one state is almost isolated, its occupancy probability falling rapidly to a value near zero. We choose as initial state

$$p = (0.002, 0.464, 0.534), \tag{7.24}$$

We propagate p up to time t via $p(t) = \exp(tW)p$. Relative entropy as a function of time is $s(t) = S(p(t) \| p^{ss}) = \sum_i p_i(t) \ln[p_i(t)/p_i^{ss}]$. A plot of $\ddot{s}(t)$ is given in Fig.7.1, showing a region where the function becomes negative.

The initial state in Eq.(7.24) is not close to p^{ss} in any reasonable acceptance of vicinity, so one might expect that this effect only occurs sufficiently far from the steady state. Instead, we are able to generate counterexamples in which the initial state is chosen arbitrarily close to the steady state. Notice that, since the system has real spectrum, after a transient time relative entropy will recover its convexity, dominated by the largest-modulo eigenvalue. We illustrate in the rest of this section the procedure by which one can generate similar counterexamples.

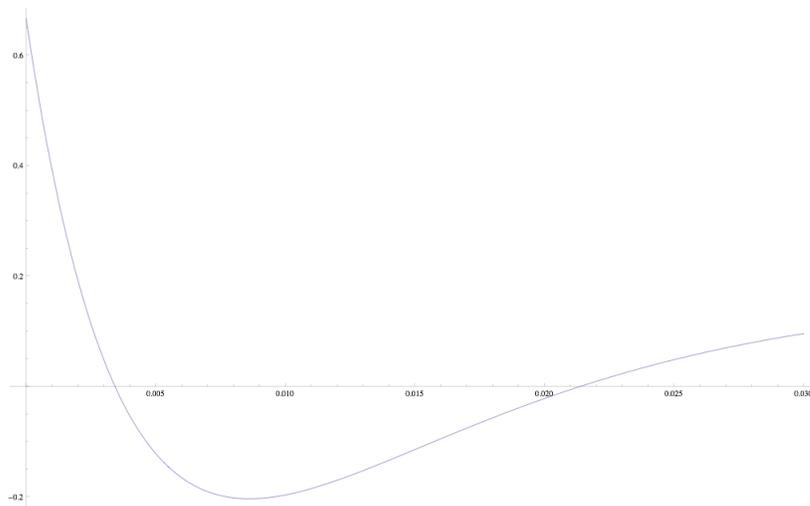


Figure 7.1: A plot of the second time-derivative of the relative entropy as a function of time in the interval $t \in [0, 0.03]$.

The most general generator of a three-state system dynamics is

$$W = \begin{pmatrix} -w_{21} - w_{31} & w_{12} & w_{13} \\ w_{21} & -w_{12} - w_{32} & w_{23} \\ w_{31} & w_{32} & -w_{13} - w_{23} \end{pmatrix}.$$

Its steady state reads

$$p^{ss} = \frac{1}{Z} \begin{pmatrix} w_{12}w_{13} + w_{32}w_{13} + w_{12}w_{23} \\ w_{21}w_{13} + w_{21}w_{23} + w_{31}w_{23} \\ w_{31}w_{12} + w_{21}w_{32} + w_{31}w_{32} \end{pmatrix} = \frac{1}{Z} \begin{pmatrix} Z_1 \\ Z_2 \\ Z_3 \end{pmatrix},$$

where the normalizing factor Z is given below:

$$\begin{aligned} T &= w_{21} + w_{31} + w_{12} + w_{32} + w_{13} + w_{23}, \\ Z &= w_{12}w_{13} + w_{32}w_{13} + w_{12}w_{23} + w_{21}w_{13} + w_{21}w_{23} \\ &\quad + w_{31}w_{23} + w_{31}w_{12} + w_{21}w_{32} + w_{31}w_{32}. \end{aligned}$$

The two non-null eigenvalues of W are given by

$$\lambda_{\pm} = -\frac{1}{2} \left(T \pm \sqrt{T^2 - 4Z} \right),$$

with relative eigenvectors

$$q_{\pm} = \begin{pmatrix} (w_{13} + w_{23} + \lambda_{\pm})(w_{12} + w_{32} + \lambda_{\pm}) - w_{23}w_{32} \\ w_{23}w_{31} + w_{21}(w_{13} + w_{23} + \lambda_{\pm}) \\ w_{32}w_{21} + w_{31}(w_{12} + w_{32} + \lambda_{\pm}) \end{pmatrix}.$$

The system has two real eigenvalues when $T^2 > 4Z$ and it has two complex conjugate eigenvalues when $T^2 < 4Z$. In the $2V$ -dimensional space of parameters $W \ni \{w_{ij} > 0\}$, these two regions are separated by a $(2V-1)$ -dimensional algebraic set \mathcal{D} determined by zeros of a polynomial,

$$\mathcal{D}: \quad T^2 - 4Z = 0.$$

On this hypersurface, the spectrum becomes degenerate and the generator is either defective or it affords a complete set of eigenvectors. Notice that $\lambda_+ \lambda_- = Z$ and $\lambda_+ + \lambda_- = -T$. Moreover, from their explicit form we have that

$$T^2 > 2Z \tag{7.25}$$

from which it follows that when the spectrum is complex, $\lambda_{\pm} = -1/2(T \pm i\sqrt{4Z - T^2})$, the real part of the eigenvalue is always bigger than the imaginary part, which implies that the conditions for conjecture (C2) to hold for normal operators is always satisfied for three-state systems.

In the real domain, the Fisher matrix reads

$$\mathbf{G} = \begin{pmatrix} \|q_+\|^2 & \langle q_+, q_- \rangle \\ \langle q_+, q_- \rangle & \|q_-\|^2 \end{pmatrix}$$

and it is positive by virtue of Schwarz's inequality $\|q_+\|^2\|q_-\|^2 > |\langle q_+, q_- \rangle|^2$. The traces of \mathbf{S}''_{irr} , \mathbf{S}'' and \mathbf{S}' is easily seen to be positive, while their determinant is positive if the following chain of inequalities holds

$$\frac{\|q_+\| \cdot \|q_-\|}{|\langle q_+, q_- \rangle|} > \frac{\lambda_+^2 + \lambda_-^2}{2\lambda_+\lambda_-} > \frac{(\lambda_+ + \lambda_-)^2}{4\lambda_+\lambda_-} > \frac{\lambda_+ + \lambda_-}{2\sqrt{\lambda_+\lambda_-}},$$

which strengthen Schwarz's inequality. According to the above discussion, only the right-hand most is known to hold.

Now suppose that we have a smooth one-parameter family of three-state systems $W(s)$, where $W(0)$ is a normal system (real or complex spectrum), for which conjecture (C2) is known to hold. At $s = 0$ the symmetric matrix \mathbf{S}'' is positive, so that all of its eigenvalues are positive, while at $s = 1$ we approach a degenerate system on \mathcal{D} . As we vary s eigenvalues of \mathbf{S}'' vary smoothly. For \mathbf{S}'' to fail to be positive definite, it is necessary to stumble into a null eigenvalue, i.e. to cross an hypersurface where $\det \mathbf{S}'' = 0$. We then identify another algebraic variety as the set of zeros of the polynomial

$$\mathcal{S}'' : \frac{Z_1 Z_2 Z_3}{Z} [16\lambda_+^2 \lambda_-^2 \|q_+\|^2 \|q_-\|^2 - \langle q_+, q_- \rangle^2 (\lambda_+^2 + \lambda_-^2)^4] = 0.$$

The factor $Z_1 Z_2 Z_3 / Z$ ensures that this is a polynomial. Now it's fairly obvious that $\mathcal{D} \subseteq \mathcal{S}''$. The converse is not true.

To find counterexamples we must then find a non-defective generator for which $\det \mathbf{S}'' = 0$, which is a simple problem that can be solved by computation. Close to such generator is a generator with a negative eigenvalue. Its relative eigenvector identifies the direction where one can pick eigenmodes so to generate a non-concave behavior of the relative entropy. One can pick the eigenmode's entries small at will, thus generating counterexamples where the initial state is arbitrarily close to the steady state.

7.8 A class of NE phase transitions?

We left out from our analysis defective generators, that is, generators that admit degenerate eigenvalues lacking a complete set of corresponding eigenvectors. This case and the phenomenology so far analyzed are better illustrated with the aid of an example. Consider the following generator, parametrized by positive rates ξ, χ

$$W(\xi, \chi) = \begin{pmatrix} -\xi - \chi & 1 & \chi \\ \chi & -1 - \chi & 1 \\ \xi & \chi & -1 - \chi \end{pmatrix}. \quad (7.26)$$

The dynamics generated by $W(\xi, \chi)$ is that of a hopping particle with a systematic bias in the counterclockwise direction, and one perturbed clockwise rate (see Fig.7.2a). Its phase space is depicted in Fig.7.2b. By Kolmogorov's criterion, transition rates satisfy detailed balance if and only if the only macroscopic affinity vanishes, $\ln \xi/\chi^3 = 0$, which traces the equilibrium line ℓ_{eq} . The model corresponding to $\chi = 1 = \xi$ is known as the unbiased hopping particle, with twice degenerate eigenvalue $\lambda = 2$ affording a complete basis of eigenvectors. The space of parameters is partitioned into two phases with real spectrum (A, in grey in Fig.7.2a) and with a couple of complex conjugate eigenvalues (B1, in white), marked out by the critical lines $\ell_1 : \chi + 3\xi = 4$ and $\ell_2 : \xi = \chi$. For the first class of models, direct calculation of the eigenvectors shows that G is diagonal only along the equilibrium line. In phase B1 one needs to turn to the complex components of the eigenmodes to be able to expand relative entropy as a positive bilinear form. Along ℓ^* are the biased hopping particle models $W(1, \chi)$, which make the complexified matrix diagonal. Their reversal is found by inverting the bias in the clockwise direction, yielding $\bar{W} = W^T$.

With the exception of $W(1, 1)$, a generator W picked along the critical lines only has one eigenvector q relative to the degenerate eigenvalue $-\tau^{-1}$. A generalized eigenvector u shall then be introduced, with

$$Wu = -\tau^{-1}u + q,$$

carrying W into Jordan's normal form. The time evolved $\exp(tW)p$ is seen to acquire a term $\propto te^{-t/\tau}q$ [132].

Consider now a path $\Gamma = \{\xi(s), \chi(s)\}$ in parameter space, as depicted in Fig.7.2b. We first traverse the complex phase. At $s = 1$ we come upon

an abrupt switch in the appropriate basis. Approaching the critical line ℓ_1 from below, the imaginary part $\text{Im} q_+(s)$ becomes smaller and smaller until it vanishes; from above, the modes $q_+(s)$ and $q_-(s)$, respectively with higher and lower eigenvalue, tend to align. At the critical line the Fisher matrix becomes degenerate and has a discontinuity

$$G^\uparrow = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \rightarrow G^\downarrow = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}. \quad (7.27)$$

An order parameter $f_s(\infty)$ —of little physical meaning though— can also be engineered. Consider two vectors $q_\pm^\perp(s)$ and u^\perp , respectively in the orthogonal complement of $q_-(s)$ and u . Projecting $\exp[tL(s)]p - p^{ss}$ along the two, and then taking the ratio, yields

$$f_{2>s>1}(t) \propto [1 + ce^{-t(\tau_-^{-1} - \tau_+^{-1})}]^{-1}, \quad (7.28a)$$

$$f_1(t) \propto 1/(1 + c't), \quad (7.28b)$$

where c and c' are some constants. The exponential decay, which reaches an arbitrary nonzero value of $f_s(\infty)$, becomes a power-law at the critical line, with $f_s(\infty) = 0$. Thence we took the liberty to refer to a class of nonequilibrium phase transitions, with an acceptance that is reminiscent of that employed for simple driven lattice models [133, Sec. 1.1]. This is also motivated by the equilibrium usage of the Fisher matrix, which coincides

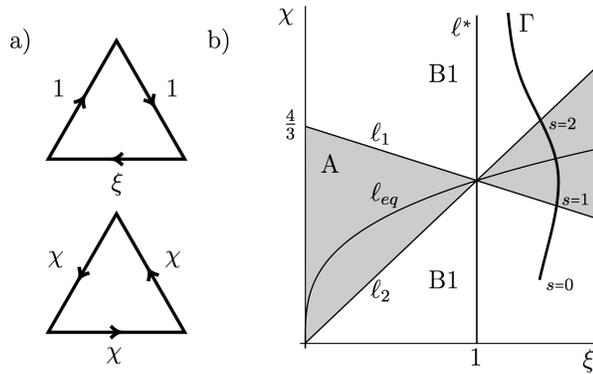


Figure 7.2: a) Transition rates for the hopping biased particle with one clockwise perturbed rate. b) The parameter space of $L(x, y)$: phases, critical and trivial lines, a path Γ .

with the covariance matrix of the observable constraints X^α that define the equilibrium ensemble

$$p \propto \exp - \sum_{\alpha} \beta_{\alpha} X^{\alpha}. \quad (7.29)$$

Crooks [134] commented that, as we vary the intensive parameters β_{α} , correlations vary smoothly except at phase transitions, where divergencies occur. On this line, further insight might come from estimation theory. Consider an unbiased estimator $\hat{\epsilon}^i = (\epsilon_{\alpha}^i)_{\alpha}$, whose average

$$\langle \hat{\epsilon} \rangle_p = \sum_i \epsilon^i p_i = \epsilon$$

yields precisely the vector of parameters $\epsilon = (\epsilon_{\alpha})_{\alpha}$ that describes state p ,

$$p = p^{ss} + \sum_{\alpha} \epsilon_{\alpha} q^{\alpha}.$$

The Crámer-Rao inequality [135], establishes a lower bound on the covariance matrix

$$\langle (\hat{\epsilon} - \epsilon)(\hat{\epsilon} - \epsilon) \rangle_p \geq G^{-1},$$

where $A \geq B$ means that $A - B$ is positive semidefinite. Multiplying by G and taking the trace we obtain

$$\langle \|\hat{\epsilon} - \epsilon\|_{G(s)}^2 \rangle_p \geq n, \quad s \neq 1, 2. \quad (7.30)$$

A degenerate metric admits non-null vectors of null norm. Hence in the limit $s \rightarrow 1$ there might exist unbiased estimators whose correlations diverge, since degeneracy of the bilinear form must be compensated by a divergence in order to verify Eq.(7.30).

7.9 Information-geometric interpretation

In this section we interpret some of the results of this chapter in the light of information theory and geometry. We establish a connection between thermodynamical aspects of nonequilibrium systems, encoded in their decay modes, and geometrical properties of the Fisher-Rao measure of distance between probability distributions.

As was already known to Kullback [136, Sec. 2.6] and thoroughly discussed by Baez in his blog [137], relative entropy is at the core of the definition of Fisher's matrix $g^{\alpha\beta}$ [138], which was reinterpreted by Rao as a metric g on the manifold of statistical states [139]. Already a standard tool in information theory and statistics [135], the Fisher-Rao metric was rediscovered in equilibrium statistical mechanics [140–142], and more recently it is drawing attention in NESM [134, 143] and in quantum information theory [144–146]. Singularities of $g^{\alpha\beta}$ have been shown to signal the insurgence of quantum phase transitions [147].

Indeed, a rich nonequilibrium phenomenology is marked by the peculiar representation of relative entropy near the invariant state, which can be interpreted as a metric on the manifold of statistical states \mathcal{P} . Let us hint at its construction. With an information-theoretical attitude, one would like to employ relative entropy as a tool to compare probability distributions. However, relative entropy is not a good distance: it is not symmetrical, and the triangle inequality can be violated [137], as one can split a path between two far-apart points into short segments whose relative entropies add up to a number smaller than $S(p'|p)$. The way out of this puzzle is to stick to nearby distributions, thus obtaining a local metric that measures the length of vectors $\varepsilon_\alpha q^\alpha$ living on the tangent space to \mathcal{P} at p . When moving to a different neighbourhood, one will shift the reference probability distribution to p' , and there define the metric in terms of $S(\cdot|p')$. If this procedure is carried on point-wise, one endows \mathcal{P} with the Fisher-Rao metric. One can then assign coordinates x^α to neighbourhoods of the manifold; associated to such coordinates is a basis of preferred tangent vectors $\partial/\partial x^\alpha$, which yield a matrix representative for the metric at each point of the neighbourhood. Notice that the Fisher-Rao metric is smoothly defined all over the manifold (except at boundaries and corners); it is its coordinatisation that might suffer from pathologies, as is the case for our critical systems.

But for $n = 1$, it can be shown that g has a non-null Riemann curvature: while one can always choose a coordinate patch that trivialises the

metric at one given point, there is no such coordinate transformation which simultaneously makes g diagonal all over a neighbourhood. Given the twice-contravariant transformation law for the metric, $g^{\alpha'\beta'} = \Lambda_{\alpha}^{\alpha'} \Lambda_{\beta}^{\beta'} g^{\alpha\beta}$, where $\Lambda_{\alpha}^{\alpha'}(x') = \partial x_{\alpha} / \partial x'_{\alpha'}$, is the inverse jacobian of the coordinate transformation $x \rightarrow x'(x)$, one realises that the components of e_i^{α} can be interpreted as the jacobian of an embedding patch, also called a frame, which trivialises the metric at p . The choice of a markovian generator L identifies a point on the manifold of statistical states and a set of decay modes. We first map the probability simplex into the surface of a sphere, then interpret the pushed-forward vectors' entries e_i^a as the jacobian of a second coordinate transformation, in such a way that an equilibrium generator corresponds to the choice of a coordinate patch which trivializes the Fisher-Rao metric at the invariant state. Given an invariant state, there exists a whole $O(n+1)$ -orbit of frame fields which trivialize the metric. Vice versa, two equilibrium generators with the same invariant state yield gauge-equivalent frames.

Hence, orthonormal frames are associated to p -normal systems; vice versa, two such systems with the same invariant state yield different orthonormal frames, which are connected by an $O(n+1)$ “gauge” transformation. This very mechanism lies at the heart of the Equivalence Principle of General Relativity. While gravity curves spacetime so as to prevent the definition of broad notions of “parallelism” and “simultaneity”, one can always find coordinates that make spacetime minkowskian at one point, and gravity indiscernible from a fictitious force. To a special observer, the frames' entries provide an inertial frame of coordinate axis: in a very precise way they measure how much the orientation of these axis differs, up to Lorentz gauge transformations, from “bent” coordinate axis. This discrepancy *is* the gravitational field [127, pp. 59-60].

In this chapter we established a close connection between the Fisher-Rao metric and markovian generators. The choice of a generator induces a natural identification of a positive semi-definite matrix representation, nested in the late-time behavior of relative entropy. A trivialized metric emerges for generators that commute with their time-reversal, including equilibrium systems. Then, using a motto, we might claim that equilibrium systems are to nonequilibrium thermodynamics what inertial frames are to gravity. Seeming nonequilibrium phase transitions are induced by degenerate coordinatizations. This study calls for a careful treatment of the algebraic varieties of critical and trivial loci in the space of generators, and for a thermody-

namical characterization of the order parameters. Normal systems seem to enjoy special properties, and deserve more in-depth study, in particular in relation to the fluctuations and large deviations of their microscopic jump trajectories. Finally, the neat framework suggests to deepen the nonequilibrium characterization of geometric objects such as Christoffel coefficients, geodesic curves, intrinsic and extrinsic curvature.

We conclude this section with some more precise and formal note on the Fisher-Rao metric. The two matrices H and $-W$ are both representations of an operator \mathbf{H} with eigenvectors

$$\mathbf{e}^a = q_i^a \frac{\partial}{\partial p_i} = e_i^a \frac{\partial}{\partial z_i}. \quad (7.31)$$

The peculiar notation employed for the basis vectors denotes that \sqrt{P} might be seen as the inverse jacobian of the coordinate transformation $p_j \mapsto z_j(p) = 2\sqrt{p_j}$, which maps the probability simplex $\{p_i \in [0, 1]^{n+1} : \sum_j p_j = 1\}$ into a portion of the hypersphere with square radius $\sum_i z_i^2 = 4$. Both are embeddings of the abstract manifold \mathcal{P} of probability distributions into \mathbb{R}^{n+1} . Each such coordinatization (say, x) of “positions” on \mathcal{P} endows the $(n+1)$ -dimensional vector space $V \cong \mathbb{R}^{n+1}$ of “velocities”, attached to p , with a preferred basis of directions $\partial/\partial x_i$. Vectors \mathbf{e}^α span the n -dimensional tangent space $T_p\mathcal{P} \subset V$, while \mathbf{e}^0 describes how a neighbourhood of p sits in the embedding space.

A metric at p is a positive semidefinite bilinear form $h_p[\mathbf{v}, \mathbf{w}]$, with vectors $\mathbf{v}, \mathbf{w} \in V$ attached to p . A choice of coordinates endows the dual space V^* with a basis of linear forms dx_a , such that $dx_a[\partial/\partial x_b] = \delta_a^b$. Vectors’ components are then obtained by projecting $v_a = dx_a[\mathbf{v}]$, while the metric in coordinates reads $h_p = h^{ab}(x)dx_a \otimes dx_b$. Again, the notation “ dx_a ” highlights the transformation properties of linear forms: if $x \mapsto x'(x)$ is a diffeomorphism, the metric’s entries transform twice contravariantly

$$h^{a'b'} = \frac{\partial x_a}{\partial x'_{a'}} \frac{\partial x_b}{\partial x'_{b'}} h^{ab}. \quad (7.32)$$

A metric is fully characterized by its action on a complete set of vectors. In our case, we define h_p via

$$h_p[\mathbf{e}^a, \mathbf{e}^b] := \delta^{ij} e_i^a e_j^b =: \delta^{ij} \mathbf{e}_i \otimes \mathbf{e}_j \left[\frac{\partial}{\partial x_a}, \frac{\partial}{\partial x_b} \right] \quad (7.33)$$

where the right-hand side helps introducing the frame forms $\mathbf{e}_i = e_i^a dx_a$ [72]. Given a metric, frames are determined up to $O(n+1)$ -rotations $\mathbf{e}_i \mapsto R_i^j \mathbf{e}_j$,

which leave the metric's coefficients unaltered. When such rotations are performed point-by-point all over a neighborhood of the manifold, in a differentiable way, one talks of a gauge transformation.

Comparison of Eq.(7.33) with Eq.(7.32) reveals that e_i^a is the inverse jacobian of a coordinate transformation $z \mapsto x(z)$ which pulls back the metric's components to the unit matrix. For example, choosing "spherical" coordinates $x_a = \delta_a^i z_i$, one obtains the euclidean length element $h_p = (dz)^{\otimes 2}$. The intrinsic metric at p , g_p , is defined as the restriction of h_p over the hypersurface \mathcal{P} , acting on the tangent space $T_p\mathcal{P}$. By construction \mathbf{e}^0 is orthogonal to all other \mathbf{e}^α 's. Finally, the Fisher-Rao metric on the manifold is simply the disjoint collection of local intrinsic metrics, $g = \bigsqcup_{p \in \mathcal{P}} g_p$.

Bibliography

- [1] F. W. Nietzsche, from the notebooks of the early 1870's, in P. Poellner, *Nietzsche and Metaphysics* (Oxford University Press, 2000).
- [2] M. Polettini, *Macroscopic constraints for the minimum entropy production principle*, Phys. Rev. E **84**, 051117 (2011).
- [3] M. Polettini, *Nonequilibrium thermodynamics as a gauge theory*, arXiv:1110.0608 (2001).
- [4] M. Polettini, *System/environment duality of nonequilibrium network observables*, arXiv:1106.1280 (2011).
- [5] M. Polettini, *Equivalence Principle and Critical Behaviour for Nonequilibrium Decay Modes*, arXiv:1105.4134 (2011).
- [6] G. Gallavotti and E. G. D. Cohen, *Dynamical ensembles in nonequilibrium statistical mechanics*, Phys. Rev. Lett. **74**, 2694 (1995).
- [7] G. E. Crooks, *Nonequilibrium measurements of free energy differences for microscopically reversible markovian systems*, J. Stat. Phys. **90**, 1481 (1998); *Entropy production fluctuation theorem and the nonequilibrium work relation for free energy differences*, Phys. Rev. E **60**, 2721 (1999).
- [8] D. J. Evans and D. J. Searles, *Equilibrium microstates which generate second law violating steady states*, Phys. Rev. E **50**, 1645 (1994).
- [9] C. Jarzynski, *Nonequilibrium equality for free energy differences*, Phys. Rev. Lett. **78**, 2690 (1997).

- [10] G. N. Bochkov and Y. E. Kuzovlev, *Nonlinear fluctuation-dissipation relations and stochastic models in nonequilibrium thermodynamics: I. Generalized fluctuation-dissipation theorem*, Physica A **106**, 443 (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 (1981).
- [11] J. Schnakenberg, *Network Theory of Microscopic and Macroscopic Behavior of Master Equation Systems*, Rev. Mod. Phys. **48**, 571 (1976).
- [12] J. Schnakenberg, *Thermodynamic Network Analysis of Biological Systems*, (Springer, Berlin, 1977).
- [13] G. R. Kirchhoff, *Ueber die Auflösung der Gleichungen, auf welche man bei der Untersuchung der linearen Vertheilung galvanischer Ströme geführt wird*, Poggendorffs Ann. Phys. Chem. **72**, 497 (1847).
- [14] A. Shapere and F. Wilczek (eds.), *Geometric Phases in Physics*, (World Scientific, 1989).
- [15] T. L. Hill, *Free Energy Transduction and Biochemical Cycle Kinetics*, (Dover, New York, 2005).
- [16] D. Andrieux and P. Gaspard, *Fluctuation theorem and Onsager reciprocity relations*, J. Chem. Phys. **121**, 6167 (2004).
- [17] D. Andrieux and P. Gaspard, *Fluctuation theorem and mesoscopic chemical clocks*, J. Chem. Phys. **128**, 154506 (2008).
- [18] S. Liepelt and R. Lipowsky, *Steady-state balance conditions for molecular motor cycles and stochastic nonequilibrium processes*, Europhys. Lett. **77**, 50002 (2007); *Kinesins network of chemomechanical motor cycles*, Phys. Rev. Lett. **98** 258102 (2007).
- [19] A. Faggionato and D. Di Pietro, *Gallavotti-Cohen-type symmetry related to cycle decompositions for Markov chains and biochemical applications*, J. Stat. Phys **143**, 11 (2011).
- [20] D. Andrieux and P. Gaspard, *Fluctuation theorem for transport in mesoscopic systems*, J. Stat. Mech.: Theory Exp., P01011 (2006).

- [21] D. Andrieux and P. Gaspard, *Fluctuation theorem for currents and Schnakenberg network theory*, J. Stat. Phys **127**, 107 (2007).
- [22] H. Qian and M. Qian, *Pumped biochemical reactions, nonequilibrium circulation, and stochastic resonance*, Phys. Rev. Lett. **84**, 2271 (2000).
- [23] H. Qian, *Cycle kinetics, steady state thermodynamics and motors – a paradigm for living matter physics*, J. Phys.: Cond. Matt. **17**, S3783 (2005).
- [24] D.-J. Jiang, M. Qian, M.-P. Qian, *Mathematical theory of nonequilibrium steady states*, (Springer, Berlin, 2004).
- [25] S. Kalpazidou, *Cycle representations of Markov processes*, (Springer, New York, 1995).
- [26] R. K. P. Zia and B. Schmittmann, *A possible classification of nonequilibrium steady states*, J. Phys. A: Math. Gen. **39**, L407 (2006).
- [27] I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, (John Wiley and Sons, New York, 1955).
- [28] T. Gowers, *My favourite pedagogical principle: examples first!*, available online at <http://gowers.wordpress.com/> (2007).
- [29] L. Onsager, *Reciprocal relations in irreversible processes. I*, Phys. Rev. **37**, 405 (1931); *Reciprocal relations in irreversible processes. II*, Phys. Rev. **38**, 2265 (1931).
- [30] A. N. Kolmogorov, *On the theory of Markov chains*, Mathematische Annalen **112**, 155 (1936).
- [31] N. Biggs, *Algebraic Graph Theory*, (Cambridge University Press, Cambridge, 1974).
- [32] T. S. K. V. Iyer, *Circuit Theory*, (Tata Mac Graw-Hill, New Dehli, 2006).
- [33] N. Nakanishi, *Graph Theory and Feynman Integrals*, (Gordon and Breach, New York, 1971).

- [34] C. D. Godsil and G. Royle, *Algebraic Graph Theory*, (Springer-Verlag, New York, 2001).
- [35] P. J. Giblin, *Graphs, Surfaces, and Homology: an Introduction to Algebraic Topology*, (Chapman and Hall, London, 1981).
- [36] M. Desbrun, A. N. Hirani, M. Leok and J. E. Marsden, *Discrete exterior calculus*, arXiv:math/0508341 (2005).
- [37] M. Desbrun, E. Kanso and Y. Tong, in *Discrete Differential Geometry*, A. I. Bobenko, J. M. Sullivan, P. Schroder and G. M. Ziegler, Eds., vol. 38 of Oberwolfach Seminars, (Birkhauser, Basel, 2008), p. 287.
- [38] A. Perez, *Determining the genus of a graph*, available online at <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.107.560&rep=rep1&type=pdf>.
- [39] M. Conder, E. Robertson and P. Williams, *Presentations for 3-dimensional special linear groups over integer rings*, Proceedings of the American Math. Soc. **115**, 19 (1992).
- [40] B. Mohar, *The laplacian spectrum of graphs*, in: Y. Alavi, G. Chartrand, O. Oellermann, A. Schwenk (Eds.), *Graph Theory, Combinatorics, and Applications*, (Wiley, New York, 1991), p. 871.
- [41] A. D. Sokal, *The multivariate Tutte polynomial (alias Potts model) for graphs and matroids*, in *Surveys in combinatorics 2005*, 173226, London Math. Soc. Lecture Note Ser., 327 (Cambridge Univ. Press, 2005).
- [42] J. Bjorken and S. Drell, *Relativistic Quantum Fields* (McGraw-Hill, New York, 1965).
- [43] M. Marcolli, *Feynman Motives*, (World Scientific, Singapore, 2010).
- [44] F. David and R. H. Tuan, *A duality property of planar Feynman diagrams*, Phys. Lett. B **158**, 435 (1985).
- [45] F. Y. Wu, *The Potts model*, Rev. Mod. Phys. **54**, 235 (1982).
- [46] M. Esposito and C. van den Broeck, *The three faces of the second law: I. Master equation systems*, Phys. Rev. E **82**, 011143 (2010).

- [47] J. M. R. Parrondo and P. Español, *Criticism of Feynman's analysis of the ratchet as an engine*, Am. J. Phys. **64**, 1125 (1996).
- [48] H. Hinrichsen, C. Gogolin and P. Janotta, *Non-equilibrium dynamics, thermalization and entropy production*, J. Phys.: Conf. Ser. **297**, 012011 (2011).
- [49] T. A. McKee, *The logic of graph-theoretic duality*, Am. Math. Mon. **92**, 457 (1985).
- [50] O. Shai and G. R. Pennock, *Extension of graph theory to the duality between static systems and mechanisms*, J. Mech. Des. **128**(1), 179 (2006); *A study of the duality between planar kinematics and statics*, J. Mech. Des. **128**(3), 587 (2006).
- [51] C. Timm, *Gauge theory for the rate equations: Electrodynamics on a network*, Phys. Rev. Lett. **98**, 070604 (2007).
- [52] K. H. Knuth, *Lattice duality: the origin of probability and entropy*, Neurocomputing **67**, 245 (2005).
- [53] J. Brunnemann and D. Rideout, *Oriented matroids – combinatorial structures underlying loop quantum gravity*, Classical and Quantum Gravity **27**, 205008 (2010).
- [54] M. Klein and P. H. E. Meijer, *Principle of minimum entropy production*, Phys. Rev. **96**, 250 (1954).
- [55] E. T. Jaynes, *Information theory and statistical mechanics. I.*, Phys. Rev. **106**, 620 (1957).
- [56] E. T. Jaynes, *Information theory and statistical mechanics. II*, Phys. Rev. **108**, 171 (1957).
- [57] H. B. Callen, *Principle of minimum entropy production*, Phys. Rev. **105**, 360 (1957).
- [58] I. Gyarmati, *Non-equilibrium Thermodynamics*, (Springer-Verlag, Berlin, 1970).

- [59] L. M. Martyushev, A. S. Nazarova and V. D. Seleznev, *On the problem of the minimum entropy production in the nonequilibrium stationary state*, J. Phys. A **40**, 371 (2007).
- [60] B. Poznaniak, M. Kotłowska and I. Danielewicz-Ferchmin, *Heat conduction and near-equilibrium linear regime*, Rev. Mex. Fís **49** (5), 477 (2003); I. Danielewicz-Ferchmin and A. R. Ferchmin, *A check of Prigogine's theorem of minimum entropy production in a rod in a nonequilibrium stationary state*, Am. J. Phys. **68** (10), 962 (2000); P. Palfy-Muhoray, *Comment on "A check of Prigogines theorem ..."*, Am. J. Phys. **69** (7), 825 (2001); W. G. Hoover, *Note on "Comment on ..."*, Am. J. Phys. **70** (4), 452 (2002).
- [61] I. Prigogine and S. Lafleur, *Sur la mécanique statistique des mélanges, I*, Bull. Acad. Roy. Belg. Cl. Sci. **40**, 481 (1954).
- [62] D. Ruelle, *Smooth Dynamics and New Theoretical Ideas in Nonequilibrium Statistical Mechanics*, Jour. Stat. Phys. **95**, 394 (1999).
- [63] R. Kalaba and R. Xu, *On the generalized inverse form of the equations of constrained motion*, Amer. Math. Monthly **102**, 821 (1995).
- [64] C. Lawson and R. Hanson, *Solving Least Squares Problems* (Prentice-Hall, Englewood Cliffs, New Jersey, 1974).
- [65] E. T. Jaynes, *On the rationale of maximum-entropy methods*, Proc. IEEE **70**, 939 (1982).
- [66] L. M. Martyushev and V. D. Seleznev, *Maximum entropy production principle in physics, chemistry and biology*, Phys. Rep. **426**, 1 (2006); H. Struchtrup and W. Weiss, *Maximum of the local entropy production becomes minimal in stationary processes*, Phys. Rev. Lett. **80**, 5048 (1998); S. Bruers, C. Maes and K. Netočný, *On the validity of entropy production principles for linear electrical circuits*, J. Stat. Phys. **129**, 725 (2007); S. Bruers, *A discussion on maximum entropy production and information theory*, J. Phys. A: Math. Theor. **40**, 7441 (2007).
- [67] E. T. Jaynes, *The minimum entropy production principle*, Ann. Rev. Phys. Chem. **31**, 579 (1980).

- [68] P. Županović, D. Kuić, Ž. Bonačić Lošić, D. Petrov, D. Juretić and M. Brumen, *The maximum entropy production principle and linear irreversible processes*, Entropy **12**, 996 (2010).
- [69] J. G. Kemeny, J. L. Snell, A. W. Knapp, *Denumerable Markov Chains*, (Springer Verlag, New York, 1976).
- [70] J. R. Norris, *Markov Chains*, (Cambridge University Press, Cambridge, 1997).
- [71] J. L. Lebowitz and H. Spohn, *A Gallavotti-Cohen-Type Symmetry in the Large Deviation Functional for Stochastic Dynamics*, J. Stat. Phys. **95**, 333 (1999).
- [72] J. Baez and J. P. Munian, *Gauge Fields, Knots and Gravity* (World Scientific, Singapore, 1994).
- [73] G. M. Schütz, *Exactly solvable models for many-body systems far from equilibrium*, in C. Domb and J. Lebowitz, Eds., *Phase Transitions and Critical Phenomena* Vol. 19 (Academic Press London, London, 2001).
- [74] R. J. Harris and G. M. Schütz, *Fluctuation theorems for stochastic dynamics*, J. Stat. Mech. (2007) P07020.
- [75] S. Mazzucchi, *Mathematical Feynman Path Integrals and Their Applications*, (World Scientific, Singapore, 2009).
- [76] C. Maes, K. Netočný and B. Wynants, *On and beyond entropy production: the case of Markov jump processes*, Markov Processes Relat. Fields **14** (2008).
- [77] T. M. Cover and J. A. Thomas, *Elements of Information Theory* (John Wiley and Sons 1991).
- [78] M. Esposito and C. Van den Broeck, *Three Detailed Fluctuation Theorems*, Phys. Rev. Lett. **104**, 090601 (2010).
- [79] S.-F. Shieh, *Eigenvalue estimates using the Kolmogorov-Sinai entropy*, Entropy **13**, 2036 (2011).
- [80] J. Lebowitz, *Boltzmann's entropy and time's arrow*, Physics Today, 32 (september 1993).

- [81] K. Sekimoto, *Langevin equation and thermodynamics*, Prog. Theor. Phys. Supplement **130**, 17 (1998).
- [82] U. Seifert, *Stochastic thermodynamics: principles and perspectives*, Eur. Phys. J. B **64**, 423 (2008).
- [83] V. Y. Chernyak, M. Chertkov and C. Jarzynski, *Path-integral analysis of fluctuation theorems for general Langevin processes*, J. Stat. Mech., P08001 (2006).
- [84] U. Seifert, *Efficiency of Autonomous Soft Nanomachines at Maximum Power*, Phys. Rev. Lett. **106**, 020601 (2011).
- [85] H. P. Breuer and F. Petruccione, *The Theory of Open Quantum Systems* (Oxford University Press, Oxford, 2002).
- [86] M. Esposito and S. Mukamel, *Fluctuation theorems for quantum master equations*, Phys. Rev. E **73**, 046129 (2006).
- [87] M. Esposito, U. Harbola and S. Mukamel, *Nonequilibrium fluctuations, fluctuation theorems and counting statistics in quantum systems*, Rev. Mod. Phys. **81**, 1665 (2009).
- [88] M. Esposito, K. Lindenberg and C. Van den Broeck, *Entropy production as correlation between system and reservoir*, New J. Phys. **12**, 013013 (2010).
- [89] A. Kossakowski, A. Frigerio, V. Gorini and M. Verri, *Quantum detailed balance and KMS condition*, Commun. Math. Phys. **57**, 97 (1977).
- [90] A. K. Rajagopal, *The principle of detailed balance and the Lindblad dissipative quantum dynamics*, Phys. Lett. A **246**, 237(1998).
- [91] F. Fagnola and V. Umanità, *Detailed balance, time reversal and generators of quantum Markov semigroups*, Mathematical Notes (Mat. Zametki) **84**, 108 (2008).
- [92] R. Chetrite and K. Mallick, *Quantum fluctuation relations for the Lindblad master equation*, arXiv:1112.1303 (2011).

- [93] T L. Hill, *Studies in irreversible thermodynamics. III. Models for steady state and active transport across membranes*, J. Theor. Biol. **10**, 442 (1996).
- [94] B. Gaveau and L. S. Schulman, *Master equation based formulation of nonequilibrium statistical mechanics*, (1996).
- [95] R. A. Horn, *Matrix Analysis* (Cambridge University Press, Cambridge, 1985).
- [96] S. Chaiken, *A combinatorial proof of the all minors matrix tree theorem*, J. Alg. Disc. Meth. **3**, 319 (1982).
- [97] B. Gaveau and L. S. Schulman, *Theory of nonequilibrium first-order phase transitions for stochastic dynamics*, (1997).
- [98] R. K. P. Zia and B. Schmittmann, *Probability currents as principal characteristics in the statistical mechanics of nonequilibrium steady states*, P07012 (2007).
- [99] P. F. Arndt, *Yang-Lee theory for a nonequilibrium phase transition*, Phys. Rev. Lett. **84**, 814-817 (2000).
- [100] R. A. Blythe and M. R. Evans, *Lee-Yang zeros and phase transitions in nonequilibrium steady states*, Phys. Rev. Lett. **89**, 080601 (2002).
- [101] R. A. Blythe and M. R. Evans, *The Lee-Yang theory of equilibrium and nonequilibrium phase transitions*, Braz. J. Phys **33**, 464 (2003).
- [102] F. Martinelli, *Lectures on Glauber dynamics for discrete spin models*, in *Lectures on probability theory and statistics* (Saint-Flour, 1997), volume 1717 of Lecture Notes in Math., pages 93 - 191. (Springer, Berlin, 1999).
- [103] K. J. Laidler, *The Development of the Arrhenius Equation*, J. Chem. Educ. **61**, 494 (1984).
- [104] A. Vulpiani, *The role of chaos for the foundation of statistical mechanics*, abstract available at <http://www.fis.unipr.it/stat/PARMA2011/welcome2011.htm>.
- [105] Bricmont, *Science of chaos or chaos in science?*, Physicalia Magazine **17** (1995).

- [106] A. Ben-Naim, *A Farewell to Entropy: Statistical Thermodynamics Based on Information*, (World Scientific, Singapore, 2008).
- [107] V. Hnizdo and M. Gilson, *Thermodynamic and differential entropy under a change of variables*, Entropy **12**, 578 (2010).
- [108] T. Tao, *What is a gauge?*, blog entry, available at <http://terrytao.wordpress.com/> (2008).
- [109] A. Caticha, *Maximum Entropy, Fluctuations and Priors*, in *Maximum Entropy and Bayesian Methods in Science and Engineering*, ed. by A. Mohammad-Djafari, A.I.P. Vol. 568, 94 (2001), arXiv.org/abs/math-ph/0008017.
- [110] H. Suyari, *Generalization of Shannon-Khinchin axioms to nonextensive systems and the uniqueness theorem for the nonextensive entropy*, IEEE Trans. Inf. Theory **50**, 1783 (2004).
- [111] C. E. Shannon and W. Weaver, *A mathematical theory of communication*, (Univ. of Illinois Press, Urbana, 1949).
- [112] H. White, *The entropy of a continuous distribution*, Bull. Math. Biophys. **27**, 135 (1965).
- [113] E. P. Northrop, *Riddles in Mathematics*, (D. Van Nostrand Company, New York, 1944).
- [114] J. Banavar J. and A. Maritan, *The maximum relative entropy principle*, arXiv:cond-mat/0703622 (2007).
- [115] S. Janson, *The numbers of spanning trees, Hamilton cycles and perfect matchings in a random graph*, Comb. Probab. Comput. **3**, 97 (1994).
- [116] B. Bollobás, *Random Graphs*, (Cambridge University Press, Cambridge, 2001).
- [117] R. Graham, *Path integral formulation of general diffusion processes*, Z. Physik B **26**, 281 (1977); *Covariant formulation of non-equilibrium statistical thermodynamics*, Z. Physik B **26**, 397 (1977).

- [118] H. Feng and J. Wang, *Potential and flux decomposition for dynamical systems and non-equilibrium thermodynamics: curvature, gauge field and generalized fluctuation-dissipation theorem*, J. Chem. Phys. **135**, 234511 (2011).
- [119] T. Sagawa and H. Hayakawa, *Geometrical Clausius equality for steady states thermodynamics*, Phys. Rev. E **84**, 051110 (2011).
- [120] S. Abe and S. Kaneko, *Geometric effect and gauge field in nonequilibrium quantum thermostatistics*, Phys. Lett. A **357**, 284 (2006); S. Abe, *Geometric effect in nonequilibrium quantum thermodynamics*, Physica A **372**, 387 (2006); S. Abe, *Gauge fields and geometric control of quantum-thermodynamic engine*, J. Stat. Mech., P09011 (2011).
- [121] H. Qian, *Vector field formalism and analysis for a class of thermal ratchets*, Phys. Rev. Lett. **81**, 3063 (1998).
- [122] R. Giles, *Reconstruction of gauge potentials from Wilson loops*, Phys. Rev. D **24**, 2160 (1981).
- [123] N. A. Sinitsyn and I. Nemenman I., *Universal geometric theory of mesoscopic stochastic pumps and reversible ratchets*, Phys. Rev. Lett. **99**, 220408, (2007); *The Berry phase and the pump flux in stochastic chemical kinetics*, Eur. Phys. Lett. **77**, 58001 (2007).
- [124] J. Ohkubo, *The stochastic pump current and the non-adiabatic geometrical phase*, J. Stat. Mech., P02011 (2008).
- [125] N. A. Sinitsyn, *The stochastic pump effect and geometric phases in dissipative and stochastic systems*, J. Phys. A: Math. Theor. **42**, 193001 (2009).
- [126] S. Weinstein, *Gravity and gauge theory*, Philosophy of Science **66**, 146 (1999).
- [127] C. Rovelli, *Quantum Gravity*, (Cambridge University Press, Cambridge, 2004).
- [128] F. W. Hehl, J. D. McCrea, E. W. Mielke and Y. Ne'Eman, *Metric-affine gauge theory of gravity: field equations, Noether identities, world spinors, and breaking of dilation invariance*, Phys. Rep. **258**, 1 (1995);

- F. Gronwald and F. W. Hehl, *On the gauge aspects of gravity*, arXiv:gr-qc/9602013 (1996).
- [129] G. E. Crooks, *Path-ensemble averages in systems driven far from equilibrium*, Phys. Rev. E **61**, 2361 (2000).
- [130] N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North Holland, Amsterdam, 1997).
- [131] C. Maes, K. Netočný and B. Wynants, *Monotonic Return to Steady Nonequilibrium*, Phys. Rev. Lett. **107**, 010601 (2011); *Monotonicity of the dynamical activity*, arXiv:1102.2690 (2011).
- [132] D. Andrieux, *Spectral signature of nonequilibrium conditions*, arXiv:1103.2243 (2011).
- [133] J. Marro and R. Dickman, *Nonequilibrium Phase Transitions in Lattice Models*, (Cambridge University Press, Cambridge, 1999).
- [134] G. E. Crooks, *Measuring thermodynamic length*, Phys. Rev. Lett. **99**, 100602 (2007).
- [135] *Algebraic and Geometric Methods in Statistics*, edited by P. Gibilisco et al., (Cambridge Univ. Press, Cambridge, 2010), Sec. 1.4; Sec. 1.5; Ch. 14.
- [136] S. Kullback, *Information Theory and Statistics*, (Wiley, New York, 1959).
- [137] J. C. Baez, *Information geometry (Part 1-7)*, available online at <http://johncarlosbaez.wordpress.com/> (2011).
- [138] R. A. Fisher, *Theory of statistical estimation*, Proc. Cambridge Phil. Soc. **22**, 700 (1925).
- [139] C. R. Rao, *Information and accuracy attainable in the estimation of statistical parameters*, Bull. Calcutta Math. Soc. **37**, 81 (1945).
- [140] F. Weinhold, *Metric geometry of equilibrium thermodynamics*, J. Chem. Phys. **63**, 2479 (1975).

- [141] B. Andresen, R. S. Berry, E. Ihrig and P. Salamon, *Inducing Weinhold's metric from Euclidean and Riemannian metrics*, Phys. Rev. A **37**, 845 (1988).
- [142] R. Mrugała, J. D. Nulton, J. C. Schön and P. Salamon, *Statistical approach to the geometric structure of thermodynamics*, Phys. Rev. A **41**, 3156 (1990).
- [143] E. H. Feng and G. E. Crooks, *Far-from-equilibrium measurements of thermodynamic length*, Phys. Rev. E **79**, 012104 (2009).
- [144] D. C. Brody and L. P. Hughston, *Statistical geometry in quantum mechanics*, Proc. R. Soc. London A **454**, 2445 (1998).
- [145] A. S. Holevo, *Probabilistic and Statistical Aspects of Quantum Theory* (North-Holland,1982).
- [146] D. Petz and C. Sudár, *Extending the Fisher metric to density matrices*, in *Geometry in Present Days Sciences*, edited by O. E. Barndorff-Nielsen, and E. B. Vendel Jensen, 2134 (World Scientific 1999).
- [147] P. Zanardi, P. Giorda and M. Cozzini, *Information-theoretic differential geometry of quantum phase transitions*, Phys. Rev. Lett. **99**, 100603 (2007).