Chapter 4

The master equation

The master equation is another particular case of the Chapman-Kolmogorov equation for a *discrete, homogeneous, Markovian* process that we denote by $n(t)$. In contrast, the Brownian motion was considered as a continuous process.

For instance, $n(t)$ can represent the number of particles at time t (photons, radioactive nuclei, molecules in a chemical reaction), the number of people in a queue or infected by a disease, etc.

In a general manner, the system contains a set of states Σ that are distinguished by an appropriate indexing (eigenstates of a quantum system, particles or spins configurations on a lattice, etc.). Throughout the rest of the document, n will denote the states indices and $n(t)$ the corresponding process.

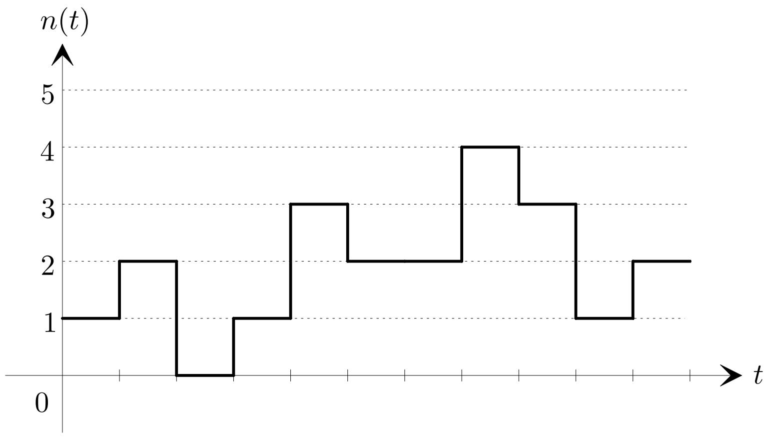

Figure 4.1: Representation of a discrete process $n(t)$. Note that we do not exclude increments larger than 1, that is $|n(t_i) - n(t_{i-1})|$ may be bigger than 1 $\forall i$.

4.1 Derivation of the master equation

We consider a homogeneous Markov process on a set of states Σ labeled by n. Our aim is to derive a differential equation, called the *master equation* that gives the transition probability $P(n_1|n_2, t)$ of the process with $P(n_1|n_2, t = 0) = \delta_{n_1,n_2}$. The basic assumption is the existence of a *transition rate* $\mathcal{W}(n_1|n_2)$ from n_1 to n_2, $n_1 \neq n_2$, defined as

$$\mathcal{W}(n_1|n_2) = \lim_{t\to 0} \frac{P(n_1|n_2,t)}{t} = \frac{\partial}{\partial t} P(n_1|n_2,t)\Big|_{t=0}. \tag{4.1}$$

This rate gives the probability per unit of time to have a transition from state n_1 into n_2. Thus, when $n_1 \neq n_2$ and $t \to 0$,

$$P(n_1|n_2,t) = \mathcal{W}(n_1,n_2)\,t + o(t). \tag{4.2}$$

To derive the master equation, we first note that

$$P(n_1|n_2,\Delta t) = \left\{ \begin{array}{l} \text{probability to stay in} \\ n_1 \text{ during } \Delta t \text{ if } n_1 = n_2 \end{array} \right\} \tag{4.3}$$

and

$$P(n_1|n_2,\Delta t) = \left\{ \begin{array}{l} \text{probability to reach } n_2 \text{ during} \\ \Delta t \text{ starting from } n_1 \text{ if } n_1 \neq n_2 \end{array} \right\} \tag{4.4}$$

Now,

$$\begin{aligned} \left\{ \begin{array}{l} \text{probability to stay in} \\ n_1 \text{ during } \Delta t \text{ if } n_1 = n_2 \end{array} \right\} &= \left\{ 1 - \begin{array}{l} \text{probability to leave} \\ n_1 \text{ during } \Delta t \end{array} \right\}_{n_1=n_2} \\ &= \Big(1 - \sum_{\substack{n_2\in\Sigma \\ n_1\neq n_2}} \mathcal{W}(n_1|n_2)\Delta t\Big)\delta_{n_1,n_2}, \end{aligned} \tag{4.5}$$

and [1]

$$\left\{ \begin{array}{l} \text{probability to reach } n_2 \text{ during} \\ \Delta t \text{ starting from } n_1 \text{ if } n_1 \neq n_2 \end{array} \right\} = \mathcal{W}(n_1|n_2)\,\Delta t\,(1-\delta_{n_1,n_2}). \tag{4.6}$$

By introducing the probability $a(n_1)$ per unit of time to leave n_1 ,

$$a(n_1) = \sum_{\substack{n_2\in\Sigma \\ n_1\neq n_2}} \mathcal{W}(n_1|n_2), \tag{4.7}$$

it follows from (4.5) and (4.6) that

$$P(n_1|n_2,\Delta t) = (1 - a(n_1)\Delta t)\delta_{n_1,n_2} + (1-\delta_{n_1,n_2})\mathcal{W}(n_1|n_2)\Delta t. \tag{4.8}$$

As the process is Markovian, the Chapman-Kolmogorov equation in the discrete case reads

$$\begin{aligned} P(n_1|n_3,t+\Delta t) &= \sum_{n_2\in\Sigma} P(n_1|n_2,t) \underbrace{P(n_2,t|n_3,t+\Delta t)}_{=P(n_2|n_3+\Delta t)} \\ &\overset{(4.8)}{=} \sum_{n_2\in\Sigma} P(n_1|n_2,t)\big((1-a(n_2)\Delta t)\delta_{n_2,n_3} + (1-\delta_{n_2,n_3})\mathcal{W}(n_2|n_3)\Delta t\big) \\ &= P(n_1|n_3,t) - P(n_1|n_3,t)a(n_3)\Delta t + \sum_{\substack{n_2\in\Sigma \\ n_2\neq n_3}} P(n_1|n_2,t)\mathcal{W}(n_2|n_3)\Delta t \\ &\overset{(4.7)}{=} P(n_1|n_3,t) - P(n_1|n_3,t)\sum_{\substack{n_2\in\Sigma \\ n_2\neq n_3}} \mathcal{W}(n_3|n_2)\Delta t + \sum_{\substack{n_2\in\Sigma \\ n_2\neq n_3}} P(n_1|n_2,t)\mathcal{W}(n_2|n_3)\Delta t. \end{aligned}$$

[1] From now on we will omit the term $o(\Delta t)$.

By rearranging the terms and taking the limit $\Delta t \to 0$, this leads to

$$\underbrace{\lim_{\Delta t \to 0} \frac{P(n_1|n_3, t+\Delta t) - P(n_1|n_3, t)}{\Delta t}}_{=\frac{\partial}{\partial t}P(n_1|n_3,t)} = \sum_{\substack{n_2 \in \Sigma \\ n_2 \neq n_3}} \left(P(n_1|n_2, t)\mathcal{W}(n_2|n_3) - P(n_1|n_3, t)\mathcal{W}(n_3|n_2)\right). \tag{4.9}$$

We see that the term $n_2 = n_3$ of the sum (4.9) is zero, hence we can remove the restriction $n_2 \neq n_3$.[2] If the initial conditions are randomly distributed with $P_0(n_0)$, then by linearity $P(n,t) = \sum_{n_0 \in \Sigma} P_0(n_0)P(n_0|n,t)$, where $P(n, t = 0) = P_0(n)$, still satisfies (4.9).

From now on, we will omit to write the initial condition, thus the master equation reads

$$\boxed{\frac{\partial}{\partial t}P(n,t) = \sum_{n' \in \Sigma} \left(P(n',t)\mathcal{W}(n'|n) - P(n,t)\mathcal{W}(n|n')\right),} \tag{4.10}$$

with

$$P(n, t = 0) = P_0(n). \tag{4.11}$$

The physical meaning of the master equation (4.10) is clear: it is a gain-loss equation for the probability of the state n. The first term is the gain due to transitions from other states n' whereas the second one is the loss due to transitions into other states n'.

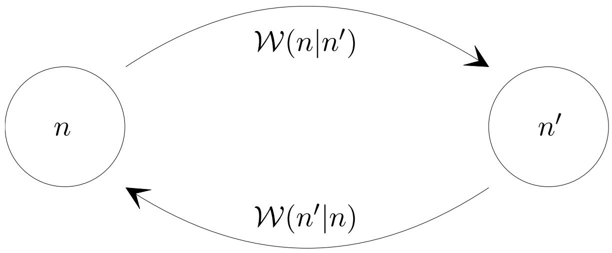

Figure 4.2: Interpretation of the mater equation. The transition rate $\mathcal{W}(n|n')$ yields a lost $-P(n,t)\sum_{n' \in \Sigma} \mathcal{W}(n|n')$ for the state n, whereas $\mathcal{W}(n|n')$ yields a gain $\sum_{n' \in \Sigma} P(n',t)\mathcal{W}(n'|n)$.

If the process is *stationary*, then there exists a distribution $P^s(n)$ such that for all time t

$$\sum_{n' \in \Sigma} \left(P^s(n')\mathcal{W}(n'|n) - P^s(n)\mathcal{W}(n|n')\right) = 0. \tag{4.12}$$

The research and the study of the properties of the steady state are a key element of the theory that we will address in section 4.3.

4.1.1 Birth-death process

Let us assume that the states of Σ can be classified in a linear order. Then, we can consider the two neighbour states $n+1$ and $n-1$ of n. The existence of this order is obvious if $n \in \mathbb{N}$ represents a number of particles. A birth-death process is a process where the transitions occur only between neighbour states within an infinitesimal time. Mathematically, this means that

$$\mathcal{W}(n|n') = 0, \qquad n' \neq n \pm 1. \tag{4.13}$$

[2]Therefore we can assign an arbitrary value to $\mathcal{W}(n|n)$.

For instance, if n describes a population, this condition means that when $\Delta t \to 0$ the probability that n increases or decreases by more than one indivudual is negligible.

From now on, we will write $\mathcal{W}(n|n+1) = g_n$, $\mathcal{W}(n|n-1) = r_n$ and $P(n,t) = P_n(t)$. The master equation then reads

$$\boxed{\frac{\partial}{\partial t} P_n(t) = g_{n-1} P_{n-1}(t) + r_{n+1} P_{n+1}(t) - (g_n + r_n) P_n(t).} \tag{4.14}$$

The first two terms of the right-hand side represent a gain for the state n, whereas the third term is a loss.

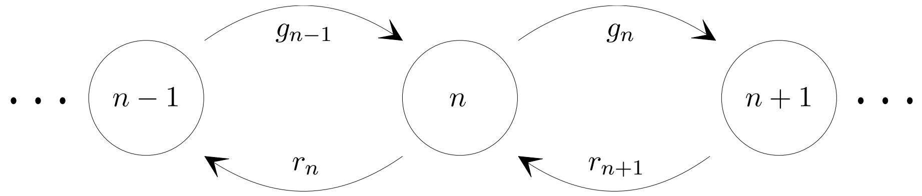

Figure 4.3: The transition between two states of a birth-death process occurs only between nearest neighbours because of the restriction $\mathcal{W}(n|n') = 0 \; \forall n' \neq n \pm 1$. We denote the gain and loss (the increment and decrement) of one unit by g_n and r_n, respectively.

4.2 Applications

We will assume that the following examples can all be treated as birth-death processes.

Example 1 (Poisson process) Suppose that some events occur independently over time with the same probability and consider the number $n(t) \in \mathbb{N} = \{0, 1, 2, \ldots\}$ of events that occured until time t. For instance, $n(t)$ is the length of a queue. Besides, we assume that $n(t)$ cannot increase by more than one increment per unit of time. Thus, it is a pure-birth process, characterized by

$$\left\{ \begin{array}{lcl} g_n &=& \alpha, \\ r_n &=& 0. \end{array} \right. \tag{4.15}$$

The master equation reduces to

$$\frac{\partial}{\partial t} P_n(t) = \alpha (P_{n-1}(t) - P_n(t)). \tag{4.16}$$

We can easily verify that

$$P_n(t) = \frac{(\alpha t)^n}{n!} \mathrm{e}^{-\alpha t} \tag{4.17}$$

is the solution of (4.16) with $P_n(t=0) = \delta_{n,0}$. (4.17) is the *Poisson distribution.* It is the particular case $\beta = 0$ of the assymetric random walk. ◇

Example 2 (Continuous-time asymmetric random walk) Let $n(t)$ be the position of a particle on a lattice $\mathbb{Z}$ and let $g_n = \alpha$ et $r_n = \beta \; \forall n$ be the uniform probabilities to jump right and left, respectively. Then, the master equation for the continuous-time random walk is given by

$$\frac{\partial}{\partial t} P_n(t) = \alpha P_{n-1}(t) + \beta P_{n+1}(t) - (\alpha + \beta) P_n(t). \tag{4.18}$$

This master equation can be solved by the method of the generating function [3]

$$G(z,t) = \sum_{n \in \mathbb{Z}} z^n P_n(t). \tag{4.19}$$

Consequently, $P_n(t)$ is given by the z^n coefficient of the Laurent series of $G(z,t)$. The corresponding equation for the generating function $G(z,t)$ is given by

$$\begin{aligned} \frac{\partial}{\partial t} G(z,t) &= \sum_{n \in \mathbb{Z}} z^n \frac{\partial}{\partial t} P_n(t) \\ &\overset{(4.18)}{=} \alpha \sum_{n \in \mathbb{Z}} \underbrace{z^n P_{n-1}(t)}_{= z z^{n-1} P_{n-1}(t)} + \beta \sum_{n \in \mathbb{Z}} \underbrace{z^n P_{n+1}(t)}_{= \frac{1}{z} z^{n+1} P_{n+1}(t)} - (\alpha + \beta) \underbrace{\sum_{n \in \mathbb{Z}} z^n P_n(t)}_{= G(z,t)} \\ &= \left(\alpha z + \frac{\beta}{z} - \alpha - \beta \right) G(z,t). \end{aligned} \tag{4.20}$$

To solve this equation, we have to fix an initial condition. If the particle is in n_1 at $t = 0$, the transition probability $P(n_1|n,t)$ of the process satisfies $P(n_1|n,t=0) = \delta_{n_1,n}$, which corresponds to

$$G(z,t=0) = \sum_{n \in \mathbb{Z}} z^n \delta_{n,n_1} = z^{n_1}. \tag{4.21}$$

In conclusion, the corresponding generating function is

$$G(z,t) = z^{n_1} \mathrm{e}^{\left(\alpha z + \frac{\beta}{z} - \alpha - \beta \right) t}. \tag{4.22}$$

Fully asymmetric case ($\beta = 0$) By expanding the generating function (4.22) in Laurent series, we find

$$P(0|n,t) = \mathrm{e}^{-\alpha t} \frac{(\alpha t)^n}{n!} = W(n,t), \tag{4.23}$$

$$P(n_1|n_2,t) = \begin{cases} \mathrm{e}^{-\alpha t} \frac{(\alpha t)^{n_2 - n_1}}{(n_2 - n_1)!}, & n_2 \geq n_1, \\ 0, & n_2 < n_1. \end{cases} \tag{4.24}$$

It is easy to verify that $W(n,t)$ and $P(n_1|n_2,t)$ define a homogeneous Markov process which corresponds to the Poisson process.

[3] Do not confuse the moment-generating function of definition 2.7 on page 25 with (4.19). They are two different definitions, however their power series provide both interesting quantities.

Fully symmetric case ($\alpha = \beta = 1$) Assuming the particle to be initially in the origin, it follows from (4.22) that

$$G(z,t) = \mathrm{e}^{-2t}\mathrm{e}^{\left(z+\frac{1}{z}\right)t}. \tag{4.25}$$

Now, $\mathrm{e}^{(z+1/z)\,t/2}$ is the generating function of the modified Bessel functions $I_n(t)$:

$$\mathrm{e}^{(z+1/z)\,t/2} = \sum_{n=-\infty}^{\infty} z^n I_n(t). \tag{4.26}$$

Therefore,

$$P(0|n,t) = \mathrm{e}^{-2t}\, I_n(2t), \tag{4.27}$$

and we have $P(0|n,t) = P(0|-n,t)$, as a consequence of the symmetry $G(z,t) = G(1/z,t)$. The series expansion of $I_n(t)$ is given by (using (4.26))

$$I_n(t) = \sum_{k=0}^{\infty} \frac{\left(\frac{t}{2}\right)^{2k+n}}{k!(k+n)!}, \qquad n \geq 0, \tag{4.28}$$

hence

$$P(0|n,t) \asymp \frac{t^n}{n!}, \qquad t \to 0. \tag{4.29}$$

It follows from the behaviour $I_n(t) \asymp \frac{\mathrm{e}^t}{\sqrt{2\pi t}}$, $t \to \infty$ that

$$P(0|n,t) \asymp \frac{1}{\sqrt{4\pi t}}, \qquad t \to \infty. \tag{4.30}$$

The probability of occupation of a point n tends to 0 as $t \to \infty$: the particle escapes to infinity. ◇

Example 3 (Radioactive decay) Let $n(t)$ be the population of radioactive nuclei, $n \in \mathbb{N}$. In this model we only have losses, thus $g_n = 0$. If the nuclei disintegrate independently with a decay rate γ, then $r_n = \gamma n$. The master equation of the process is given by

$$\frac{\partial}{\partial t} P_n(t) = \gamma(n+1)P_{n+1}(t) - \gamma n P_n(t). \tag{4.31}$$

This equation can also be solved by the method of the generating function (4.19), by writing down a differential equation for $G(z,t)$ with an appropriate initial condition for $P_n(0)$. The generating function $G(z,t)$ satisfies

$$\begin{aligned} \frac{\partial}{\partial t} G(z,t) &= \gamma \left(\sum_{n=0}^{\infty} (n+1) z^n P_{n+1}(t) - \sum_{n=0}^{\infty} n z^n P_n(t) \right) \\ &= \gamma(1-z)\frac{\partial}{\partial z} G(z,t). \end{aligned} \tag{4.32}$$

The general solution of (4.32) is a linear combination

$$G(z,t) = \sum_{n=0}^{\infty} a_n \left((z-1)\mathrm{e}^{-\gamma t} \right)^n. \tag{4.33}$$

The particular solution corresponding to $P_n(t=0) = \delta_{n,n_0}$, that is $G(z, t=0) = z^{n_0}$, reads

$$\begin{aligned} G_{n_0}(z,t) &= \left((z-1)\mathrm{e}^{-\gamma t} + 1\right)^{n_0} \\ &= \left(z\mathrm{e}^{-\gamma t} + \left(1 - \mathrm{e}^{-\gamma t}\right)\right)^{n_0} \\ &= \sum_{n=0}^{n_0} \binom{n_0}{n} z^n \mathrm{e}^{-\gamma t n} \left(1 - \mathrm{e}^{-\gamma t}\right)^{n_0 - n} . \end{aligned} \tag{4.34}$$

Therefore, the probability to find n nuclei at time t with an initial population equal to n_0 is given by

$$P(n_0|n,t) = \binom{n_0}{n} \mathrm{e}^{-\gamma t n} \left(1 - \mathrm{e}^{-\gamma t}\right)^{n_0 - n}, \qquad n \leq n_0, \tag{4.35}$$

◇

Example 4 (photons-matter equilibrium) Let $n(t)$ be the number of photons inside a cavity at time t, $n(t) \in \mathbb{N}$. Suppose that the photons are monochromatic and that they interact with atoms having two energy levels E_1 and E_2. The energy conservation implies $E_1 - E_2 = \hbar\omega$, where ω is the photon frequency. The gains and losses of the process are due to photons emission and absorption.

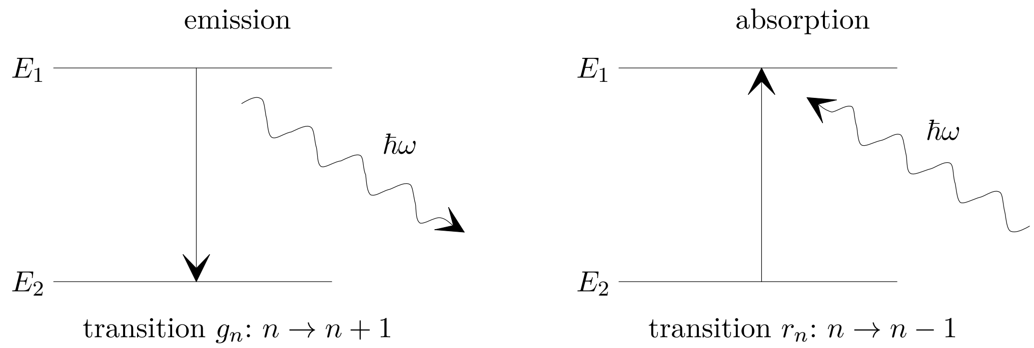

Figure 4.4: A photon emission corresponds to a gain $n \to n+1$, whereas a photon absorption is a loss $n \to n-1$.

The *gain term* is

$$g_n = \lambda n + \lambda = \lambda(n+1), \tag{4.36}$$

where λn describes the stimulated emission and λ the spontaneous emission.

The *loss term* is

$$r_n = \mu n, \tag{4.37}$$

which describes atomic absorption. We further assume that atoms emit and absorb photons independently from each other, thus

$$\lambda = \gamma N_{E_1}, \qquad \mu = \gamma N_{E_2}, \tag{4.38}$$

where N_{E_1} and N_{E_2} are the populations of levels E_1 and E_2, and γ is the probability of emission or absorption per unit of time. These rates are deduced from quantum mechanics and one can show that they are equal. Therefore, the master equation reads

$$\frac{\partial}{\partial t} P_n(t) = \lambda n P_{n-1}(t) + \mu(n+1) P_{n+1}(t) - ((\mu+\lambda)n + \lambda) P_n(t). \tag{4.39}$$

In reality, we should take into account the fact that the atomic populations N_{E_1} and N_{E_2} are also random quantities over time. In this example we neglect their fluctuations ΔN_{E_i}, so N_{E_i} represent their average at a given time. Moreover, if we are only interested in the stationary solution P_n^s, the populations are constant, as well as λ and μ. Thus,

$$P_n^s = C \left(\frac{\lambda}{\mu}\right)^n, \tag{4.40}$$

where $C \in \mathbb{R}$ is a normalization constant. Indeed, by inserting (4.40) in the master equation (4.39) we have

$$\begin{aligned} \lambda n \left(\frac{\lambda}{\mu}\right)^{n-1} + \mu(n+1)\left(\frac{\lambda}{\mu}\right)^{n+1} - ((\mu+\lambda)n+\lambda)\left(\frac{\lambda}{\mu}\right)^n \\ = n\frac{\lambda^n}{\mu^{n-1}} + (n+1)\frac{\lambda^{n+1}}{\mu^n} - (n+1)\frac{\lambda^{n+1}}{\mu^n} - n\frac{\lambda^n}{\mu^{n-1}} \\ = 0. \end{aligned} \tag{4.41}$$

Let us assume that this stationary solution corresponds to the thermal equilibrium of atoms and photons. Then it follows from the Boltzmann statistics that

$$\frac{\lambda}{\mu} \overset{(4.38)}{=} \frac{N_{E_1}}{N_{E_2}} = \mathrm{e}^{-\beta(E_1 - E_2)} = \mathrm{e}^{-\beta\hbar\omega}. \tag{4.42}$$

Thus,

$$P_n^s = C\mathrm{e}^{-\beta\hbar\omega n}. \tag{4.43}$$

The condition $\sum_{n=0}^{\infty} P_n^s = 1$ fixes the normalization constant to

$$C = 1 - \mathrm{e}^{-\beta\hbar\omega}, \tag{4.44}$$

and therefore

$$P_n^s = \left(1 - \mathrm{e}^{-\beta\hbar\omega}\right)\mathrm{e}^{-\beta\hbar\omega n}. \tag{4.45}$$

The average number of photons $\langle n \rangle_s$ in the steady state is given by

$$\begin{aligned} \langle n \rangle_s &= \sum_{n=0}^{\infty} n P_n^s \\ &= \left(1 - \mathrm{e}^{-\beta\hbar\omega}\right) \frac{\partial}{\partial(-\beta\hbar\omega)} \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega n} \\ &= \frac{1}{\mathrm{e}^{\beta\hbar\omega} - 1}, \end{aligned} \tag{4.46}$$

which corresponds to the thermal distribution of a quantum harmonic oscillator (Bose-Einstein statistics). The purely quantum effect of spontaneous emission λ in (4.36) is absolutely necessary to recover the Bose-Einstein statistics, as Einstein had already noted. ◇

Example 5 (Chemical reaction) Consider the chemical reaction $A \underset{\gamma'}{\overset{\gamma}{\rightleftarrows}} B$ with rates γ and γ'. The process that we are interested in is the number of particles B, $n(t) = n_B(t) \in \mathbb{N}$. We assume that the number of particles $n_A(t)$ of the species A is constant, $n_A(t) = n_A$ (this can be realized by a flow of particles that compensates the variation due to the reaction $A \rightleftarrows B$). Therefore, the gain and loss rates of B molecules are given by $g_n = \gamma n_A$ and $r_n = \gamma' n$, respectively. The master equation reads

$$\frac{\partial}{\partial t} P_n(t) = \gamma\, n_A P_{n-1}(t) + \gamma'(n+1)P_{n+1}(t) - (\gamma\, n_A + \gamma' n)P_n(t). \tag{4.47}$$

The stationary regime is given by the Poisson distribution,

$$P_n^s = \frac{\lambda^n}{n!}\mathrm{e}^{-\lambda}, \qquad \lambda = \frac{\gamma}{\gamma'} n_A. \tag{4.48}$$

Indeed, inserting (4.48) in (4.47) yields

$$\gamma\, n_A \frac{\lambda^{n-1}}{(n-1)!}\mathrm{e}^{-\lambda} + \gamma'(n+1)\frac{\lambda^{n+1}}{(n+1)!}\mathrm{e}^{-\lambda} - (\gamma\, n_A + \gamma' n)\frac{\lambda^n}{n!}\mathrm{e}^{-\lambda} = 0, \tag{4.49}$$

that is,

$$\frac{\lambda^n}{n!}\mathrm{e}^{-\lambda}(\lambda\gamma' - \gamma\, n_A) + \frac{\lambda^{n-1}}{(n-1)!}\mathrm{e}^{-\lambda}(\gamma\, n_A - \lambda\gamma') = 0. \tag{4.50}$$

This relation implies $\lambda = \frac{\gamma}{\gamma'} n_A$, which is the average number of B particles. This is an intuitive result: the production of B molecules increases with the ration γ/γ'. ◇

Example 6 (Malthus-Verhulst logistic equation) Consider a population of n individuals $n = 0, 1, 2, \ldots$ occupying a territory Ω. Each of them has a probability α to die and β to reproduce per unit of time. Moreover, because of the competition, each individual has a further probability $\gamma(n-1)$ to die that is proportional to the population size. The loss and gain terms r_n and g_n are then given by

$$r_n = \alpha n + \gamma n(n-1), \tag{4.51}$$
$$g_n = \beta n. \tag{4.52}$$

Therefore, the master equation of the system reads

$$\frac{\partial}{\partial t} P_n(t) = \beta(n-1)P_{n-1}(t) + (\alpha(n+1) + \gamma n(n+1))\, P_{n+1}(t) - ((\beta+\alpha)n + \gamma n(n-1))\, P_n(t). \tag{4.53}$$

This equation is difficult to solve because of the non-linearity of r_n. However, in the limit of an extensive territory Ω, we can study the asymptotic behaviour of (4.53).

Our aim is to derive a differential equation for the population density and its fluctuations, starting from (4.53). If $\langle n(t)\rangle$ is the average population at time t in the territory Ω, then the density is defined by

$$\rho(t) = \lim_{\Omega\to\infty} \frac{\langle n(t)\rangle}{\Omega} \tag{4.54}$$

We assume that the population fluctuations around its mean value $\rho(t)\Omega$ is of order $\sqrt{\Omega}$,

$$\sqrt{\langle (n(t) - \rho(t)\Omega)^2\rangle} = \mathcal{O}\left(\sqrt{\Omega}\right), \tag{4.55}$$

by analogy with thermal fluctuations. Note that in this case, the process $\frac{n(t)}{\Omega}$ has no fluctuations in the limit $\Omega \to \infty$:

$$\left\langle \left(\frac{n(t)}{\Omega}\right)^2 \right\rangle - \rho^2(t) = \frac{\left\langle (n(t) - \rho(t)\Omega)^2 \right\rangle}{\Omega^2} = \mathcal{O}\left(\frac{1}{\Omega}\right) \overset{\Omega\to\infty}{=} 0. \tag{4.56}$$

Let us now study the evolution of the average population. Substituting $n \to n-1$ and $n \to n+1$ in the sums, we find from equation (4.53)

$$\frac{\partial}{\partial t} \langle n(t) \rangle = \sum_{n=0}^{\infty} n \frac{\partial}{\partial t} P_n(t) = (\beta - \alpha) \langle n(t) \rangle - \gamma \left\langle (n(t))^2 \right\rangle. \tag{4.57}$$

If we want a well-defined asymptotic behaviour, it is necessary to assume that the competition rate γ is of order Ω^{-1}. Thus, we write $\gamma = \frac{\mathcal{X}}{\Omega}, \mathcal{X} > 0$. Dividing equation (4.57) by Ω and taking (4.56) into account, we find in the limit $\Omega \to \infty$

$$\frac{\partial}{\partial t} \rho(t) = (\beta - \alpha)\rho(t) - \mathcal{X}\rho^2(t), \tag{4.58}$$

which is a deterministic differential equation for the density.

Let us assume that the birth rate is higher than the death rate, $\beta > \alpha$. Besides the trivial point $\rho = 0$, the equation (4.58) has the stationary point

$$\rho_s = \frac{\beta - \alpha}{\mathcal{X}} > 0 \tag{4.59}$$

that represents the population equilibrium density in the presence of a competition rate $\mathcal{X}$. By linearizing (4.58) around this equilibrium point, $\rho(t) = \rho_s + X(t)$, we have

$$\frac{\mathrm{d}}{\mathrm{d}t} X(t) = -(\beta - \alpha) X(t), \tag{4.60}$$

hence $X(t) = \mathrm{e}^{-(\beta-\alpha)t} X(0)$, i.e. the equilibrium is reached exponentially fast.

Note that if $\mathcal{X} = 0$ $(\beta > \alpha)$, the solution of (4.58) is given by $\rho(t) = \mathrm{e}^{(\beta-\alpha)t}\rho(0)$, i.e. the population grows exponentially without competition (Malthus law). If the death rate is higher than the birth rate, $\beta < \alpha$, the only stationary point of (4.58) is $\rho = 0$ and the population extinguishes.

Looking at (4.54) and (4.55), it is natural to write

$$n(t) = \Omega\rho(t) + \sqrt{\Omega}\, \xi(t), \tag{4.61}$$

where $\xi(t)$ is the first-order fluctuations process. The fluctuations distribution $\Pi(\xi, t)$ is defined by

$$\Pi(\xi, t) = P_n(t) = P_{\Omega\rho(t)+\sqrt{\Omega}\,\xi}(t). \tag{4.62}$$

Note that with the change of variables (4.61) we have

$$\begin{aligned} \frac{\partial}{\partial t} \Pi(\xi, t) &= \Omega \frac{\mathrm{d}}{\mathrm{d}t}\rho(t) \frac{\partial}{\partial n} P_n(t) + \frac{\partial}{\partial t} P_n(t) \\ &= \sqrt{\Omega} \frac{\mathrm{d}}{\mathrm{d}t}\rho(t) \frac{\partial}{\partial \xi} \Pi(\xi, t) + \frac{\partial}{\partial t} P_n(t). \end{aligned} \tag{4.63}$$

By inserting (4.61), (4.62) and (4.63) in (4.53), we can write the equation that rules the evolution of the fluctuations distribution $\Pi(\xi, t)$. It follows from (4.63) that

$$P_{n\pm 1}(t) = P_{\Omega\rho(t)+\sqrt{\Omega}\left(\xi\pm\frac{1}{\sqrt{\Omega}}\right)}(t) = \Pi\left(\xi \pm \frac{1}{\sqrt{\Omega}}, t\right). \tag{4.64}$$

Thus, for a fixed $\mathcal{X}$, equation (4.53) becomes

$$\begin{aligned}\frac{\partial}{\partial t}\Pi(\xi,t) - \sqrt{\Omega}\frac{\mathrm{d}}{\mathrm{d}t}\rho(t)\frac{\partial}{\partial\xi}\Pi(\xi,t) &= \beta\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi-1\right)\Pi\left(\xi-\frac{1}{\sqrt{\Omega}},t\right)\\ &+\left[\alpha\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi+1\right)+\frac{\mathcal{X}}{\Omega}\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi\right)\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi+1\right)\right]\Pi\left(\xi+\frac{1}{\sqrt{\Omega}},t\right)\\ &-\left[(\beta+\alpha)\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi\right)+\frac{\mathcal{X}}{\Omega}\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi\right)\left(\Omega\rho(t)+\sqrt{\Omega}\,\xi-1\right)\right]\Pi(\xi,t).\end{aligned} \tag{4.65}$$

For large Ω we expand Π in powers of $\Omega^{-1/2}$

$$\Pi\left(\xi\pm\frac{1}{\sqrt{\Omega}},t\right) = \Pi(\xi,t) \pm \frac{1}{\sqrt{\Omega}}\frac{\partial}{\partial\xi}\Pi(\xi,t) + \frac{1}{2\Omega}\frac{\partial^2}{\partial\xi^2}\Pi(\xi,t) + \mathcal{O}\left(\frac{1}{\Omega^{3/2}}\right). \tag{4.66}$$

By inserting the latter expression in (4.65), we can identify the power coefficients separately.

Order Ω. The terms compensate each other.

Ordre $\sqrt{\Omega}$. We find

$$-\sqrt{\Omega}\frac{\partial}{\partial\xi}\Pi(\xi,t)\frac{\mathrm{d}}{\mathrm{d}t}\rho(t) = \sqrt{\Omega}\frac{\partial}{\partial\xi}\Pi(\xi,t)\left(-\beta\rho(t)+\alpha\rho(t)+\mathcal{X}\rho^2(t)\right), \tag{4.67}$$

which is the deterministic equation (4.58).

Ordre Ω^0. We find

$$\begin{aligned}\frac{\partial}{\partial t}\Pi(\xi,t) &= -(\beta-\alpha)\Pi(\xi,t) - (\beta-\alpha)\xi\frac{\partial}{\partial\xi}\Pi(\xi,t) + 2\mathcal{X}\rho(t)\xi\,\frac{\partial}{\partial\xi}\Pi(\xi,t)\\ &\quad +2\mathcal{X}\rho(t)\Pi(\xi,t) + \frac{1}{2}\left((\alpha+\beta)\rho(t)+\mathcal{X}\rho^2(t)\right)\frac{\partial^2}{\partial\xi^2}\Pi(\xi,t)\\ &= -\frac{\partial}{\partial\xi}\left(h(\xi,t)\Pi(\xi,t)\right) + \frac{D(t)}{2}\frac{\partial^2}{\partial\xi^2}\Pi(\xi,t),\end{aligned} \tag{4.68}$$

with

$$h(\xi,t) = (\beta-\alpha-2\mathcal{X}\rho(t))\xi \tag{4.69}$$

$$D(t) = (\beta+\alpha)\rho(t) + \mathcal{X}\rho^2(t). \tag{4.70}$$

The equation (4.68) is a linear Fokker-Planck equation (with time-depending coefficients) that describes a distribution of the Gaussian fluctuations around the average population density $\rho(t)$. In particular, at equilibrium $\frac{\partial}{\partial t}\Pi(\xi,t)=0$, we have

$$h_s(\xi) = ((\beta-\alpha)-2\mathcal{X}\rho_s)\,\xi \overset{(4.59)}{=} -(\beta-\alpha)\xi \tag{4.71}$$

and

$$D_s = \frac{\rho_s}{2}\left(\alpha + \beta + \mathcal{X}\rho_s\right) = \frac{\beta(\beta-\alpha)}{\mathcal{X}}. \tag{4.72}$$

The steady state equation is obtained by inserting (4.71) in (4.68):

$$-(\beta-\alpha)\frac{\partial}{\partial\xi}(\xi\Pi_s(\xi)) + \frac{D_s}{2}\frac{\partial^2}{\partial\xi^2}\Pi_s(\xi) = 0. \tag{4.73}$$

Multiplying this by ξ^2 and integrating by parts, we find

$$\left\langle \xi^2 \right\rangle = \frac{D_s}{2(\beta-\alpha)} = \frac{\beta}{2\mathcal{X}}. \tag{4.74}$$

Thus, for large Ω, the fluctuations around the average population $\rho_s\Omega$ are of order $\sqrt{\frac{\beta\Omega}{2\mathcal{X}}}$. ◇

Example 7 (Quantum states evolution) Consider a quantum system described by the Hamiltonian $H = H_0 + V$. The unperturbed part H_0 leads to the time-indepedent Schrödinger equation $H_0\phi_n = E_n\phi_n$. The transition probability from an initial state n to a final state n' can be calculated from the time-dependent perturbation (Fermi's golden rule)

$$\mathcal{W}(n|n') = \frac{2\pi}{\hbar}\left|\langle\phi_n|V|\phi_{n'}\rangle\right|^2 \rho(E_n), \tag{4.75}$$

where $\rho(E_n)$ is the density of states. By inserting these transition probabilities (which were calculated for short times) in the master equation and assuming the Markov property, we can find the evolution for long times. The resulting equation is the *Pauli equation.* ◇

4.3 The detailed balance

The master equation is fully determined by the transition probabilities $\mathcal{W}(n|n')$. Before studying the dynamics, we should examine if the latter give rise to a steady state, satisfying

$$\sum_{n'\in\Sigma}\left(P^s_{n'}\mathcal{W}_{n',n} - P^s_n\mathcal{W}_{n,n'}\right) = 0, \tag{4.76}$$

with $\mathcal{W}_{n,n'} = \mathcal{W}(n|n')$. For instance, an *isolated system* (or a system in contact with a *heat reservoir*) must approach the microcanonical (or canonical) equilibrium distribution P^e_n, in agreement with the second law of thermodynamics.[4] In that case, the $\mathcal{W}_{n,n'}$ must be such that equation (4.76) admits a solution P^e_n. A particular solution of (4.76) is the one where each term vanishes separately.

Definition 4.1 (Detailed balance) *The process is said to have detailed balance with respect to the steady state P^s if the transition probabilities $\mathcal{W}_{n,n'}$ obey*

$$\boxed{P^s_{n'}\mathcal{W}_{n',n} = P^s_n\mathcal{W}_{n,n'}, \qquad \forall\, n, n'.} \tag{4.77}$$

This condition implies (4.76).

[4] P^s_n refers to a steady state whereas P^e_n indicates thermodynamic equilibrium. Thermodynamic equilibrium is a steady state, however there are many non-equilibrium steady states.

The detailed balance means that for each pair of states n, n', the transitions per unit of time from n into n' must be balanced by the transitions from n' into n. If the system is

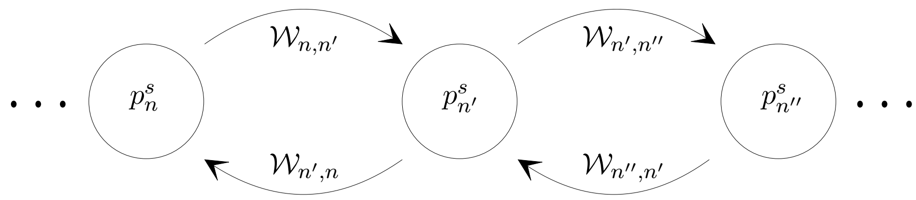

Figure 4.5: The detailed balance asserts that each pair of states is in mutual equilibrium, that is $P^s_{n'}\mathcal{W}_{n',n} = P^s_n\mathcal{W}_{n,n'}$, $P^s_{n''}\mathcal{W}_{n'',n'} = P^s_{n'}\mathcal{W}_{n',n''}$, and so forth.

in thermal contact with a heat reservoir, the stationary distribution corresponds to that of thermal equilibrium

$$P^s_n = P^e_n = Q^{-1}\, d_n\, \mathrm{e}^{-\beta E_n}, \tag{4.78}$$

where Q is the partition function, E_n the energy of the state n and d_n its degeneracy. Thus, the detailed balance condition takes the form

$$\boxed{d_{n'}\mathrm{e}^{-\beta E_{n'}}\mathcal{W}_{n',n} = d_n\mathrm{e}^{-\beta E_n}\,\mathcal{W}_{n,n'}, \qquad \forall\, n, n',} \tag{4.79}$$

which provides a specific relation between the transition rates and the energies of the system.

Remark (Microscopic foundations of the detailed balance) The relation (4.79) can be derived from quantum or classical mechanics under several conditions, in particular the time-reversal invariance of the microscopic dynamics (see section 5.1). It is characteristic for a master equation that leads to the thermalization of the system. ◇

4.3.1 Monte-Carlo Metropolis algorithm

The master equation is often used as a tool to describe the thermal equilibrium distribution $\lim_{t\to\infty} P_n(t) = P^e_n$. We suppose that the states of energy E_n are known and we construct the rates $\mathcal{W}_{n,n'}$ and $\mathcal{W}_{n',n}$ such that the detailed balance is verified. Assuming $d_n = d_{n'} = 1$, we have

$$\frac{P^e_{n'}}{P^e_n} = \frac{\mathcal{W}_{n,n'}}{\mathcal{W}_{n',n}} = \mathrm{e}^{-\beta(E_{n'}-E_n)}. \tag{4.80}$$

As we are only interested by thermal equilibrium, we can choose the rates $\mathcal{W}_{n,n'}$ that we want, even if they are not physical, as long as equation (4.80) is satisfied. The idea is then to simulate the realizations $n(t)$ of the process (whose evolution is described by the master equation), while respecting (4.80).

Method. Let us choose a function F such that

$$F(x) = x\,F\left(\frac{1}{x}\right), \tag{4.81}$$

and write

$$F\left(\frac{P^e_{n'}}{P^e_n}\right) = \mathcal{W}_{n,n'} \tag{4.82}$$

so that the detailed balance condition (4.80) is satisfied:

$$\frac{\mathcal{W}_{n,n'}}{\mathcal{W}_{n',n}} \overset{(4.82)}{=} \frac{F\left(\frac{P^e_{n'}}{P^e_n}\right)}{F\left(\frac{P^e_n}{P^e_{n'}}\right)} \overset{(4.81)}{=} \frac{P^e_{n'}}{P^e_n} \underbrace{\frac{F\left(\frac{P^e_n}{P^e_{n'}}\right)}{F\left(\frac{P^e_n}{P^e_{n'}}\right)}}_{=1}. \tag{4.83}$$

Two simple choices of F are given by

$$F(x) = \min(x, 1), \qquad x > 0, \tag{4.84}$$
$$F(x) = \frac{x}{1+x}. \tag{4.85}$$

The first choice (4.84) gives rise to the Monte Carlo Metropolis algorithm. By inserting (4.80) in (4.82), we have

$$\mathcal{W}_{n,n'} = \begin{cases} 1, & E_{n'} - E_n \leq 0, \\ \mathrm{e}^{-\beta(E_{n'}-E_n)}, & E_{n'} - E_n > 0. \end{cases} \tag{4.86}$$

Thus, the rates $\mathcal{W}_{n,n'}$ are fully determined by the energy differences $E_{n'} - E_n$ of the system, a quantity that the physicist is accustomed to calculating.

Algorithm.

(i) Following a random or a determined procedure, create a state n' starting from a first state n.

(ii) Calculate $\Delta E = E_{n'} - E_n$.

(iii) (a) If $\Delta E \leq 0$, then $\mathcal{W}_{n,n'} = 1$ and retain n'.
 (b) If $\Delta E > 0$, then $\mathcal{W}_{n,n'} = \mathrm{e}^{-\beta\Delta E}$ and choose a number r at random in the interval $[0, 1]$. Retain the state n' if $r \geq \mathrm{e}^{-\beta\Delta E}$ and reject it in the opposite case.

(iv) Repeat the procedure

In this way, we can construct a realization of the process $n(t)$ that is governed by the master equation. The random drawing of r simulates the arbitrary nature of the process, by analogy with the one-dimensional random walk for which there are only two possible situations (jump left or right depending on whether $r \gtrless 1/2$). Going through this procedure a lot of times, we can construct a large number of realizations of the stochastic process. Their average taken for sufficiently long times reproduce the thermal means and allow to find the absolute probabilities W as explained in section 2.1.1. For a system with a large number of degrees of freedom, this procedure is often more efficient than calculating the average by summing over all the configurations with weights P^e_n (4.78).

4.3.2 Stochastic dynamics of the Ising model

- *Configurations.* The states $\omega \in \Sigma = \{-1, 1\}^N$ correspond to the 2^N spin configurations of a set of N lattice sites, $\omega = \{\sigma_1, \ldots, \sigma_N\}$, $\sigma_i = \pm 1$. A realization of the multi-dimensional process consists in the evolution $\omega(t) = \{\sigma_1(t), \ldots, \sigma_N(t)\}$ of one spin configuration over time.
- *Energy.* Let $J_{ij} \geq 0$ be the coupling constants such that $\lim_{|i-j| \to \infty} J_{ij} = 0$, then the energy of a configuration is given by the Ising Hamiltonian

$$H(\omega) = -\frac{1}{2} \sum_{i \neq j}^{N} J_{ij} \sigma_i \sigma_j. \tag{4.87}$$

- *Possible configurations.* We assume that only one spin at a time can be flipped between two successive states ω and ω'. Let $\omega^{(k)} = \{\sigma_1, \ldots, -\sigma_k, \ldots, \sigma_N\}$ be the configuration obtained by flipping the spin k of ω, then the transition rates satisfy the relations $\mathcal{W}(\omega|\omega') = 0$ if $\omega' \neq \omega^{(k)}$ and

$$\frac{\mathcal{W}(\omega|\omega^{(k)})}{\mathcal{W}(\omega^{(k)}|\omega)} = \mathrm{e}^{-\beta\left(H\left(\omega^{(k)}\right) - H(\omega)\right)}, \qquad H(\omega^{(k)}) - H(\omega) = 2m_k(\omega), \tag{4.88}$$

  where

$$m_k(\omega) = \sum_{j \neq k}^{N} J_{kj} \sigma_j \tag{4.89}$$

  is the local magnetization of the site k in the configuration ω.

The master equation associated to this process reads

$$\frac{\partial}{\partial t} P(\omega, t) = \sum_{k=1}^{N} \left[\mathcal{W}(\omega^{(k)}|\omega) P(\omega^{(k)}, t) - W(\omega|\omega^{(k)}) P(\omega, t)\right]. \tag{4.90}$$

We now construct the evolution of a configuration $\omega(t)$ by applying the Metropolis algorithm. If t is large enough, we obtain in this way a typical configuration for the Gibbs distribution $\rho(\omega) = \frac{1}{Q} \mathrm{e}^{-\beta H(\omega)}$, where Q is the partition function.

The problem can be solved analytically in two particular cases, the one-dimensional spin chain and the mean field approximation. Let us begin by specifying the transition rates in the form

$$\mathcal{W}(\omega|\omega^{(k)}) = \frac{\gamma}{2} \left[1 - \sigma_k \,\mathrm{th}\left(\beta m_k(\omega)\right)\right], \tag{4.91}$$

where $m_k(\omega)$ is the local magnetization (4.89), and $2/\gamma$ determines the time scale in which the process occurs. By using the relation $(1 - \mathrm{th}\, x)/(1 + \mathrm{th}\, x) = \exp(-2x)$ we can easily verify that these rates satisfy the detailed balance condition (4.88). Thus, the master equation (4.90) becomes

$$\frac{\partial}{\partial t} P(\omega, t) = \frac{\gamma}{2} \sum_{j=1}^{N} \left[(1 + \sigma_j \,\mathrm{th}\, \beta m_j(\omega)) P(\omega^{(j)}, t) - (1 - \sigma_j \,\mathrm{th}\, \beta m_j(\omega)) P(\omega, t)\right]. \tag{4.92}$$

Consider the average value of the kth spin,

$$\langle \sigma_k \rangle (t) = \sum_{\omega} \sigma_k P(\omega, t). \tag{4.93}$$

It obeys the equation of motion

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\sigma_k\rangle(t) = -\gamma\left[\langle\sigma_k\rangle(t) - \langle\operatorname{th}\beta m_k\rangle(t)\right]. \tag{4.94}$$

Indeed, inserting (4.92) and isolating the term $j = k$ leads to

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle\sigma_k\rangle(t) &= \sum_\omega \sigma_k \frac{\partial}{\partial t}P(\omega,t)\\ &= \frac{\gamma}{2}\sum_\omega(\sigma_k + \operatorname{th}\beta m_k(\omega))P(\omega^{(k)},t) - \sum_\omega(\sigma_k - \operatorname{th}\beta m_k(\omega))P(\omega,t)\\ &+\frac{\gamma}{2}\sum_\omega\sigma_k\sum_{j\neq k}\Big[(1+\sigma_j\operatorname{th}\beta m_j(\omega))P(\omega^{(j)},t)\\ &\qquad -(1-\sigma_j\operatorname{th}\beta m_j(\omega))P(\omega,t)\Big]. \end{aligned}\tag{4.95}$$

We change the dummy variable σ_k to $-\sigma_k$ in the first sum, which then becomes identical to the second one ($m_k(\omega)$ is independent of σ_k), hence (4.94). The third sum vanishes because its terms are odd under $\sigma_k \to -\sigma_k$.

One-dimensional spin chain

We consider a one-dimensional, infinite chain of spins σ_i. The spins are labeled by $i = \dots, -2, -1, 0, 1, 2, \dots$ and coupled to their nearest neighbours: $J_{ii-1} = J_{ii+1} = J > 0$, $J_{ik} = 0$, $k \neq i-1, i+1$. In these conditions, we have

$$m_j(\omega) = J(\sigma_{j+1} + \sigma_{j-1}), \qquad \operatorname{th}\beta m_j(\omega) = \frac{1}{2}(\sigma_{j+1}+\sigma_{j-1})\operatorname{th}2\beta J, \tag{4.96}$$

so that (4.94) reduces to the finite difference equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\sigma_i\rangle(t) = -\gamma\left[\langle\sigma_i\rangle(t) - \frac{1}{2}\Big(\langle\sigma_{i-1}\rangle(t) + \langle\sigma_{i+1}\rangle(t)\Big)\operatorname{th}2\beta J\right]. \tag{4.97}$$

The problem is basically the same as the continuous-time random walk that we discussed about in section 4.2 and can be solved by the method of the generating function $G(z,t)$ as in the second example. In our case, the generating function is given by

$$\frac{\partial}{\partial t}G(z,t) = \left[\frac{\gamma}{2}\operatorname{th}(2\beta J)\left(z+\frac{1}{z}\right) - \gamma\right]G(z,t). \tag{4.98}$$

If we take the initial condition $\langle\sigma_i\rangle(0) = 0$, $i \neq 0$, $\langle\sigma_0\rangle(0) = 1$, we find

$$G(z,t) = \mathrm{e}^{-\gamma t}\exp\left[\frac{\gamma}{2}\operatorname{th}(2\beta J)\left(z+\frac{1}{z}\right)t\right], \tag{4.99}$$

and equation (4.26) leads to

$$\langle\sigma_i\rangle(t) = \mathrm{e}^{-\gamma t}I_j[\gamma\operatorname{th}(2\beta J)t]. \tag{4.100}$$

The behaviours (4.29) and (4.30) of the modified Bessel function (4.28) show that

$$\langle\sigma_i\rangle(t) \overset{t\to 0}{\asymp} Ct^i, \qquad i\neq 0, \quad C\in\mathbb{R}, \tag{4.101}$$

$$\langle\sigma_i\rangle(t) \overset{t\to\infty}{\asymp} \frac{\exp[-\gamma t(1-\operatorname{th}2\beta J)]}{\sqrt{2\pi(\gamma\operatorname{th}2\beta J)t}}. \tag{4.102}$$

For small times, the spins that are close to σ_0 flip in the positive direction because of the ferromagnetic coupling. For long times, the average value of each spin tends exponentially to zero (regardless of the temperature) because there is no spontaneous magnetization in the one-dimensional Ising model with $T \neq 0$.

Mean field approximation

We choose the coupling constants to be independent of the distance, written as $J_{ik} = \frac{J}{N}$, $J > 0$, and we consider the average magnetization per spin in the macroscopic limit $N \to \infty$

$$\mu(t) = \lim_{N\to\infty} \langle \overline{m}_N \rangle (t), \qquad \overline{m}_N(\omega) = \frac{1}{N}\sum_{i=1}^{N} \sigma_i. \tag{4.103}$$

We assume that at any times, the fluctuations of $\overline{m}_N(\omega)$ are negligible when $N \to \infty$, that is

$$\lim_{N\to\infty} \langle (\overline{m}_N)^p \rangle (t) = \mu(t)^p, \qquad p = 2, 3, \dots. \tag{4.104}$$

We see that the local magnetization (4.89) is equal to the magnetization per spin up to a term of order $1/N$.

$$m_k(\omega) = \sum_{i\neq k} \frac{J}{N}\sigma_i = J\left(\overline{m}_N(\omega) - \frac{1}{N}\sigma_k\right). \tag{4.105}$$

Thus, taking (4.104) into account, it follows from (4.94) that in the limit $N \to \infty$

$$\frac{\mathrm{d}}{\mathrm{d}t}\mu(t) = -\gamma[\mu(t) - (\mathrm{th}\,\beta J)\mu(t)]. \tag{4.106}$$

The stationary points of this non-linear differential equation are given by the solutions of $\mu - (\mathrm{th}\,\beta J)\mu = 0$, one of which is the point $\mu = 0$. Using the Taylor expansion $\mathrm{th}\,x \simeq x - x^3/3$ around $x = 0$, the equation becomes in the vicinity of $\mu = 0$

$$\frac{\mathrm{d}}{\mathrm{d}t}\mu(t) = -\gamma\left[(1-\beta J)\mu(t) + \frac{(\beta J)^3}{3}\mu(t)^3\right]. \tag{4.107}$$

If $1 - \beta J > 0$, or equivalently if $T > T_c = J/k_B$, the stationary point $\mu = 0$ is unique and stable, and the relaxation is exponential

$$\mu(t) \overset{t\to\infty}{\asymp} \mu(0)\mathrm{e}^{-t/\tau(T)}, \qquad \tau(T) = \frac{T}{\gamma(T - T_c)}. \tag{4.108}$$

If $T < T_c$, the point $\mu = 0$ becomes unstable and two new stable points appear,

$$\mu_+ = -\mu_- = \sqrt{\left(\frac{T_c}{T}\right)^3 \frac{T}{3(T_c - T)}}. \tag{4.109}$$

The latter correspond to the two possible values of the spontaneous magnetization, T_c being the Curie temperature of the ferromagnetic phase transition of the Ising model in the mean field approximation. Their approach is also exponential, however the relaxation time $\tau(T)$ given by equation (4.108) diverges when $T \to T_c$. At the critical point $T = T_c$, the equation (4.107) reduces to

$$\frac{\mathrm{d}}{\mathrm{d}t}\mu(t) = -\frac{\gamma}{3}\mu(t)^3, \tag{4.110}$$

whose solution is given by

$$\mu(t) = \sqrt{\frac{3\mu(0)^2}{2\gamma\mu(0)^2 t + 3}} \overset{t\to\infty}{\asymp} \sqrt{\frac{3}{2\gamma t}}. \tag{4.111}$$

The decreasing is not exponential anymore: this is the phenomenon of critical slowdown of the equilibrium approach at the phase transition.

4.3.3 Resolution by the spectral theory

The detailed balance allows to solve the master equation by using the spectral theory. We make the following assumptions.

Hypothesis 4.1

(i) There exists a unique steady state $P_n^s > 0\ \forall n$.

(ii) The detailed balance is satisfied for the steady state P^s.

(iii) The number of states N is finite.

The assumption (iii) is made for mathematical simplicity. Let us write the master equation

$$\frac{\partial}{\partial t} P_n(t) = \sum_{n'} \left(P_{n'}(t)\mathcal{W}_{n',n} - P_n(t)\mathcal{W}_{n,n'} \right) \tag{4.112}$$

in the form of a linear system

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}(t) = \boldsymbol{M}\cdot\mathbf{P}(t), \tag{4.113}$$

where $\mathbf{P}(t) \in \mathbb{R}^N$ is a vector

$$\mathbf{P}(t) = \begin{pmatrix} P_1(t) \\ \vdots \\ P_N(t) \end{pmatrix}, \tag{4.114}$$

and $\boldsymbol{M} \in M_N(\mathbb{R})$ is a real $N \times N$ matrix whose components are given by

$$M_{nm} = \mathcal{W}_{m,n} - \delta_{m,n}\sum_{k=1}^{N} \mathcal{W}_{n,k}. \tag{4.115}$$

Definition 4.2 (Stochastic matrix) *A matrix $\boldsymbol{M} \in M_N(\mathbb{R})$ is said to be* stochastic *if it satisfies the two following conditions.*

(i) $M_{nm} \geq 0\ \forall n \neq m$

(ii) $\sum_{k=1}^{N} M_{km} = 0\ \forall m$

We can verify that the matrix $\boldsymbol{M}$ with components (4.115) satisfies these two conditions. Let us define the matrix $\widetilde{\boldsymbol{M}}$ by

$$\widetilde{M}_{nm} = \frac{1}{\sqrt{P_n^s}} M_{nm}\sqrt{P_m^s}. \tag{4.116}$$

Lemma 4.1 *The detailed balance holds if and only if the matrix $\widetilde{\boldsymbol{M}}$ is symmetric.*

Proof (Lemma 4.1) Suppose that $\widetilde{\boldsymbol{M}}$ is symmetric, $\widetilde{M}_{nm} = \widetilde{M}_{mn}$, and consider the non-trivial case $n \neq m$. According to the definitions (4.116) and (4.115), we have

$$\frac{1}{\sqrt{P_n^s}}\left(\mathcal{W}_{m,n} - \underbrace{\delta_{m,n}}_{=0}\sum_{k=1}^{N}\mathcal{W}_{n,k}\right)\sqrt{P_m^s} = \frac{1}{\sqrt{P_m^s}}\left(\mathcal{W}_{n,m} - \underbrace{\delta_{n,m}}_{=0}\sum_{k=1}^{N}\mathcal{W}_{m,k}\right)\sqrt{P_n^s}, \tag{4.117}$$

which is equivalent to the detailed balance condition

$$\mathcal{W}_{m,n}P_m^s = \mathcal{W}_{n,m}P_n^s. \tag{4.118}$$

The same calculus holds for the converse, and this completes the proof. ∎

As the matrix $\widetilde{\boldsymbol{M}}$ is real and symmetric, it is diagonalizable and has N orthogonal eigenvectors $\widetilde{\boldsymbol{\phi}}^{(k)} \in \mathbb{R}^N$

$$\widetilde{\boldsymbol{\phi}}^{(k)} = \begin{pmatrix} \widetilde{\phi}_1^{(k)} \\ \vdots \\ \widetilde{\phi}_N^{(k)} \end{pmatrix}, \tag{4.119}$$

with eigenvalues λ_k, $k = 1, \ldots, N$, and such that $\langle \widetilde{\boldsymbol{\phi}}^{(k_1)} | \widetilde{\boldsymbol{\phi}}^{(k_2)} \rangle = \delta_{k_1,k_2}$. The vectors $\boldsymbol{\phi}^{(k)}$ with components $\phi_n^{(k)} = \sqrt{P_n^s}\,\widetilde{\phi}_n^{(k)}$ diagonalize $\boldsymbol{M}$,

$$\boldsymbol{M}\cdot\boldsymbol{\phi}^{(k)} = \lambda_k\boldsymbol{\phi}^{(k)}, \tag{4.120}$$

and we have the orthonormality relation

$$\sum_{n=1}^{N}\frac{\phi_n^{(k_1)}\phi_n^{(k_2)}}{P_n^s} = \langle \widetilde{\boldsymbol{\phi}}^{(k_1)} | \widetilde{\boldsymbol{\phi}}^{(k_2)} \rangle = \delta_{k_1,k_2}. \tag{4.121}$$

Note that $\widetilde{\boldsymbol{M}}$ (or $\boldsymbol{M}$) always has the eigenvalue zero. Indeed, if we set $\widetilde{\phi}_n^{(1)} = \sqrt{P_n^s}$, or $\phi_n^{(1)} = P_n^s$, then by definition of the steady state $\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{P}^s = 0$, the equation (4.113) implies

$$\boldsymbol{M}\cdot\boldsymbol{\phi}^{(1)} = 0, \tag{4.122}$$

and thus the associated eigenvalues is $\lambda_1 = 0$.

Lemma 4.2 *Let λ_k be the eigenvalues of the matrix $\widetilde{\boldsymbol{M}}$, then $\lambda_k < 0$, $k = 2, \ldots, N$.*

Proof (Lemma 4.2) Let us show that $\widetilde{\boldsymbol{M}}$ defines a negative-definite quadratic form $\langle \widetilde{\boldsymbol{\phi}} | \widetilde{\boldsymbol{M}} | \widetilde{\boldsymbol{\phi}} \rangle \leq 0$.

$$\begin{aligned}
\langle \widetilde{\boldsymbol{\phi}} | \widetilde{\boldsymbol{M}} | \widetilde{\boldsymbol{\phi}} \rangle &= \sum_{n,m=1}^{N} \widetilde{\phi}_n \widetilde{M}_{nm} \widetilde{\phi}_m \\
&\overset{(4.116)}{=} \sum_{n,m=1}^{N} \widetilde{\phi}_n \frac{1}{\sqrt{P_n^s}} M_{nm} \sqrt{P_m^s}\,\widetilde{\phi}_m \\
&\overset{(4.115)}{=} \sum_{n,m=1}^{N} \left(\widetilde{\phi}_n \frac{1}{\sqrt{P_n^s}} \mathcal{W}_{m,n} \sqrt{P_m^s}\,\widetilde{\phi}_m - \widetilde{\phi}_n^2 \mathcal{W}_{n,m} \right)
\end{aligned} \tag{4.123}$$

Defining $x_n = \frac{\widetilde{\phi}_n}{\sqrt{P_n^s}}$, (4.123) becomes

$$\begin{aligned}
\langle\widetilde{\boldsymbol{\phi}}|\widetilde{\boldsymbol{M}}|\widetilde{\boldsymbol{\phi}}\rangle &= \sum_{n,m=1}^{N} x_n x_m \mathcal{W}_{m,n} P_m^s - \sum_{n,m=1}^{N} x_n^2 \mathcal{W}_{n,m} P_n^s \\
&= \sum_{n,m=1}^{N} x_n x_m \mathcal{W}_{m,n} P_m^s - \frac{1}{2}\sum_{n,m=1}^{N} x_n^2 \underbrace{\mathcal{W}_{n,m} P_n^s}_{\overset{(4.118)}{=}\mathcal{W}_{m,n} P_m^s} - \frac{1}{2} \underbrace{\sum_{n,m=1}^{N} x_n^2 \mathcal{W}_{n,m} P_n^s}_{\overset{n\leftrightarrow m}{=}\sum_{n,m=1}^{N} x_m^2 \mathcal{W}_{m,n} P_m^s} \\
&= -\frac{1}{2}\sum_{n,m=1}^{N} \mathcal{W}_{m,n} P_m^s \left(-2x_n x_m + x_n^2 + x_m^2\right) \\
&= -\frac{1}{2}\sum_{n,m=1}^{N} \underbrace{\mathcal{W}_{m,n}}_{\geq 0} \underbrace{P_m^s}_{>0} \underbrace{(x_n - x_m)^2}_{\geq 0} \\
&\leq 0. \qquad (4.124)
\end{aligned}$$

Moreover, as the stationary solution is assumed to be unique, the multiplicity of the zero eigenvalue is 1. Thus, the other eigenvalues are strictly negative $\lambda_k < 0$, $k = 2, \ldots, N$, and this completes the proof. ■

Remark A sufficient condition to ensure the unicity of the steady state is that all the rates are strictly positive: $\mathcal{W}_{m,n} > 0\ \forall\, n, m$. Indeed, in that case (4.124) implies $x_n = x_m$ $\forall\, n, m$, that is $\frac{\widetilde{\phi}_n}{\sqrt{P_n^s}} = \frac{\widetilde{\phi}_m}{\sqrt{P_m^s}} = C$ is independent of n. Thus, $\widetilde{\phi}_n = C\sqrt{P_n^s} = C\widetilde{\phi}_n^{(1)}$ is proportional to the vector of eigenvalue $\lambda_1 = 0$, and the latter is not degenerate. ◇

Any initial distribution $\mathbf{P}(0)$ can be represented in the basis of eigenvectors $\boldsymbol{\phi}^{(k)}$

$$\mathbf{P}(0) = \sum_{k=1}^{n} c_k \boldsymbol{\phi}^{(k)}, \qquad (4.125)$$

and according to (4.121),

$$c_k = \sum_{n=1}^{N} \frac{\phi_n^{(k)} P_n(0)}{P_n^s}, \qquad c_1 = \sum_{n=1}^{N} \frac{\overbrace{\phi_n^{(1)}}^{=P_n^s} P_n(0)}{P_n^s} = 1. \qquad (4.126)$$

Thus, the *general solution* of (4.113) is given by

$$\begin{aligned}
\mathbf{P}(t) &\overset{(4.113)}{=} \mathrm{e}^{\boldsymbol{M}t}\cdot\mathbf{P}(0) \\
&= \sum_{m=0}^{\infty}\frac{1}{m!}t^m\boldsymbol{M}^m\cdot\mathbf{P}(0) \\
&\overset{(4.125)}{=} \sum_{m=0}^{\infty}\frac{1}{m!}t^m\boldsymbol{M}^m\cdot\sum_{k=1}^{n}c_k\boldsymbol{\phi}^{(k)} \\
&= \sum_{m=0}^{\infty}\frac{1}{m!}t^m\sum_{k=1}^{n}c_k\lambda_k^m\boldsymbol{\phi}^{(k)} \\
&= \sum_{k=1}^{N}\boldsymbol{\phi}^{(k)}c_k\mathrm{e}^{\lambda_k t} \\
&\overset{(4.126)}{=} \sum_{k=1}^{N}\boldsymbol{\phi}^{(k)}\mathrm{e}^{\lambda_k t}\sum_{n=1}^{N}\frac{\phi_n^{(k)}P_n(0)}{P_n^s}.
\end{aligned} \tag{4.127}$$

We know that $\lambda_k < 0\ \forall\, k = 2,\ldots,N$, which implies the exponential approach to the equilibrium

$$\lim_{t\to\infty}\mathbf{P}(t) = c_1\boldsymbol{\phi}^{(1)} = \mathbf{P}^s \tag{4.128}$$

for any initial condition $\mathbf{P}(0)$.

The *transition probability* $P(n,0|m,t)$ of the Markov process from a state n into a state m during time t is obtained by specifying the initial condition $P_m(0)=\delta_{n,m}$, hence

$$P(n,0|m,t) = \sum_{k=1}^{N}\frac{\phi_m^{(k)}\phi_n^{(k)}}{P_n^s}\mathrm{e}^{\lambda_k t}. \tag{4.129}$$

The joint distribution of the process with steady state $W(n)=P_n^s$ is given by

$$W(n,0|m,t) = P_n^s\,P(n,0|m,t) = \sum_{k=1}^{N}\phi_m^{(k)}\phi_n^{(k)}\mathrm{e}^{\lambda_k t}. \tag{4.130}$$

Let us calculate the *autocorrelation function* of the process, defined as

$$K(t) = \langle n(0)n(t)\rangle - \langle n(0)\rangle\,\langle n(t)\rangle\,. \tag{4.131}$$

As the process is stationary,

$$\langle n(0)\rangle = \langle n(t)\rangle = \sum_{n=1}^{N}n\,P_n^s = \sum_{n=1}^{N}\phi_n^{(1)}, \tag{4.132}$$

and

$$\begin{aligned}
\langle n(0)n(t)\rangle &= \sum_{n,m=1}^{N}n\,m\,W(n,0|m,t) \\
&\overset{(4.130)}{=} \sum_{n,m=1}^{N}n\,m\sum_{k=1}^{N}\phi_m^{(k)}\phi_n^{(k)}\mathrm{e}^{\lambda_k t} \\
&= \sum_{k=1}^{N}\mathrm{e}^{\lambda_k t}\left(\sum_{n=1}^{N}n\,\phi_n^{(k)}\right)^2,
\end{aligned} \tag{4.133}$$

then by inserting (4.133) and (4.132) in (4.131) we have

$$K(t) = \sum_{k=2}^{N} \mathrm{e}^{\lambda_k t} \left(\sum_{n=1}^{N} n\, \phi_n^{(k)} \right)^2 . \tag{4.134}$$

$K(t)$ tends exponentially to zero as $t \to \infty$, which means that the time correlations of the system decrease exponentially.

4.4 The H-theorem

Whether the detailed balance holds or not, the master equation possess a remarkable general property: there exists a functional of the state that is monotonic over time. Such a functional is said to be Lyapunov in mathematics. In physics, it provides a model for non-equilibrium entropy.

Theorem 4.1 (H-theorem) *Assume that the number of states is finite* [5] *and that the master equation admits a stationary distribution P_n^s such that $P_n^s > 0$, $n \in \Sigma$. Let $f(x)$ be a strictly convex ($f''(x) > 0$), bounded below ($f(x) \geq a \in \mathbb{R}$) function for $x \geq 0$. Then, the functional*

$$H(t) = \sum_{n \in \Sigma} P_n^s\, f\left(\frac{P_n(t)}{P_n^s} \right) \tag{4.135}$$

is monotonically decreasing over time.

Proof (H-theorem) We have to prove that $\frac{\mathrm{d}}{\mathrm{d}t} H(t) \leq 0$. We start by noting that for any sequence of numbers $\{a_n\}_{n \geq 1}$, we have

$$\sum_{n,m \in \Sigma} P_m^s \mathcal{W}_{m,n} (a_n - a_m) = 0. \tag{4.136}$$

This follows directly from the fact that P_m^s satisfies the stationary master equation,

$$\sum_{n,m \in \Sigma} P_m^s \mathcal{W}_{m,n} (a_n - a_m) = \sum_{n \in \Sigma} a_n \underbrace{\sum_{m \in \Sigma} \left(P_m^s \mathcal{W}_{m,n} - P_n^s \mathcal{W}_{n,m} \right)}_{\overset{(4.12)}{=} 0} = 0. \tag{4.137}$$

[5] This will avoid us the problems of the limit and convergence of infinite sums.

Let us now set $x_n(t) = \frac{P_n(t)}{P_n^s}$, and calculate

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}H(t) &= \sum_{n\in\Sigma} P_n^s \frac{\mathrm{d}}{\mathrm{d}t} f\left(\frac{P_n(t)}{P_n^s}\right) \\
&= \sum_{n\in\Sigma} f'(x_n)\,\frac{\partial}{\partial t} P_n(t) \\
&\overset{(4.10)}{=} \sum_{n\in\Sigma} f'(x_n) \sum_{m\in\Sigma} \left(P_m(t)\mathcal{W}_{m,n} - P_n(t)\mathcal{W}_{n,m}\right) \\
&= \sum_{n\in\Sigma} f'(x_n) \sum_{m\in\Sigma} P_m(t)\mathcal{W}_{m,n} - \underbrace{\sum_{n\in\Sigma} f'(x_n) \sum_{m\in\Sigma} P_n(t)\mathcal{W}_{n,m}}_{n\leftrightarrow m} \\
&= \sum_{n,m\in\Sigma} P_m(t)\mathcal{W}_{m,n}\left(f'(x_n) - f'(x_m)\right) \\
&= \sum_{n,m\in\Sigma} P_m^s\mathcal{W}_{m,n}\left(x_m f'(x_n) - x_m f'(x_m)\right). \qquad (4.138)
\end{aligned}$$

We choose

$$a_n = f(x_n) - x_n f'(x_n), \qquad (4.139)$$

in (4.137). This choice leads to

$$\sum_{n,m\in\Sigma} P_m^s\mathcal{W}_{m,n}\left(f(x_n) - f(x_m) - \left(x_n f'(x_n) - x_m f'(x_m)\right)\right) = 0, \qquad (4.140)$$

that we add to (4.138) to obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}H(t) = -\sum_{n,m\in\Sigma} \underbrace{P_m^s}_{\geq 0}\underbrace{\mathcal{W}_{m,n}}_{\geq 0}\Big(\underbrace{f(x_m) - f(x_n) - (x_m - x_n)f'(x_n)}_{>0}\Big) < 0. \qquad (4.141)$$

The result $f(x_m) - f(x_n) - (x_m - x_n)f'(x_n) > 0$ stems from the strict convexity of $f(x)$, as depicted in figure 4.6.

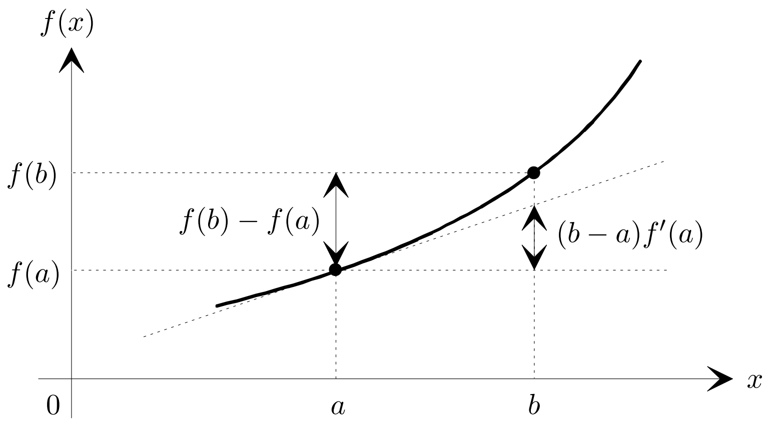

Figure 4.6: The strict convexity of $f(x)$ implies $f(b)-f(a) > (b-a)f'(a)$, thus $f(b)-f(a)-(b-a)f'(a) > 0$.

■

Corollary 4.1 (Equilibrium approach) *Furthermore, if all the rates are strictly positive $\mathcal{W}_{n,n'} > 0 \; \forall \, n, n'$, then for any initial condition $P_n(0)$ we have*

$$\lim_{t\to\infty} P_n(t) = P_n^s. \tag{4.142}$$

Therefore, the steady state is unique.

The corollary demands that transitions may occur between any pair of states. This assumption is in fact too restrictive. The result remains true if each pair of states is connected by a chain having a non-zero transition rate. The latter condition ensures that all the components of $\mathbf{P}(t)$ may evolve towards those of $\mathbf{P}^s$ by successive transitions. If it were not satisfied, the system might have several stationary distributions, each of them having an initial conditions' attraction area.

Proof (Equilibrium approach corollary) By the H-theorem, $H(t)$ is bounded below and decreasing, therefore $\lim_{t\to\infty} H(t)$ exists and $\lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} H(t) = 0$. Consequently, it follows from (4.141) that

$$\lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t} H(t) = -\lim_{t\to\infty} \sum_{n,m\in\Sigma} P_m^s \mathcal{W}_{m,n} \left(f(x_m) - f(x_n) - (x_m - x_n) f'(x_n)\right) = 0. \tag{4.143}$$

Since each term of the sum in (4.143) is positive and $P_m^s \neq 0$, $\mathcal{W}_{m,n} \neq 0$, we have

$$\lim_{t\to\infty} \left(f(x_m) - f(x_n) - (x_m - x_n) f'(x_n)\right) = 0. \tag{4.144}$$

The Taylor expansion of $f(x_m)$ around $x_m = x_n$ gives

$$\begin{aligned} & f(x_m) = f(x_n) + f'(x_n)(x_m - x_n) + \frac{1}{2} f''(\overline{x}_n)(x_m - x_n)^2, \quad \overline{x}_n \in [x_m, x_n] \\ \Longrightarrow \quad & f(x_m) - f(x_n) - (x_m - x_n) f'(x_n) = \frac{1}{2} \underbrace{f''(\overline{x}_n)}_{=\delta>0} (x_m - x_n)^2, \quad \overline{x}_n \in [x_m, x_n]. \end{aligned} \tag{4.145}$$

The strict inequality $\delta > 0$ is ensured because of the assumption of strict convexity for $f(x)$. By inserting (4.145) in (4.144), we obtain with $x_n(t) = \frac{P_n(t)}{P_n^s}$

$$\begin{aligned} & \lim_{t\to\infty} (x_m - x_n) = 0 \\ \Longrightarrow \quad & \lim_{t\to\infty} \left(\frac{P_m(t)}{P_m^s} - \frac{P_n(t)}{P_n^s} \right) = 0 \\ \Longrightarrow \quad & \lim_{t\to\infty} \left(P_n(t) - P_n^s \frac{P_m(t)}{P_m^s} \right) = 0. \end{aligned} \tag{4.146}$$

By summing over the states n with the normalization condition $\sum_{n\in\Sigma} P_n(t) = \sum_{n\in\Sigma} P_n^s = 1$ $\forall \, t$, (4.146) becomes

$$\begin{aligned} & \lim_{t\to\infty} \left(\underbrace{\sum_{n\in\Sigma} P_n(t)}_{=1} - \frac{P_m(t)}{P_m^s} \underbrace{\sum_{n\in\Sigma} P_n^s}_{=1} \right) = 0 \\ \Longrightarrow \quad & \lim_{t\to\infty} \frac{P_m(t)}{P_m^s} = 1 \\ \Longrightarrow \quad & \lim_{t\to\infty} P_m(t) = P_m^s, \end{aligned} \tag{4.147}$$

and this completes the proof. ■

Remark In the proof we have assumed that the existence of $\lim_{t\to\infty} H(t)$ implies $\lim_{t\to\infty} \dot{H}(t) = 0$. In principle this is not true if $\dot{H}(t) = dH(t)/dt$ is non-monotonic and starts to oscillate when $t \to \infty$. In that case, the demonstration remains valid provided that we replace $\dot{H}(t)$ by its average over a time interval τ: $\frac{1}{\tau}\int_t^{t+\tau} \mathrm{d}s\, \dot{H}(s) = \frac{H(t+\tau)-H(t)}{\tau}$. ◇

There is a model for equilibrium approach that is analogous to the second law of thermodynamics. Let us assume that the steady state corresponds to the equilibrium state of the system, $P_n^s = P_n^e$. We choose $f(x) = x\ln(x)$, so that

$$H(t) = \sum_{n\in\Sigma} P_n(t)\ln\left(\frac{P_n(t)}{P_n^e}\right). \tag{4.148}$$

This function has the following properties:

(i) It is strictly decreasing.

(ii) It is extensive: if Σ_a and Σ_b are twoo independent systems, $(P_n(t) = P_n^a(t)P_n^b(t))$, we have

$$H(\Sigma_a \cup \Sigma_b) = H(\Sigma_a) + H(\Sigma_b). \tag{4.149}$$

(iii) $\lim_{t\to\infty} H(t) = 0$.

Let us consider the *equilibrium entropy* S^e, defined as usual by

$$S^e = -k_B \sum_{n\in\Sigma} P_n^e \ln\left(P_n^e\right), \tag{4.150}$$

where k_B is the Boltzmann constant. We define the *non-equilibrium entropy* function of the process as

$$\begin{aligned} S(t) &= -k_B H(t) + S^e \\ &= -k_B\left(\sum_{n\in\Sigma} P_n(t)\ln\left(\frac{P_n(t)}{P_n^e}\right) + \sum_{n\in\Sigma} P_n^e \ln\left(P_n^e\right)\right). \end{aligned} \tag{4.151}$$

By the H-theorem, the non-equilibrium entropy function is monotonically increasing, and we have $\lim_{t\to\infty} S(t) = S^e$.

It should be emphasized that these considerations constitute by no means a demonstration of the second law of thermodynamics, because they rely on an evolution that is described by an irreversible Markov process and not by a reversible microscopic motion.