Physics of complex systems

Prof. *Antonio Trovato*
University of Padova

Written by: *Giovanni Piccolo*

Academic Year 2020/21

Compiled on January 11, 2021

Contents

Chapter 1

Introduction

1.1 Notion of complexity

(Lesson 1 of 30/09/2020) Compiled: January 11, 2021

In order to talk about notion of complexity we will look at three different papers:

- Anderson "more is different" and "emergence"
- Goldenfeld and Kadanoff: "structure with variations", "complexity vs. chaos", universality allows choice of "most convenient minimal model"
- Newman: survey of complex systems; examples and theories

1.1.1 Anderson's "More is different"

To introduce the concept of *complexity* we will start looking at the Anderson's critique of the *reduction hypothesis*: dividing research in **intensive** basic research and **extensive** applied research he states that *reductionism* is different from **constructionism**.
In other words we may know everything about *simple fundamental laws* but does not imply the ability to reconstruct the actual behaviour of the universe.

Simple fundamental laws $\neq$ behaviour of the universe

But why is that? There are two main problems that are due to this disconnection:

- **Scale**: at a first glance this problem seems to be very practical because of the high number of microscopic constituents necessary to describe an ordinary piece of macroscopic matter ($\sim 10^{23}$) $\rightarrow$ this leads to *Statistical Mechanics*. Another important problem related to the scale of the system is due to the *available amount of computer power*: we may think that this is not a real problem (again, only a practical one). The real problem is the following.
- **Complexity**: the point is that we have an emergent behaviour if we deal with a very large number of elementary units what happens is that at macroscopic level we observe *novel emergent behaviours* of the system taking place. In other words this *complex emergent behaviour can't be understood as a simple extrapolation from small systems.*

What follows from these points is a **hierarchy** of complexity levels where -at each level of complexity- there is a new novel emergent property.

As we can read from Anderson's paper *More is Different* we can't say that **solid state physics** is just applied **elementary particle physics** or that **cell biology** is just applied **molecular biology**: let's explore the first example.

$$\text{Elementary particles} \rightarrow \text{Solid state physics}$$

From the prospective of elementary particle physics the aim is to solve the Schrödinger equation but in the 60s physicist discovered the whole idea of *phase transitions*: this emergent property happends at the thermodynamic limit. What is the general lesson that we can learn from phase transitions? In general we discover phase transitions from disordered "fully symmetric[1]" phase (typically **time** and **space** invariance).
What we have learnt is that this symmetry is broken (in these transitions) to an **ordered phase** with a reduced symmetry. This is a quite general statement: we can think of the mechanism by which the Higg's boson produces the masses of particles, of the transition phases in the Ising model and of crystals.
Crystals are object whose full space invariance is lost but it maintains some discrete symmetries. The key point here is the **spontaneous symmetry breaking**, a novel idea that we came up with while studying those particular systems.
These are some example of what Anderson's **emergent problems**.

1.1.2 Goldenfeld and Kadanoff's "Simple Lessons from Complexity"

In the second paper the basic idea is that we are dealing again with big systems whose elementary units follow simple elementary laws but the result of that is that the world we observe is **complex** and **chaotic**. What does *complex* mean according to Goldenfeld and Kadanoff?

To them *complexity* is associated to what they call "structure with variations". Here follow two examples of this concept:

- **Cells in different tissues** in an organism: at the very beginning are equal because they all start from the same genetic information encoded in the DNA but neurons have a very different shape from muscle cells and so on. The important point is that at the beginning the elementary basic rules are the same.

- **Turbulence**: we have a fluid made up of molecules/atoms and we know the simple rules by which the different molecules/atoms can bind (?) each other but at the very end we can have a turbulent regime and we can see very complex patterns, each time different from the previous one (this is the structure variation).

---

[1] ∧Meaning: displaying the full symmetry that is present in the simple elementary laws.

To sum up: the basic rules can be the same but do observe a great variety of possible complex structures.

Chaotic instead refers to the *sensitive dependence* on *initial conditions*: even in the case of deterministic systems where we know the rules and even if we know how to solve the equations, still in chaotic regime changing by a very small amount the initial conditions will produce a very different behaviour.
A chaotic systems however still have some properties that can be predicted: an example is climate but we can predict the existence of seasons. Again the point (similarly to Anderson) is that complexity may emerge (or does emerge) from very simple ingredients: for example we can setup a very simple computer simulation with three general rules

1. *local interactions of atoms*;
2. *conservation laws* [for a fluid: particle number, momentum];
3. *symmetry* [rotational invariance],

As we have from point 1 to 3 we do observe emergent turbulent behaviour INDEPENDENT OF DETAILS (very important point to stress). This is not a trivial thing and that's what people refers to with the expression *no model chaos*: the behaviour of a simulation is not crucially depending on the details of how we define rules in our simulation on in our theoretical model.
This can be summarized as **universality** → independence on details at microscopic scale.
But why is it so? Why do we observe that there is no model chaos?

No model chaos

We do observe no model chaos because in the systems that we are studying we have what physicist call *separations of length,time, energy scales.* This is the real reason why what happens at the macroscopic level does not depend too much on the microscopic details. Let's see and example of this:

Brownian motion the whole idea of Einstein to describe brownian particles is based on the separation between what happens in the ***collision time scale*** and the ***dissipative time scale***. If this separation didn't exist then a theory of brownian motion would not be possible. The crucial point is that if our goal is to develop a theory to describe the property of a complex system (with a large number of units) then the universality feature tells us that out game should be to model our system with a correct level of details: we must discard the detail that are irrelevant for the properties of the system that we wish to model and maintain the features (such as in the case of turbulent fluids the previous 1 to 3 points) that are crucial to the behaviours that we want to describe.

We must chose the relevant details in a model description

This depends on the kind of systems that we are studying but also on the kind of questions that we want to ask.

1.1.3 Newmann's "A survey of complex systems"

When physicist refers to complex systems, each of us think very different systems: it is an immense field! For example:

- Networks;
- Dynamical systems (typical approach in studying complex systems, chaotic behaviour and bifurcation theory);
- Discrete dynamics (cellular automata - CA: we place objects on a lattice and then we define some interactions and update tools letting the simulation go);
- **Scaling and criticality** (existence of power law behaviour, especially in the context of non-equilibrium phase transitions);
- Adaptation (complex adaptive systems and game theory);
- **Information theory** (pattern detection/pattern communication: a pattern is such exactly because it tells a low information content);
- **Computational complexity** (polynomial vs. NP-complete problems);
- Agent-based models.

1.2 Random walk and brownian motion

(Lesson 2 of 01/10/2020) Compiled: January 11, 2021

1.2.1 Reference books and important concepts

Livi - Politti

Reference book: *Non equilibrium statistical physics: a modern perspective* by Livi and Politi: From chapter one is important to check Brownian motion, Langevin, FP, FP formalism in order to calculate the escape time from an energy barrier, which leads to Arrhenius equation. We will treat the issue on Markov chains (always chapter one), master equations, detailed balance condition. From chapter two we will look at *linear response theory* and the connection of LRT with transport phenomena. the central issue in LRT is the idea that we have a weak perturbation driving the system out of equilibrium behaviour, it can be described in terms of equilibrium correlation function (computed in thermodynamic equilibrium). Actually the point is that, using LRT, one can derive some equations known as *Kubo relations* (or *Green-Kubo relations*) such as:

$$D = \lim_{t\to\infty} \int_0^t d\tau < v_x(t) v_x(0) > \tag{1.1}$$

The diffusion coefficient is a quantity related to a transport phenomena and can be actually expressed using the Kubo relation in a way that involves equilibrium velocity correlation function.
We will then talk about:

- *Kramers-Kronij relations* which are the either way to express the fluctuation-dissipation theorem;
- *Osager theory* and *Osager repression relation* (always in the weak perturbation limit). The idea here is to study the coupling between different observables
- ...

Mezad - Montanari

Qui continua a parlare di cosa guardare nel libro ...
Poi nella seconda parte useremo il libro su informazione e computazione che si chiama: mezad montanari

Introduzione seconda parte

1.2.2 Random Walk

A typical way of defining a random walk is to define a single step: we deal with a sequence of steps labeled by i, the step i has a length l_i and proceeds along a given direction:

$$\vec{x_i} = l_i \hat{x}_i \tag{1.2}$$

We will sample the length of each step i from a probability distribution $g(l)$, which is normalized PDF.
We are interested in the total movement $\vec{X}$, defined as the sum of all steps:

$$\vec{X} = \sum_{i=1}^{N} \vec{x_i} \tag{1.3}$$

In particular we are interested in the squared distance:

$$X^2 = \vec{X} \cdot \vec{X} = \sum_{ij} \vec{X}_i \cdot \vec{X}_j \overset{(a)}{=} \sum_i x_i^2 + \sum_{i \neq j} \vec{x_i} \cdot \vec{x_j} \tag{1.4}$$

where in (a) we split the terms the diagonal terms. Let's now consider an average over different realizations: the idea is that step direction is chosen *randomly* at each step and the most important thing is that is chosen independently on the previous steps. More formally:

$$\vec{x_i} \cdot \vec{x_j} = l_i l_j \cos(\theta_{ij}) \tag{1.5}$$

where θ_{ij} is the angle between the two directions. To sum up now at each step I chose the length of a step from a PDF AND the random angle direction independently from the previous choices.

Let's now consider the average over different realizations

$$\left\langle X^2 \right\rangle = \vec{X} \cdot \vec{X} = \sum_i \left\langle x_i^2 \right\rangle + \sum_{i \neq j} \left\langle \vec{x_i} \cdot \vec{x_j} \right\rangle \overset{(b)}{=} \sum_{i=1}^{N} \left\langle l_i^2 \right\rangle = N \left\langle l^2 \right\rangle \tag{1.6}$$

where in (b) the term $\sum_{i \neq j} \left\langle \vec{x_i} \cdot \vec{x_j} \right\rangle = 0$ is due to the assumption of independence in the choice of direction for each step because there is no correlation between difference steps on average.

Let's say now that the PDF $g(l)$ is a *poisson distribution*:

$$g(l) = \frac{1}{\lambda} e^{-\frac{l}{\lambda}} \tag{1.7}$$

In the contest of kinetic theory λ is known as the **mean free path** (the average length of each step) because if we evaluate the average value of l given the poisson distribution we get $\langle l \rangle = \lambda$.
Let's introduce the total length travelled by the walker on average[2]:

$$\langle L \rangle = \lambda N \overset{(c)}{:=} \langle v \rangle t \tag{1.8}$$

If we are interested in the average value of $\left\langle l^2 \right\rangle = 2\lambda^2$ and in the MSD of the total distance travelled by the random walker from the starting point of the random walk as a function of time:

$$\left\langle X^2 \right\rangle = 2N\lambda^2 = 2\lambda \langle v \rangle t = 2dDt \tag{1.9}$$

where d is the space dimension and $D := \lambda < v >$ is the **diffusion coefficient**. In this way we have found the expected diffusion behaviour. In this way we can connect the diffusion coefficient with λ and with the average velocity.

Let's make now an example with an air molecule @$T = 20°C$: we can divide the average velocity from the Maxwell velocities distribution:

$$\langle v \rangle = \sqrt{\frac{8T}{\pi m}} \sim 450 m/s \tag{1.10}$$

where m is the mass of the molecule and assuming *as in the rest of the course* $k_B = 1$. Then, from kinetic theory, we can derive the following equation:

$$\lambda = \langle v \rangle \tau = \frac{1}{\sqrt{2} n \sigma} \tag{1.11}$$

where $\sigma = 4\pi r^2$ is the collision cross section (with r molecular size $\sim$ radius if the molecule is spherical) and n is the density (we can calculate it from the perfect gas law). At this point we can estimate the mean free path $\lambda \sim 60\, nm$;: τ is called instead **collision time** and it's the typical time between subsequent collisions in the gas which is of the order of $\sim \mathcal{O}(10^{-11})\, s$. In the end we can estimate $D \sim 9\, mm^2/s$ for a molecule in a gas.

---

[2] ∧I.e. the sum of all steps, which is different from X^2: the latter is the final distance at which the walker is found from the starting point. In (c) we defined the average velocity, but it is also a trick to introduce time in this formulation of the random walk problem.

1.2.3 Brownian motion

We are dealing now with mesoscopic[3], particles of size $R \sim 1 - 10\,\mu m$ moving in a fluid. The trick of the separation between time scales is based on the mesoscopic nature of brownian particles: on one hand we treat them as macroscopic objects and in this sense *dissipation* is described using **Stoke's law** which states:

$$\vec{F} = m\frac{d\vec{v}}{dt} = -\tilde{\gamma}\vec{v} \overset{(*)}{=} -6\pi\eta R\vec{v} \tag{1.12}$$

$$\tag{1.13}$$

where $\tilde{\gamma}$ is the *friction coefficient.* In the Stoke's regime we can express the friction coefficient with the viscosity η and the size of browninan particles; (*) works with spherical particles assumption only.
We can observe that $\tilde{\gamma}/m$ is just the inverse of a time scale (that we will call $\mathbf{t_d} := \frac{\mathbf{m}}{}$) (*dissipation timescale*, typical time in which dissipation takes place).

$$\frac{d\vec{v}}{dt} = -\frac{\tilde{\gamma}}{m}\vec{v} \tag{1.14}$$

Using the Stoke's relation for the friction coefficient we can write that (using the water's viscosity):

$$t_d = \frac{m}{6\eta\pi R} \sim \mathcal{O}(10^{-7})\,s \tag{1.15}$$

as we can see $t_d >> \tau$ so the typical time in which dissipation takes place is much larger than the typical time between two subsequent collisions of the brownian particles. Again, the idea is the same we have to deal with particles whose size is much bigger than the fluid's constituents and the key is the separation between the two timescales.
To be explicit:

$$\begin{cases} t >> t_d & \textbf{Diffusive regime} \\ t << t_d & \textbf{Balistic regime} \end{cases}$$

To sum up: brownian motion and diffusive behaviour emerges because the two scales are separated. We can describe these equations in a macroscopic way and somehow the emergence of brownian motion/random walk behaviour for a physical brownian particle is an example of a *emergent behaviour.*

1.3 Langevin equation and FP approach

1.3.1 The Langevin equation

(Lesson 3 of 07/10/2020) Compiled: January 11, 2021

There are two theoretical ways to deal with the description of brownian particles: the first one is the Langevin equation.

$$m\frac{dv_i}{dt} = -\underbrace{\tilde{\gamma}v_i(t)}_{\mathbf{I}} + \underbrace{\tilde{\eta}_i(t)}_{\mathbf{II}} \tag{1.16}$$

---

[3] ∧Much larger than the size of the fluid constituents, namely $\sim \mathring{A}$

where **I** is the term referred to the *macroscopic dissipation*, while **II** is the term referred to the *stochastic microscopic noise term.* What we know about the noise η is that:

$$\langle \tilde{\eta}_i(t) \rangle = 0 \tag{1.17}$$

$$\left\langle \tilde{\eta}_i(t)\tilde{\eta}_j(t') \right\rangle \ = \tilde{\Gamma}\delta_{ij}\delta(t-t') \tag{1.18}$$

which means that the noise is different from zero only if we are dealing with the same component and at the same time. Let's now introduce some rescaled variables:

$$\text{where} \qquad \gamma := \frac{\tilde{\gamma}}{m}; \qquad \eta_i := \frac{\tilde{\eta}_i}{m}; \qquad \Gamma := \frac{\tilde{\Gamma}}{m^2} \tag{1.19}$$

Now we can rewrite the Langevin equation in a more compact way, without the mass of the particle entering the equation:

$$\frac{dv_i}{dt} = -\gamma v_i(t) + \eta_i(t); \quad \langle \eta_i(t) \rangle = 0 \vee \left\langle \eta_i(t)\eta_j(t') \right\rangle \ = \Gamma\delta_{ij}\delta(t-t') \tag{1.20}$$

It is important to stress that, when we take the average of the noise, we average *over different realizations of the system* (realizations in the sense of stochasticity). For a given realization I chose some explicit value for the stochastic variable η, then I repeat this over a different realization.

One can formally integrate the Langevin equation. A formal solution can be written in this way (starting the integral from 0):

$$v_i(t) = \exp(-\gamma t)[v_i(0) + \int_0^t d\tau \exp(\gamma\tau)\eta_i(\tau)] \tag{1.21}$$

Taking the average velocities over the different realizations (i.e. over noises) we get:

$$\langle v_i(t) \rangle = v_i(0)\exp(-\gamma t) \tag{1.22}$$

$$\left\langle v_i^2(t) \right\rangle = v_i^2(0)\exp(-2\gamma t) + \frac{\Gamma}{2\gamma}[1-\exp(-2\gamma t)] \tag{1.23}$$

$$\xrightarrow{t\to\infty} \frac{\Gamma}{2\gamma} \tag{1.24}$$

Now we can relate this result to the behaviour at the thermodynamic equilibrium: assuming that asymptotically my system reaches thermodynamic equilibrium, we can use the equipartition theorem, which states that: [4]

$$\left\langle \frac{1}{2} m v_i^2(t) \right\rangle = T/2 \tag{1.25}$$

By comparing (1.61) and (1.25) we can get a relation between the Γ parameter and the temperature:

$$\frac{m\Gamma}{2\gamma} = T \quad \Longrightarrow \quad \Gamma = \frac{2\gamma}{m}T \quad \Longrightarrow \quad \tilde{\Gamma} = 2\tilde{\gamma}T \tag{1.26}$$

---

[4] ∧Remember that k_B is set to 1 for all the entire course!

This kind of relation is a first example of **fluctuation-dissipation relation**: the idea is that this relation connects *dissipation* (the friction coefficient $\tilde{\gamma}$) and *thermal fluctuation at equilibrium* $\tilde{\Gamma}$ (strenght of the noise). To derive this the assumption of thermal equilibrium was crucial.

Let's now compute the MDS (more precisely the MDS part related to the i-th component:

$$\left\langle (x_i(t)-x_i(0))^2 \right\rangle = \left\langle [\int_0^t v_i(\tau)d\tau]^2 \right\rangle = \tag{1.27}$$

$$= (v_i(0)^2 - \frac{\gamma}{2\gamma})[\frac{1-\exp(-\gamma t)}{\gamma}]^2 + \frac{\Gamma}{\gamma^2}t- \tag{1.28}$$

$$- \frac{\Gamma}{\gamma^3}(1-\exp(-\gamma t)) \tag{1.29}$$

What is relevant here is that we can clearly see the two different regimes:

- $\sim v_i^2(0)t^2$ BALLISTIC REGIME[5] $t << t_d = \frac{1}{\gamma}$
- $\sim \Gamma/\gamma^2 t := 2Dt$ DIFFUSIVE REGIME[6] $t >> t_d$

$$D = \frac{\Gamma}{2\gamma^2} = \frac{T}{\gamma}m = \frac{T}{\tilde{\gamma}} \tag{1.30}$$

where $D = \frac{T}{\tilde{\gamma}}$ is the **Einstein relation**.

One formally defines the diffusion coefficient D as:

$$\lim_{t\to\infty} \frac{\left\langle (\vec{x}(t)-\vec{x}(0))^2 \right\rangle}{t} = 2dD \tag{1.31}$$

1.3.2 Langevin equation with an external conservative force

Let's now consider an extension of the Langevin equation in the presence of a conservative force. As we know if a force is conservative (not necessarily uniform) $\vec{F}(\vec{x}) = -\vec{\nabla}U(\vec{x})$, where U is a potential energy and essentially now we will introduce the position x (previously the Langevin equation was a differential equation fro the velocities):

$$m\frac{d\vec{v}}{dt} = m\frac{d^2\vec{x}}{dt^2} = -\vec{\nabla}U(\vec{x}) - \tilde{\gamma}\frac{d\vec{x}}{dt} + \tilde{\eta}(t) \tag{1.32}$$

The fluctuations due to the thermal noise is the case of a brownian particle are provided by microscopic collisions of the particle with the constituents of the fluids [thermal fluctuations] and those fluctuations are described using the stochastic (noise term)/force η.

---

[5] ∧Taylor expanding the exponential terms we get that distance is scaling linearly with time depending on the initial velocity.

[6] ∧All the exponential terms go away and the leading term is the one which is linear in time (the second one): asymptotically the MSD is linear in time and so distance scales as the square root of time.

1.3.3 Fokker Plank approach

In this case the idea of dealing with stochasticity is to deal with probability distribution for the position of the brownian particles at time t $p(\vec{x},t)$ PDF IN $\vec{x}$ at time t. Once we know this PDF we can sample it and in this way we can sample different realization of our system.

Notation: with $W(\vec{x},t|\vec{x}',t+\Delta t)$ [7] we describe a conditional probability: it is the probability of getting to position $\vec{x}'$ at time $t+\Delta t$ given condition to the fact that at time t my particle was in position $\vec{x}$.

We can use this conditional probability to calculate the *transition rate* $R(\vec{x}',\vec{x})$ [8] $[s^{-1}]$.

$$R(\vec{x},\vec{x}') = \lim_{\Delta t\to 0}\frac{1}{\Delta t}W(\vec{x},t|\vec{x}',t+\Delta t) \tag{1.33}$$

This rate is a PDF in $\vec{x}'$, even if it is an object in $\vec{x}'$ and $\vec{x}$ because is a PDF considered over the possible arriving points: it originates from a conditional probability so $\vec{x}$ is somehow fixed but I can consider all possible arrival points (not clear).

I can use these rates to write a *master equation*: I want to write an equation for the rate of change of my PDF $p(\vec{x},t)$ on how the PDF is changing in time and then I can use my transition rates to write the following equation. The point is that I will have two different terms: the **gain term**, meaning that the rate of change of the probability of finding the particle in $\vec{x}$ is increasing from processes where the particle is coming from $\vec{x'}$ to $\vec{x}$:. This describes a rate transition from $\vec{x}'$ to $\vec{x}$: this is the gain term, I integrate over all the starting points. Now $\vec{x'}$ is the starting point, while $\vec{x}$ is the arrival point.
On the other hand the **loss term** were we deal with particles that leave $\vec{x}$ and go to $\vec{x}'$. In this case I am integrating all over the possible arrival points.

$$\frac{\partial p(\vec{x},t)}{\partial t} = \int d^3x' \,[\underbrace{p(\vec{x}',t)R(\vec{x},\vec{x}')}_{\text{Gain term}} - \underbrace{p(\vec{x},t)R(\vec{x}',\vec{x})}_{\text{Loss term}}] \tag{1.34}$$

The way the FP equation is derived is based on the assumption that the rates are practically non zero only for small values of $\vec{\chi} := \vec{x}' - \vec{x}$.
This is reasonable: the probability of growing from $\vec{x}$ to $\vec{x}'$ per unit time will be smaller when the distance between the two points involved in the transition becomes larger.

Therefore the idea is to Taylor expand the gain term around $\vec{\chi} = 0$ (zero movement) up to the second order:

$$\frac{\partial p(\vec{x},t)}{\partial t} = -\sum_i \frac{d}{dx_i}(a_i(\vec{x})p(\vec{x},t)) + \frac{1}{2}\sum_{ij}\frac{\partial^2}{\partial x_i \partial x_j}(b_{ij}(\vec{x})p(\vec{x},t)) \tag{1.35}$$

---

[7] ∧W(Starting point|arrival point)

[8] ∧Switched order: R(arrival point|starting point)

The zero order expansion cancels the loss term and one is left with the first and second order expansion terms. Formally I can relate the quantities a, b to the transition rates such that:

$$a_i(\vec{x}) = \int d^3\chi R(\vec{x}', \vec{x})\chi_i \tag{1.36}$$

$$b_{ij}(\vec{x}) = \int d^3\chi R(\vec{x}', \vec{x})\chi_i\chi_j \tag{1.37}$$

If we consider as example a brownian particle, $\Delta x_i = \chi_i$ is the displacement and the factor a is defined as $\vec{a} = \frac{\langle \Delta\vec{x} \rangle}{\Delta t}$: it's the average displacement per unit of time.
In the general formulation $\vec{a}, b_{ij}, R$ could also depend on the time t. In the brownian particle case I don't have a dependence on time nor a dependence from $\vec{x}$ and the quantity $\vec{a}$ is uniform and constant (see the following example, a is not always uniform and constant).
Similarly, $b_{ij} = \frac{\langle \Delta x_i \Delta x_j \rangle}{\Delta t}$ is the average squared displacement per unit of time. How do we relate these quantities to real physical quantities?
If we think about brownian particles subjected to gravity, we have an uniform constant force $\vec{F}_0 = -m\vec{g}$, therefore the average displacement $\vec{a}$ is just the *sedimentation speed* (or *drift velocity*):

$$\vec{a} = \vec{v_0} = \frac{\vec{F_0}}{\tilde{\gamma}} \tag{1.38}$$

On the other hand we can relate the quantity b_{ij} to the diffusion coefficient: if we assume an homogeneus and isotropic medium then we can say that

$$b_{ij} = 2\delta_{ij}D \tag{1.39}$$

In this simple example (constant uniform force + isotropic and homogeneus solvent) the FP equation is:

$$\frac{\partial p(\vec{x}, t)}{\partial t} = -\vec{v_0} \cdot \vec{\nabla} p(\vec{x}, t) + D\nabla^2 p(\vec{x}, t) \tag{1.40}$$

If we simplify even more, setting to zero the external force, then the FP equation becomes the standard diffusion equation:

$$\frac{\partial p(\vec{x}, t)}{\partial t} = D\nabla^2 p(\vec{x}, t) \tag{1.41}$$

If we assume the initial condition [in 1d] $p(x, 0) = \delta(x - x_0)$ then the solution to the diffusion equation is a gaussian profile whose variance is increasing with time:

$$p(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{(x - x_0)^2}{4Dt}\right) \tag{1.42}$$

As a result we can compute the average MSD:

$$\left\langle (x - \langle x \rangle)^2 \right\rangle = \left\langle x^2 \right\rangle - \langle x \rangle^2 = 2Dt \tag{1.43}$$

the equation we wrote down for the MSD is exact for any time t but this is just because we chose properly the initial conditions: in general if we chose another non-gaussian initial conditions ($\delta$is gaussian) then what happens is that the PDF becomes a gaussian only asimptotically and therefore also this relation for the MSD (1.43) holds only asimptotically. This is how we deal with the diffusive behaviour of the FP case.

Let's now go back to the more general way to write the FP equation, in order to point out an interesting property: let's derive again the fluctuation-dissipation relation in the contest of FP.

$$\frac{\partial p(\vec{x},t)}{\partial t} = -\vec{\nabla}\cdot(\vec{a}(\vec{x},t)p(\vec{x},t)) + \frac{1}{2}\sum_{ij}\frac{\partial^2}{\partial x_i \partial x_j}(b_{ij}(\vec{x},t)p(\vec{x},t)) \tag{1.44}$$

Now I can write the FP in the form of a conservation law:

$$\frac{\partial p}{\partial t} = -\vec{\nabla}\cdot\vec{J}(\vec{x},t) \tag{1.45}$$

In this way we have found the *continuity equation*: the rate of change of my probability density is associated to the flow of the current $\vec{J}$, where

$$J_i(\vec{x},t) = a_i(\vec{x},t)p(\vec{x},t) - \frac{1}{2}\sum_j \frac{\partial}{\partial x_j}(b_{ij}(\vec{x},t)\cdot p(\vec{x},t)) \tag{1.46}$$

Considering a conservative (constant but not uniform) external force $\vec{a}(\vec{x},t) = \frac{F(\vec{x})}{\tilde{\gamma}} = \vec{v_0}(\vec{x})$ and $b_{ij} = 2d\delta_{ij}$ for an isotropic/homogeneus medium. If the force is conservative it amits a potential U, so (1.46) becomes:

$$\vec{J}(\vec{x},t) = \underbrace{\frac{\vec{F}(\vec{x})}{\tilde{\gamma}}p(\vec{x},t)}_{\text{Drift current}} \quad - \quad \underbrace{D\vec{\nabla}p}_{\text{Diffusive current (Fick's law)}} \tag{1.47}$$

NB: there is a distincion between *stationary states* and *equilibrium states*. A **stationary condition** means that our PDF has no dependence on time: $\frac{\partial p}{\partial t} = 0$, which physically is what we expect for $t \to \infty$: whatever happens to our system does not depend on time. The stationary condition for (1.45) can be expressed as a vanishing condition on the divergence of the current: $\vec{\nabla}\cdot\vec{J} = 0$

A **(thermodynamic) equilibrium condition** is a stronger one: equilibrium condition implies that no curren s are flowing in the system, so $\vec{J} = 0$; as we can see equilibrium implies stationarity.

Let's calculate our FP approach at equilibrium (which implies that (1.47) must be zero) and this equation results in an expression for the probability density (whose solution is p^*):

$$\frac{\vec{\nabla}p^*}{p^*} = \frac{\vec{F}(\vec{x})}{\tilde{\gamma}D} = -\frac{\vec{\nabla}U(\vec{x})}{\tilde{\gamma}D} \tag{1.48}$$

Being $p^* = p^*(\vec{x})$ stationary, it doesn't depend on t.

$$\vec{\nabla}((\ln(p^*))) = -\frac{\vec{\nabla}U}{\tilde{\gamma}D} \implies p^*(\vec{x}) = A\exp\Big(-\frac{U(\vec{x})}{\tilde{\gamma}D}\Big) \tag{1.49}$$

What we have written is nothing but the *Boltzmann distribution* provided that $\tilde{\gamma}D = k_BT = T$: in this way we are back to Einstein's relation $D = \frac{T}{\tilde{\gamma}}$.

1.4 Chapman-Kolmogorov equation

(Lesson 4 of 08/10/20) Compiled: January 11, 2021

Let's see an application of the FP approach related to the *first exit time* from a metastable state. The idea is to have a situation like the one in Figure 1.1, where we have two minima, x_A, x_B and a barrier located at position x_M that separates the two minima. We want to know - if my brownian particle is located in the metastable state around x_A - how much time it takes on average to go over the energy barrier towards the stable state around x_B. We will call the exit time τ.

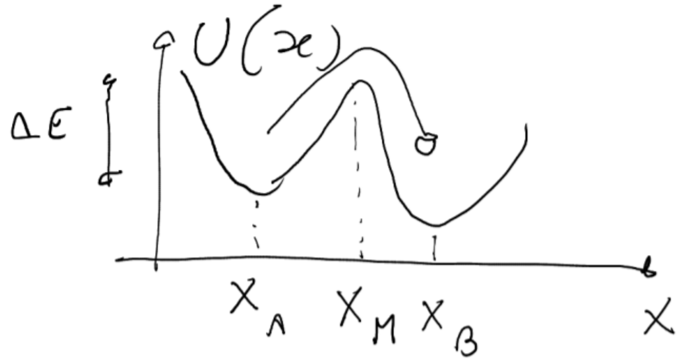


Figure (1.1) – Physical system with energy barrier $\Delta\epsilon$ and two minima used to calculate τ.

Arrhenius proposed a very simple formula: if we call $\Delta\epsilon$ the height of the energy barrier, according to Arrhenius $\tau \sim \exp\Big(\frac{\Delta\epsilon}{k_BT}\Big)$. Using the FP formalism we will derive this formula and also a more precise formula, called *Kramer's formula*, which include also the prefactors that are not present in the Arrhenius formula.

Let's start from the FP formalism in the contest of the *Chapman-Kolmogorov* (CK) equation. Let's stress the fact that we are considering stochastic processes that are continuous in time, so we will write the continuous version of the CK equation in d=1. The idea is to express the probability W decomposing the steps going from time t_0 up to time $t + \Delta t$ in an interval that goes from t_0 to t and then from t to $t + \Delta t$. Since we are in a continuous time and in a continuous space we have to integrate on all possible spatial locations of the intermediate steps y:

$$W(x_0, t_0|x, t + \Delta t) = \int dy W(x_0, t_0|y, t)W(y, t|y, t + \Delta t) \tag{1.50}$$

Starting from this CK equation, one can derive a FP equation for W that is known as **forward Kolmogorov equation** (FKE):

$$\frac{\partial W(x_0, t_0|x, t)}{\partial t} = -\frac{\partial}{\partial x}(a(x, t)W(x_0, t_0|x, t)) + \frac{1}{2}\frac{\partial^2}{\partial x^2}(b(x, t)W(x_0, t_0|x, t)) \tag{1.51}$$

where W is a function of the starting position and of the starting time and of the arrival position/time. Forward means that we are considering FP with space and time derivatives with respect the arrival time and position. The expressions for a and b are similar to the ones described in the previous lectures.

One can derive this FKE but what we actually need is that we can use the same approach deriving a **Backward Kolmogorov equation** (BKE)[9] with time and space derivatives with respect initial time and location:

$$\frac{\partial W(x_0,t_0|x,t)}{\partial t_0} = -a(x_0,t_0)\frac{\partial}{\partial x_0}[W(x_0,t_0|x,t)] - \frac{1}{2}b(x_0,t_0)\frac{\partial^2}{\partial x_0^2}[W(x_0,t_0|x,t)] \tag{1.52}$$

The BKE will be our starting point in order to calculate our ***first*** *average exit time*. Let us define formally this problem: in general we are interested in the *escape time* (or *first exit time*) problem from an interval with x_1 and x_2 boundaries, $I = [x_1, x_2]$ (we are in 1d). Our brownian particle is initially located in that in interval and we want to compute how much time it takes to the particle in order to escape from this interval. One key point in this computation is that we need at least one *absorbing boundary*, for instance x_2, such that the probability of finding a particle at the boundary is zero for all times: $x_2 \to p(x_2,t) = 0$.
Physically, if we think of probability as related to a concentration profile, saying that concentration at one boundary is zero means that once the particles reach that boundary they are immediatly taken away from the system.
We enphasize the fact that we are talking about *first* exit time because the is **no reantrance** of the particles from outside of the system. It is also important to point out that the first exit time is a stochastic random variable.

The probability of remaining in the interval I at time t after having started in x_0 is defined as (using the conditional probability W):

$$\mathbb{P}_{x_0}(t) = \int_{x_1}^{x_2} W(x_0,t_0|y,t)dy \tag{1.53}$$

In this way we are integrating over all possible locations of the particle at time t within the interval and this gives me the probability of the particle of being in the interval at time t. The point is having an absorbing boundary and with the condition of no rentrance of the particles in the system, this probability is similar to a cumulative distribution function (CDF), but why?
The first observation is that $\mathbb{P}_{x_0}(t)$ decreases with t increasing; at the initial time t_0 the conditional probability is a Dirac delta, so:

$$\mathbb{P}_{x_0}(t_0) = \int_{x_0}^{x_1} \delta(y-x_0)dy = 1 \tag{1.54}$$

and on the other hand, considering the limit of infinite time, we get that $\mathbb{P}_{x_0}(t) \xrightarrow{t\to\infty} 0$ because we have absorbing boundaries and no rentrance in the interval!

---

[9] ∧to see calculations appendix E: Kramer-Moyal expansion

In other words we can say that $\mathbb{P}_{x_0}(t)$ is the probability that the exit time $\mathbb{T}_I(x_0) > t$.

Since $\mathbb{P}_{x_0}(t)$ is more similar to a CDF, we will call $\pi(t)$ its the corresponding PDF for the random variable $\mathbb{T}_I(x_0)$: we can obtain $\pi(t)$ as follows. To be precise the correct CDF is $1 - \mathbb{P}$.

$$\begin{cases} \pi(t) = -\frac{d\mathbb{P}_{x_0}(t)}{dt} \\ \mathbb{P}_{x_0} = \int_t^{+\infty} \pi(\tau) d\tau \end{cases}$$

The quantity we are interested in is:

$$\langle \mathbb{T}_I \rangle = \int_{t_0}^{+\infty} \tau \pi(\tau) d\tau \overset{(a)}{=} t_0 + \int_{t_0}^{+\infty} \mathbb{P}_{x_0}(\tau) d\tau \tag{1.55}$$

where in (a) we performed an integration BP and we used the assumption that $\lim_{t \to \infty} t\mathbb{P}_{x_0} = 0$.

Now the idea is to consider the BKE and to perform the integration (1.53) in order to change it into an equation for $\mathbb{P}$. In doing this we are simplifing the situation too the case of the presence of constant drift force (the a term doesn't depend on time) and of homogeneus medium (D doesn't depend on space and time).

$$\frac{\partial W(x_0, t_0 | y, t)}{\partial t} = a(x_0) \frac{\partial W(x_0, t_0 | y, t)}{\partial x_0} + D \frac{\partial^2}{\partial x_0^2} [W(x_0, t_0 | y, t)] \tag{1.56}$$

Here we changed the sign because ($\frac{\partial W}{\partial t_0} = -\frac{\partial W}{\partial t}$) due to the time translation invariance, which means that W depends on $(t - t_0)$.

Now we integrate over y from x_1 to x_2 and in this way we get an equation for our CDF:

$$\frac{\partial \mathbb{P}_{x_0}(t)}{\partial t} = a(x_0) \frac{\partial}{\partial x_0} \mathbb{P}_{x_0}(t) + D \frac{\partial^2}{\partial x_0^2} \mathbb{P}_{x_0}(t) \tag{1.57}$$

It is important to stress that we have used the BKE because we are interested in the dependence from the initial position of the particle. To simplify the notation from now $x_0 \mapsto x$, where x is the initial starting position, while we set $t_0 = 0$.
Integrating the previous equation over t (with $\mathbb{P}_x(0) = 1$ and $\mathbb{P}_x(+\infty) = 0$) we get an equation for $\langle \mathbb{T}_I(x) \rangle$ as a function of the initial position x:

$$a(x) = \frac{\partial}{\partial x} \langle \mathbb{T}_I(x) \rangle + D \frac{\partial^2}{\partial x^2} \langle \mathbb{T}_I(x) \rangle = -1 \tag{1.58}$$

Let's solve this equation. The general solution is: $\Phi(x) := \exp\left[\frac{1}{D} \int_{\bar{x}}^{x} a(y) dy\right]$, where $\bar{x} \in I$ is any choice and doesn't really matter, the important thing is that the integration must stop at the initial position x (which defines Φ as a function of x).

$$\frac{d}{dx}[\Phi(x)\frac{d}{dx}\left\langle \mathbb{T}_I \right\rangle (x)] = -\frac{1}{D}\Phi(x) \tag{1.59}$$

If we substitute the expression of Φ in here we can notice that the two equations are equivalent. This expression can be solved with multiple integrations taking into account the appropriate boundary conditions:

$$\frac{d\left\langle \mathbb{T} \right\rangle_I (x)}{dx} = -\frac{1}{D}\frac{1}{\Phi(x)}\int_{x_1}^{x} dy\Phi(y) \tag{1.60}$$

Here we are considering x_1 i.e. a *reflecting boundary* which means that if $x = x_1 \implies \frac{d\langle \mathbb{T}_I(x)\rangle}{dx}|_{x=x_1} = 0$: this is the first integration step.
The second integration step is the following: here we get an equation for the first exit time as a function of x

$$\langle \mathbb{T}_I(x)\rangle = -\frac{1}{D}\int_{x_2}^{x} \frac{dy}{\Phi(y)}\int_{x_1}^{y} dz\Phi(z) \tag{1.61}$$

The previous integration over y becomes an integration over z. Here we are fixing the upper boundary condition: before we have used the BC at x_1, now we will fix the BC at x_2. In this way $\langle \mathbb{T}_I(x_2)\rangle = 0$ because x_2 is an *absorbing boundary* and it makes sense because if we start at x_2 the particle is already out and the exit time is zero.

What we had in mind since from the beginning was a situation like the one represented in Figure 1.1 in order to compute the time it takes to the particle to go from the metastable state to the stable state: in the developed formalism we identify x_2 as the position of the stable state ($x_2 = x_B$). On the other hand x_1 is a position somewhere in the steepest location where the potential energy is rising very quickly. The average exit time is not increasing moving x_1 further to the left in the limit of very high slope of the potential (reflecting BC).

The idea is that we are considering an initial position x_0 in the basin of the metastable state. The usual connection between the a term with the drift velocity and external force is:

$$a(x) = v_0(x) = \frac{F(x)}{\tilde{\gamma}} = -\frac{1}{\tilde{\gamma}}\frac{dU}{dx} \tag{1.62}$$

Now we will rewrite the equation for $\Phi(x)$ using the previous definition of the a coefficient:

$$\Phi(x) = \exp\Big[-\frac{1}{D\tilde{\gamma}}(U(x) - U(\bar{x}))\Big] \tag{1.63}$$

and finally the average exit time can be written in this way

$$\langle \mathbb{T}(x)\rangle = \frac{1}{D}\int_{x}^{x_B} dy \exp\Big(\frac{U(y)}{T}\Big)\int_{x_1}^{y} dz \exp\Big(-\frac{U(z)}{T}\Big) \tag{1.64}$$

The '-' sign disappeared from (1.61) because we inverted the boundaries of the first integral (x_2 is now on top and it is equal to x_B). On the other hand $U(\bar{x})$ doesn't enter in the final expression for the average exit time and so far it is an exact equation and the only two assumptions that we made were about the BCs.

Now we will start doing an approximation: the relevant point is to understand how to approximate the y dependence in the integral

$$\exp\Big(\frac{U(y)}{T}\Big)\int_{x_1}^{y}\exp\Big(-\frac{U(z)}{T}\Big)dz \tag{1.65}$$

The point is that integrand is dominated by the first factor $\exp\Big(\frac{U(x_M)}{T}\Big)$ for $y \sim x_M$ (i.e. when y corresponds to the height of the barrier). The second factor doesn't contribue because, provided $\Delta\epsilon \overset{*}{>>} (U(x_A) - U(x_B))$, then in this case we are interested in the position where the potential energy is minimum (because we have $-U(z)$) and I am integrating from x_1 to y and so when $y = x_M$ I already took into account the metastable state. Provided that the previous condition that we wrote is true and reminding that the stable state has less potential energy that the metastable state, the gain that I would have considering y moving towards x_B is not much because the energy difference between the stable and metastable states is much less than the height of the barrier. It is because of this assumption that we can say that the y dependence is dominated by the first term of (1.65).

If we consider $y > x_M$ the gain that I have from the second term of (1.65) is much less that the decrease that I have from the first factor. Physically this is the condition that makes the approximation (*) a sensible one.

$$\langle \mathbb{T}_t(x)\rangle \approx \frac{1}{D}\int_{x}^{x_B} dy\,\exp\Big(\frac{U(y)}{T}\Big)\int_{x_1}^{x_M} dz\,\exp\Big(-\frac{U(z)}{T}\Big) \tag{1.66}$$

To sum up the crucial point was to approximate $y \approx x_M$ in the second integral: now we have two separate integrals and we can evaluate both of them as gaussian integrals, considering a Taylor expansion around the local maximum (which implies no first order) of the energy barrier of the potential energy, doing it for example for the first one

$$U(x) = U(x_M) - \frac{1}{2}\alpha_2(y - x_M)^2 \quad \textbf{where} \quad \alpha_2 = -U''(x_M) > 0 \tag{1.67}$$

$$\approx \exp\Big(\frac{U(x_M)}{T}\Big)\int_{x\to-\infty}^{x_1\to+\infty} dy\,\exp\Big(-\frac{\alpha_2}{2T}(y - x_M)^2\Big) \tag{1.68}$$

$$\approx \sqrt{\frac{2\pi T}{\alpha_2}}\exp\Big(\frac{U(x_M)}{T}\Big) \tag{1.69}$$

Then we can do similar approximation for the second integral (the only difference is that now we are expanding around the metastable state x_A and $\alpha_1 := U''(x_A) > 0$) and we get that $I_2 \approx \sqrt{\frac{2\pi T}{\alpha_1}}\exp\Big(-\frac{U(x_A)}{T}\Big)$.

Our final (approximate) result is:

$$\langle \mathbb{T}_I(x)\rangle \approx \frac{2\pi}{\sqrt{\alpha_1\alpha_2}}\frac{T}{D}\exp\Big(\frac{\Delta U}{T}\Big) \tag{1.70}$$

where $\Delta U = U(x_M) - U(x_A)$ and in this way we recovered the Arrhenius equation: as we can see if the diffusion coefficient is increasing the average exit time is decreasing (because particles can diffuse faster).

(Lesson 5 of 14/10/20) Compiled: January 11, 2021

Let's see another application for the equation used to compute the average exit time: in the last lesson we derived an exact equation for the AET Average exit time, $\beta := (k_B T)^{-1}$:

$$\langle \mathbb{T}(x) \rangle = \frac{1}{D} \int_{x}^{x_B} dy \exp(\beta U(y)) \int_{x_1}^{x_M} dz \exp(-\beta U(z)) \tag{1.71}$$

Where x is the starting point of the brownian particle, in x_B we placed the absorbing boundary and x_1 is the reflecting boundary.
An application of equation (1.71) can be found in the computations of *Polymers' translocation time*: the general idea is that we have a wall with a hole separating in half spaces and our polymer is translocating going from the left to the right, as shown in *****.

METTI FIGURAaaaa

We define as:

- N: total number of monomers;
- n: number of already translocated monomers;
- $F(n)$: effective free energy;
- $D(n)$: effective diffusion coefficient.

The variable n is an example of *reaction coordinate* and in principle the idea is to derive an *effective free energy* as a function of the translocated monomers; along with the effective free energy one can derive an *effective diffusion coefficient* $D(n)$.

Here the idea is to study what happened in the $1d$ space as a function of n using the FP formalism obtaining an expression that is very similar to (1.71):

$$\tau = \int_{\colorbox{red}{1}}^{\colorbox{blue}{$N-1$}} dn \frac{\colorbox{green}{b^2}}{D(n)} \exp(\beta F(n)) \int_{\colorbox{violet}{1}}^{n} dm \exp(-\beta F(m)) \tag{1.72}$$

where τ is the *average translocation time* (which is a random variable) and the map colour is referred to:

- Blue: absorbing boundary condition (end of the chain);
- Red: starting point;
- Green: unit length of a monomer (length scale associated to a single monomer);
- Violet: reflective boundary condition (start of the chain).

Here we are assuming that the only important parameter is the reaction coordinate (coarse-graning approach) and we are using the effective free energy as if we were dealing with an external potential energy.

CHAPTER 2

Markov chains

2.1 Markov chains (Markov process)

So far, discussing the Langevin and FP approaches we considered *continuous time stochastic processes* and also *space* was a continuous variable.
Now we will move to stochastic processes with discrete time and discrete state space.

We define $x(t)$ as a stochastic random variable that will be chosen in a discrete (finite) space state, so $x \in S = \{S_A, \dots, S_N\}$[1] and we will label time such as: $t = 1, 2, \dots, n, \dots$.
The basic quantity we are interested in is the *probability* that (at a given time t) our process takes the value S_i:

$$p(x(t) = S_i) = p_i(t) \tag{2.1}$$

The probability $p_i(t)$ doesn't depend on previous events and that means that there is **no correlation**, so stochastic processes have no memory.

The next step is to introduce some correlations: we will introduce memory in such a way that the probability depends on the previous history of a stochastic process. In general we can deal with conditional probabilities such as[2]:

$$\Omega(x(t) = S_i | x(t-1) = S_{i_1}; x(t-2) = S_{i_2}, \dots, x(t-n) = S_{i_n}) \tag{2.2}$$

where I decided to stop the memory at time $(t-n)$. This is a general way to take into account of what happens in a process with memory n.

When we talk about of a*Markov process/chain*, this means that memory is restricted just to the previous step, so $n = 1$. The conditional probability takes this form:

$$\Omega(x(t) = S_j | x(t-1) = S_i) := W_{ji} \tag{2.3}$$

---

[1] ∧We will also generalize for $N \to \infty$.

[2] ∧The notation S_{i_1} with the i_1 index has the meaning of "state at (t-1)".

where W_{ji} are the *transition rates*[3] and the index i is the initial state, j the arrival one.

2.1.1 Homogeneous MC

In order to specify a MC I need to specify the transition rates. In the most general case the rates can depend on time but we won't consider it: we will consider only *homogeneous MC*, where the rates W_{ij} don't depend on time. We can see the elements we introduced previously (p, W) as:

$$p_i(t) \rightarrow \textit{probability vector} \text{ (N elements)} \implies \begin{cases} \sum_{i=1}^{N} p_i(t) = 1 \; \forall t \\ p_i(t) \geq 0 \, \forall i, t \end{cases}$$

$$W_{ij}(t) \rightarrow \textit{stochastic matrix} \text{ (N} \times \text{N elements)} \implies \begin{cases} \sum_{i=1}^{N} W_{ij}(t) = 1 \; \forall j \\ W_{ij} \geq 0 \; \forall i, j \end{cases}$$

When we specify the stochastic matrix, I know everything about the MC and in particular I can express the:

Stochastic dynamic rule : In order to know what is the probability of being the state j we have to sum all over the possible previous states multiplying the corresponding probability p_i for the probability to go from i to j (our transition rate):

$$p_j(t+1) = \sum_i W_{ji} p_i(t) \rightarrow \vec{p}(t+1) = W\vec{p}(t) \tag{2.4}$$

We can iterate the expression (2.4) for n steps and what we get is:

$$\vec{p}(t+n) = W^n \vec{p}(t) \tag{2.5}$$

one can show that W^n is a stochastic matrix again, so:

$$W^n \vec{p}(t) = W^n W^t \vec{p}(0) = W^{n+t} \vec{p}(0) \tag{2.6}$$

And from here we can get the **CK equation** for discrete processes:

$$\boxed{W^{n+t} = W^n W^t} \tag{2.7}$$

How can we study in general the properties of a MC?
All the properties of a MC are stored in the W_{ji} matrix, so we will consider an eigenvalue problem for W: $det(W - \lambda \mathbb{1}) = 0$.
There is a complication: the stochastic matrix W in general is **not** symmetric:, so the eigenvalues may be complex and we must distinguish between right and left eigenvectors.

---

[3] ∧To be more precise they are probabilities but since $\Delta t = 1$ we can call W_{ji} rates in analogy to FP.

$$W\bar{w}^{(\lambda)} = \lambda\bar{w}^{(\lambda)} \qquad \text{right eigenvector associated to the EGV} \quad \lambda \tag{2.8}$$

One can prove (for W stochastic matrix):

1. $|\lambda| \leq 1$;
2. At least one EGV is real and $\lambda = 1$;
3. If $\bar{w}^{(\lambda)}$ for $\lambda \neq 1 \implies \sum_i w_i^{(\lambda)} = 0$.

Point (2) is fundamental because the corresponding right eigenvector $\bar{w}^{(1)}$ is a *stationary distribution* for the Markov chain.
The eigenvalue equation for the case $\lambda = 1$ becomes:

$$W\bar{w}^{(1)} = \bar{w}^{(1)} \qquad \implies \quad \text{if} \quad \bar{p}(0) = \bar{w}^{(1)}, \quad \bar{p}(t) = \bar{p}(0)\,\forall t \tag{2.9}$$

In this case the probability vector stays the same for all times; this is why all the focus in dealing with MC properties is looking for the stationary distributions.

Let's now state the properties of MC (and stochastic matrices) in order to study the conditions for **uniqueness** and **convergence** to stationary distributions.

1. **Accessibility**: the state S_j is said to be 'accessible' from another state S_i if it is possible to go from one state to another in a finite time, i.e. $\exists\, t > 0 | (W^t)_{ji} > 0$;
2. **Irreducibility**: MC is said to be 'irreducible' if all states are accessible from any other state;
3. **Period**: we say that a given state S_i has a period[4]

   $$T := gcd\{t > 0 | (W^t)_{ii} > 0\} \tag{2.10}$$

   So we consider all possible times such that I have a finite probability to go back to the same state. If $T = 1$ we say that state S_i is *aperiodic*, while a whole MC is aperiodic if all states are aperiodic. If a MC is irreducible then all states share same T;
4. A state S_i is **persistent (recurrent)** if the probability to return to S_i in finite time is 1.

   Let's call T_i = the *first return time* to S_i (random variable):

   $$T_i := inf\{t \geq 1 | x(t) = S_i\} \quad \text{given} \quad x(0) = S_i \tag{2.11}$$

   Let's define the probability[5] $q_i^{(n)}$ that $T_i = n$ given that we are starting at $x(0) = S_i$ such that:

   $$\sum_i^{\infty} q_i^{(n)} = \begin{cases} = 1 \rightarrow \text{recurrent/persistent} \\ < 1 \rightarrow \text{transient}^6 \end{cases} \tag{2.12}$$

---

[4] ∧The term 'gdc' stays for *greatest common divisor*.

[5] ∧This is not a PDF because we are in the case with discrete time.

5. **Positive-Recurrent**: the distinction between recurrent and positive-recurrent is possible only for an infinite-state space; if $N < \infty$ recurrent $\implies$ positive-recurrent.

   We define as *mean recurrence time*:

   $$\langle T_i \rangle = \sum_{n=1}^{\infty} n q_i^{(n)} \quad \text{(this makes sense only for recurrent stages)} \tag{2.13}$$

   If $\langle T_i \rangle < \infty \implies S_i$ is called **positive-recurrent**. If $N = \infty$ positive-recurrent $\implies$ recurrent but not viceversa.

   In the end, a MC is **(pos)-recurrent** if all states are (pos)-recurrent. In other words recurrent means that we can ensure that the process always go back to the initial state in a finite time and if it is true for all states then the whole MC is recurrent; positive-recurrent means that the process is recurrent and the average of return time is finite. A MC is positive recurrent if its states are all positive-recurrent.

Theorem 1: Uniqueness If we have an *irreducible* and *positive-recurrent* MC then we can prove that a unique stationary distribution exists.

$$W\bar{w}^{(1)} \overset{\text{stat.}}{=} \bar{w}^{(1)} \quad \overset{\text{Th. 1}}{\Longrightarrow} \quad W_i^{(1)} = \frac{1}{\langle T_i \rangle} > 0 \tag{2.14}$$

which we know it's finite because the MC is pos-recurrent.

Theorem 2: Convergence For an ergodic[7] MC it can be proved that $\vec{p}(t)$ converges to the unique stationary distribution $\bar{w}^{(1)}$ (that we know for sure it exists thanks to Th. 1) for any choice of the initial condition $\bar{p}(0)$.
Formally:

$$\forall \vec{p}(0),\, \forall j \quad \sum_i (W^n)_{ji}\, p_i(0) = p_j(n) \tag{2.15}$$

And the theorem states that:

$$\boxed{\lim_{n \to \infty} p_j(n) = w_j^{(1)}} \tag{2.16}$$

Given this convergence, from a physical prospective, if ergodicity holds it allows us to exchange *ensamble averages* with *time averages.*
As a matter of fact one can show (**Th. 2 corollary**) that for a generic observable f it is actually true that the ensamble average ($\langle . \rangle$) is equal to the time average ($\bar{.}$):

$$\langle f \rangle = \bar{f} \tag{2.17}$$

Formally:

$$\sum_i f(x_i) w_i^{(1)} = \lim_{t \to \infty} \frac{1}{t} \sum_{i=1}^{t} f(x(t)) \tag{2.18}$$

---

[7] ∧Irreducible, positive-recurrent and aperiodic.

This at the base of the use of MC in the context of numerical simulations (*Monte Carlo simulations*): the goal of a simulation is to compute an average thermodinamic value at a thermal equilibrium and simulate a MC in my computer such that the stationary distribution is the Boltzmann distribution. If was able to set up an ergodic MC then I can compute the ensable average over the Boltzmann distribution just using the time average over the states that my simulation is sampling.

Going back to **Th. 1** we know that:

$$\boxed{\langle T_j \rangle = \frac{1}{w_j^{(1)}}} \tag{2.19}$$

and this relation is called **Kac's lemma**: the less time it takes to go back to the same state the more probable will be to visit the state, therefore the corresponding component in the stationary distribution will be larger.

Let us introduce a new quantity, $T_j^{(n)}$, which is the n-th return time to state S_j i.e. is the time needed to return to S_j the n-th time after the (n-1)-th visit. The total time instead is called $\mathbb{T}_M$: it's the total time needed to visit state S_j M times. From the way we described those two quantities we can relate them such that:

$$\mathbb{T}_M \sum_{n=1}^{M} T_j^{(n)} \tag{2.20}$$

Moreover, let's define $\Phi_j(\mathbb{T}_M)$ as the fraction of time spent in S_j during time $\mathbb{T}_M$. Putting together all the definitions that we introduced previously:

$$\Phi_j(\mathbb{T}_M) = \frac{M}{\mathbb{T}_M} \tag{2.21}$$

and then we can state that:

$$\langle T_j \rangle \overset{\text{time average}}{=} \lim_{M\to\infty} \frac{\mathbb{T}_M}{M} = \lim_{M\to\infty} \frac{1}{\Phi_j(\mathbb{T}_M)} \overset{\text{ensamble average}}{=} \frac{1}{w_j^{(1)}} \tag{2.22}$$

This relation shows us how (2.19) is related to the connection between time average and ensamble average in a non trivial way.

(Lesson 6 of 15/10/20) Compiled: January 11, 2021

2.2 Time-scale of convergence to equilibrium

We have seen that MC is a stochastic process with memory oneb, which means that the update rule, which tells us how to find the probability of visiting state j at time $t+1$ can be obtained with the sum of all the previous states i and multipling it by the transition rate from i to j:

$$p_j(t+1) = \sum_i W_{ji} p_i(t) \tag{2.23}$$

$$\vec{p}(t+1) = W\vec{p}(t) \tag{2.24}$$

where W_{ji} is stochastic matrix, which encodes the properties of the MC; if we find a solution of the eigenvalue problem for the stochastic matrix with eigenvalue $\lambda = 1$, then this implies that the right eigenvector is a stationary distribution for the MC:

$$W\bar{w}^{(1)} = \bar{w}^{(1)} \quad \Longrightarrow \quad \bar{w}^{(1)} = \text{stationary distribution} \tag{2.25}$$

The theorems we have seen in the last lecture are:

Theorem 1: if a MC is irreducible and positive recurrent - which means that the average return time to any state i is finite - then, upon these conditions

$$\langle T_i \rangle < +\infty \implies \bar{w}^{(1)} \textit{ unique} \text{ stationary distribution and } w_i^{(1)} = \frac{1}{\langle T_i \rangle} \tag{2.26}$$

Theorem 2: if a MC is irreducible, positive recurrent and aperiodic - meaning period (2.11) is equal to unity - then, upon these conditions we have convergence: for any choice of initial conditions we have that

$$p_j(t) = \sum_i (W^t)_{ji} p_i(0) \overset{t\to\infty}{\longrightarrow} w_i^{(1)} \tag{2.27}$$

Let's now characterize the time scale of convergence: let's study the MC in the case in which **Theorem 2** holds, whichmeans that we are dealing with a irreducible, positive recurrent and aperiodic MC (ergodic MC). Using the Perron-Frobenius theorem, which states that

$$\lambda^{(1)} = 1 > |\lambda^{(2)}| \geq |\lambda^{(3)}| \geq \dots \tag{2.28}$$

(the first eigenvalue is related to the the stationary distribution), we can use in general the set of right eigenvectors to express the probability vector as a linear combinations of all eigenvectors. The stochastic matrix is in general not symmetric and the eigenvalues can be complex numbers and we have right and left eigenvectors, where k is referred to the corresponding eigenvalue and in this contex eigenvalues are ranked according to their norm:

$$\vec{p}(t) = \sum_k \alpha_k \vec{w}^{(k)}, \quad \vec{w}^{(k)} \text{ right eigenvectors} \tag{2.29}$$

$$\alpha_k(t) = \vec{p}(t) \cdot \vec{w}_l^{(k)}, \quad \vec{w}_l^{(k)} \text{ left eigenvectors} \tag{2.30}$$

We can express the probability vector at time t as the action of the t power of the stochastic matrix on the initial condition:

$$\vec{p}(t) = W^t \vec{p}(0) = W^t [\sum_k \alpha_k(0) \vec{w}^{(k)}] \tag{2.31}$$

$$= \sum_k \alpha_k(0) (\lambda^{(k)})^t \vec{w}^{(k)} \tag{2.32}$$

From here we can see that the time dependence of the α_k coefficients can be expressed as:

$$\alpha_k(t) = \alpha_k(0)[\lambda^{(k)}]^t \tag{2.33}$$

In general eigenvalues are complex numbers, so:

$$\lambda^{(k)} = |\lambda^{(k)}| \exp(i\phi_k) \tag{2.34}$$

Now we are interested in evaluating the time dependence of these coefficients:

$$\alpha_k(t) = \alpha_k(0) \exp(it\phi_k) |\lambda^{(k)}|^t \tag{2.35}$$

$$= \alpha_k(0) \exp(it\phi_k) \exp\left(\frac{-t}{\tau_k}\right) \tag{2.36}$$

where we introduced a characteristic time $\tau_k = -1/\ln(|\lambda_k|) > 0$ since $|\lambda_k| < 1$ for $(k \geq 2)$. We are dealing then with an exponential decay in time of the α_k coefficient.

At this point we can isolate the term corresponding to the first eigenvalue, which corresponds to the stationary distribution, (and being stationary there is no time dependence in this term) and then we find:

$$\vec{p}(t) = \alpha_1(0)\vec{w}^{(1)} + \underbrace{\alpha_2(0) \exp(it\phi_2) \exp(-t/\tau_2)}_{\text{Leading term!}} + \dots \tag{2.37}$$

If we assume *no degeneracy* the leading term is the second one, because $|\lambda^{(2)}| > |\lambda^{(k)}|$ and that means $\tau_2 > \tau_k$. All other terms decay to zero exponentially and the term with the longest characteristic time is the one corresponding to the second largest normed eigenvalue.

To sum up, the characteristic time for convergence to stationarity is given by:

$$\boxed{\tau_2 = -\frac{1}{\ln\left(|\lambda^{(2)}|\right)}} \tag{2.38}$$

2.3 Detailed balance

In the infinite time limit we have discussed about *stationary* conditions but to characterize *equilibrium* we will need a stronger condition provided by detailed balance.

We will start by writing a master equation for MC. Let's write the update rule by adding and subtracting $p_i(t)$:

$$p_i(t+1) = \sum_j W_{ij} p_j(t) + p_i(t) - p_i(t) \underbrace{\sum_{ij} W_{ji}}_{=1} \tag{2.39}$$

$$= p_i(t) + \sum_j [W_{ij} p_j(t) - W_{ji} p_i(t)] \tag{2.40}$$

and taking $p_i(t)$ to the left:

$$\underbrace{p_i(t+1) - p_i(t) = \sum_{j \neq 1} [\underbrace{W_{ij} p_j}_{\text{gain term}} - \underbrace{W_{ji} p_i}_{\text{loss term}}]}_{\text{Master Equation}} \tag{2.41}$$

where the gain term is the sum over all possible previous states, while in the loss term we sum all over the possible arrival states.

Now it is immediate to see that the stationarity condition (which means $p_i(t+1) - p_i(t) = 0$) is related to:

$$\text{Stationarity condition} \iff \sum_{j \neq 1} [W_{ij} p_j - W_{ji} p_i] = 0 \; \forall \, i \tag{2.42}$$

but we can have a stronger condition, called **detailed balance**, where each single summands in the above term must be zero:

$$\text{Detailed balance} \iff W_{ij} p_j = W_{ji} p_i \; \forall \, i \neq j \tag{2.43}$$

Obviously detailed balance implies stationarity but not the other way.

2.3.1 Connection between detailed balance and reversibility

A MC for which a detailed balance is satisfied is called ***reversible MC*** and reversibility is connected to *time reversal invariance*: thermodinamic equilibrium is connected to microscopic reversibility.

When we talk about time reversal invariance essentially we say that the probability of a forward trajectory is equal to the probability of a backwards trajectory using the same dynamical rule i.e. the same stochastic matrix.
Let's consider a forward trajectory: we divide the time in $t_i = \{t_1, t_2, \ldots, t_n\}$ and we have a sequence of corresponding states $\{s_{i_0}, s_{i_1}, s_{i_2}, \ldots, s_{i_n}\}$. What is the probability of observing such trajectory for a given MC/stochastic matrix?

we want to write the probability that we observe the state s_{i_n} at time n and so on:

$$p(x(n) = s_{i_n}; x(n-1) = s_{i_{n-1}}; \ldots; x(1) = s_{i_1}; x(0) = s_{i_0}) \tag{2.44}$$

How we write this? For the initial state we have to chose an initial condition: we will chose the stationary distribution p_{i_0} for which detailed balance holds:

$$p_{i_0} \cdot W_{i_1,i_0} \cdot W_{i_2,i_1} \cdot \; \ldots \; \cdot W_{i_n,i_{n-1}} = \tag{2.45}$$

Th point is now that we can use detailed balance and we can rewrite $p_{i_0} \cdot W_{i_1,i_0}$ switching the indices of the stochastic matrix and getting $W_{i_0,i_1} \cdot p_{i_1}$ using (2.43). We can do this subsequently for all terms considering now $\{p_{i_1} \cdot W_{i_2,i_1} \rightarrow W_{i_1,i_2} \cdot p_{i_2}\}$ and so on.
In the end we will obtain the following expression for the probability of a forward trajectory (2.45):

$$= W_{i_0,i_1} \cdot W_{i_1,i_2} \cdot \; \ldots \; \cdot W_{i_{n-1},i_n} \cdot p_{i_n} \tag{2.46}$$

and this is just the expression for the backward trajectory, because now we can start from the right side of this product and it is just the probability of starting in the i_n state and then going to the i_{n-1} one and so one until we get to state i_0:

$$\underbrace{p(x(n) = s_{i_0}; x(1) = s_{i_1}; \ldots; x(0) = s_{i_n})}_{\text{Probability of backward trajectory}} \tag{2.47}$$

This is crucial because it shows the connection between detailed balance and microscopic reversibility.

Detailed balance $\Longleftrightarrow$ equilibrium (microscopic reversibility)
stronger condition than just stationarity

2.3.2 MC example: Random Walk on a ring

We will see now an example of a Random walk on a ring in one dimension: we are dealing with N states (finite space states) and our dynamical rule is such that for a given state i we can go either on the previous state $i-1$ with probability $r-1$ or to the next state $i+1$ and this may happen with probability r. the schematics of our example is represented in Figure (2.1). In this problem state $N+1$ is equal to state 1, we are using PBC.

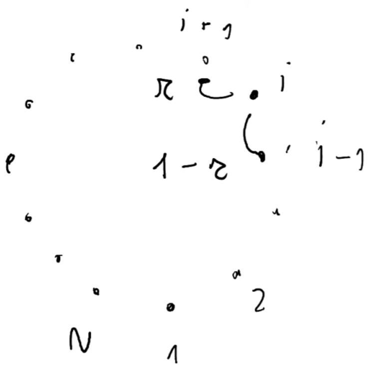


Figure (2.1) – Random Walk on a ring using with states, forward probability r and backwards probability $r-1$.

$$\text{More formally:} \begin{cases} W_{i_{i+1},i_i} = r & (2.48) \\ W_{i_{i-1},i_i} = 1 - r & (2.49) \\ W_{i.j} = 0 \qquad \text{otherwise} & (2.50) \end{cases}$$

An important observation is that the diagonal elements $W_{i,i} = 0$ so is not possible to remain in the same state: we have either go the the right or to the left.Obviously $0 \leq r \leq 1$ because it's a probability.
If we chose:

- $r = \frac{1}{2} \longrightarrow$: **symmetric (unbiased) random walk**;
- $r \neq \frac{1}{2} \longrightarrow$: **asymmetric (biased) random walk**.

We can explicitly visualize our stochastic matrix associated to a random walk on a ring:

$$W = \begin{pmatrix} 0 & 1-r & 0 & 0 & 0 & \dots & r \\ r & 0 & 1-r & 0 & 0 & & 0 \\ 0 & r & 0 & 1-r & 0 & & \vdots \\ \vdots & 0 & \ddots & \ddots & 1-r & & \vdots \\ \vdots & & \ddots & \ddots & \ddots & \ddots & \vdots \\ \vdots & & & \ddots & \ddots & \ddots & 1-r \\ 1-r & \dots & \dots & \dots & 0 & r & 0 \end{pmatrix}$$

The last entry on the first row is r due to PBC.

Let's now have a look to the stochastic update rule:

$$p_i(t+1) = (1-r)p_{i+1}(t) + r\,p_{i-1}(t) \tag{2.51}$$

We are interested in the stationary distribution, $\hat{p}_i$, which has to satisfy equation (3.107) without any dependence in time:

$$\hat{p}_i = (1-r)\hat{p}_i + r\,\hat{p}_i \tag{2.52}$$

The obvious solution is the one with constant probability $\hat{p}_i = \frac{1}{N}$: all the vector components are equal each other and each component is N^{-1} for normalization, because we want that the probability vector is normalized such that $\sum_{i=1}^{N} \hat{p}_i = 1$. Obviously, considering this solution, the stationarity condition holds $\forall\, i$.

Now the issue is *uniqueness* and *convergence*: let's have a look to the whole spectrum of the stochastic matrix W.
Starting from the eigenvalue equation:

$$W\bar{w} = \lambda\bar{w} \tag{2.53}$$

In our specific example the eigenvalue problem becomes (using k to label the states on the ring[8]):

$$(1-r)w_{k+1} + r\,w_{k-1} = \lambda w_k \tag{2.54}$$

Ansatz for the solution that will allow us to find the solution: let's rewrite the k component of the eigenvector w as follows:

$$w_k := \omega^k \tag{2.55}$$

where ω is determined by PBC. Using this ansatz we impose that:

$$w_{N+1} = w_1 \tag{2.56}$$

and this conditions tells us that

$$\boxed{\omega^N = 1} \tag{2.57}$$

---

[8] ∧We will not use i anymore because we will deal with complex eigenvalues.

We have N solutions of this equation and we need to deal with complex numbers:

$$\omega_j = \exp\left(\frac{2\pi i}{N}j\right) \tag{2.58}$$

where i is the imaginary unite, while j is an integer going from zero to $N-1$: $j = \{0, 1, \ldots, N-1\}$. These are all the possible solutions to the condition implied by the PBC on the ring, so now j labels eigenvalues and eigenvectors.

Let's now use Eq. (2.54): if we substitute the ansatz for the eigenvector component we can see that the j^{th} eigenvalue (remember that j labels different eigenvalues) can be written in this way:

$$\lambda_j = (1-r)\,\omega_j + r\frac{1}{\omega_j} = \tag{2.59}$$

then, using (2.58) and the Euler equation to express the exponential of the imaginary number as a sum of sin and cos functions:

$$= \cos\left(\frac{2\pi j}{N}\right) + i(1-2r)\sin\left(\frac{2\pi j}{N}\right) \tag{2.60}$$

Let's now have a look to what happens in the symmetric and asymmetric case

Symmetric case, $r = 1/2$: we can see in this case that, in the eigenvalues, the imaginary part vanishes: the eigenvalues are always real numbers:

$$\lambda_j = \cos\left(\frac{2\pi j}{N}\right) \in \mathbb{R} \tag{2.61}$$

Considering the transition rates then

$$r = \frac{1}{2} \qquad \Longrightarrow \qquad W_{ij} = W_{ji} \tag{2.62}$$

The fact that we get real eigenvalues is not surprising: in fact the stochastic transition matrix is symmetric in this case.

Asymmetric case, $r \neq 1/2$: Let's start by considering the eigenvalue λ_0[9]. If $j = 0$ then:

$$\lambda_0 = 1 \tag{2.63}$$

and the eigenvectors have in general components of this type (using ansatz (2.55)):

$$(1, \omega_j, \omega_j^2, \ldots, \omega_j^N) \tag{2.64}$$

In the case with $j = 0$ the corresponding eigenvector[10] is:

$$\bar{w}^{(0)} = (1, 1, \ldots, 1) \tag{2.65}$$

---

[9] ∧In this passage we need to be careful: the labeling of eigenvalues that we are using now depends on the way we enforce the PBC and is not consistent with the ranking used at the beginning of this section.

[10] ∧I'm not considering normalization in the way we wrote this eigenvector.

because $\omega_0 = 1$, as we can see from Eq. (2.58).
In the asymmetric case the imaginary part is non vanishing for $j \neq 0$. In general $\lambda_j \in \mathbb{C}$ for $j > 1$ and as we can see $W_{ij} \neq W_{ji}$.
The interesting point of this example is:

- in the symmetric case the detailed balance holds because (2.43) is verified but we need to remember that the stationary distribution is the constant one and the transition matrix is symmetric and we have *no currents in the system*: the fact that random walk is unbiased implies that *the average velocity of the random walker is zero.*

  $$\text{equilibrium and D.B. holds} \implies \text{no currents in the system}$$

- in the asymmetric case we don't have detailed balance because $p_i W_{ji} \neq p_j W_{ij}$: the stationary distribution $\hat{p}_i = 1/N$ is the same in both cases but the stochastic matrix isn't symmetric anymore. A current is flowing in the system (the random walker has a drift velocity).

This is a specific example in which we have *stationarity* but *no equilibrium.* If we compute explicitly the average velocity:

$$v = \underbrace{(+1)\,r}_{\text{Moving to R}} + \underbrace{(-1)\,(1-r)}_{\text{Moving to L}} = \tag{2.66}$$

$$= 2r - 1 = \begin{cases} > 0 & r > \frac{1}{2} \quad (2.67) \\ = 0 & r = \frac{1}{2} \quad (2.68) \\ < 0 & r = \frac{1}{2} \quad (2.69) \end{cases}$$

Problems with convergence: this example provides a case in which the assumptions needed to prove convergence in Theorem 2 are not satisfied if N is even.
In this case we can realize that we have periodicity with period 2: let's say we start at state 1, then on the next step we either go the the R or to the L. At even times we will always be at odd states and at odd times we will always be at even states *and this is true for any given time.*
Since the hypotheses of Theorem 2 are not satisfied we expect no convergence and what happens as a matter of fact is that:

$$p_i(t) \underset{t\to\infty}{\longrightarrow} \frac{1}{N} \; (= \hat{p}_i) \quad \text{does not hold for all initial conditions} \tag{2.70}$$

We can take as an example the one in which the initial condition is localized in the first state:

$$p_i(0) = \delta_{i,1} \tag{2.71}$$

and the fact that we don't see convergence is actually related to the presence of a second eigenvalue with norm equal to one and so the time scale convergence goes up to infinity. In fact, if $j = N/2$

$$\lambda_{N/2} = -1 \to \bar{w}^{(N/2)} = (+1, -1, +1, -1, \dots) \tag{2.72}$$

Nevertheless, even if we are in a situation in which we don't have formal convergence in the sense just discussed, we have a sort of *weak convergence*. In fact, considering the limit:

$$\lim_{t\to\infty} \frac{1}{t} \sum_{r_i=1}^{t} p_j(r_i) = \frac{1}{N} \tag{2.73}$$

it converges to the stationary distribution. In this way we average over the odd and even times and we recover the correct stationary distribution.

(Lesson 7 of 15/10/20) Compiled: January 11, 2021

2.4 Normalization of eigenvectors of a stochastic matrix

We were talking of MCs and of the convergence to the stationary distribution $\bar{w}^{(1)}$, where $\bar{w}^{(1)}$ is the right eigenvector of the stochastic matrix W with $\lambda = 1$:

$$W\bar{w}^{(1)} = \bar{w}^{(1)} \tag{2.74}$$

For a general initial condition of the stochastic vector at $t = 0$ we can express $\vec{p}(0)$ as a linear combination over the eigenvectors of the stochastic matrix,

$$\vec{p}(0) = \sum_k \alpha_k \bar{w}^{(k)} \tag{2.75}$$

such that, for $t \to \infty$, we get:

$$\vec{p}(t) = W^t \vec{p}(0) \underset{t\to\infty}{\to} \alpha_1 \bar{w}^{(1)} \tag{2.76}$$

But what about the normalization? What is the value of α_1?
In order to be consistent with what we've said $\alpha_1 = 1$ and now we will explain why.

In general the stochastic matrix is not symmetric and for this reason is not granted that we actually find (thinking about the finite case, $N \times N$ matrix) N eigenvectors: just the fact we wrote a linear combination in terms of N eigenvectors is not granted.
Theorems about the convergence to the stationary distribution can be proven also in these cases and in general if there is at least a second eigenvector with a second eigenvalue which is smaller than 1 then the time scale of convergence is anyway given by the mechanism that we saw in the last section.
The second point is how we defined the α_k coefficients: in general if W is asymmetric the eigenvalues/eigenvectors can be complex and therefore we need to be careful to the order in which we write the scalar product, the α_k coefficients are defined as the projection of the initial condition on the *left eigenvector*

$$\alpha_k \overset{(a)}{=} \vec{w}_l^{(k)} \cdot \vec{p}(0) = \sum_i (w_{l,i}^{(k)})^* p_i(0) \tag{2.77}$$

Where in (a) we used the usual vectors orthonormalization:

$$\vec{w}_l^{(k)} \cdot w^{(j)} = \delta_{k,j} \tag{2.78}$$

apparently there is a conflict between the orthonormalization condition (a) and the fact that $\bar{w}^{(1)}$ is a stochastic vector, therefore there is another normalization condition:

$$\sum_i w_i^{(k)} \overset{!}{=} 1 \tag{2.79}$$

How may we proceed now?
For the largest eigenvalue $\lambda^{(1)} = 1$ is easy to show that the left eigenvector is such that all its components are equal to one:

$$\boxed{w_{l,j}^{(1)} = 1} \tag{2.80}$$

And this is how you prove, for any stochastic matrix, that there is at least one stationary state distribution with eigenvalue 1.

To do that let's prove the following equation:

$$\sum_i w_{l,i}^{(1)} W_{i,j} = w_{l,j}^{(1)} \tag{2.81}$$

This is the equation that holds for a left eigenvector corresponding to eigenvalue 1, but if all components are equal to 1 we get the normalization condition for a given column of the stochastic matrix and we get:

$$\sum_i W_{ij} = 1 \tag{2.82}$$

The we can go back to the normalization condition (2.78) to write the linear combination but now this means that:

$$\sum_i \underbrace{(w_{l,i}^{(1)})^*}_{=1} \cdot w_i^{(1)} = \sum_i w_i^{(1)} \overset{(2.79)}{=} 1 \tag{2.83}$$

In this way we've shown that the normalization of the right eigenvectors as probability vectors is consistent with the usual ON condition (2.78).

The final point is to compute α_1 using (2.77) and knowing that all components of the left eigenvector are equal to 1:

$$\alpha_1 = \sum_i p_i(0) = 1 \tag{2.84}$$

For more informations about Markov chains: `Markov_chain_notes.pdf`.

Chapter 3

Linear response theory and transport phenomena

3.1 Detailed balance and Einstein relation

In this section we want to show the connection between detailed balance, microscopic reversibility and thermodynamic equilibrium in the context of Langevin equation with a conservative force (with an external potential $U(x)$). We can write the Langevin equation in this way:

$$m\ddot{x}(t) = -U'(x) - \tilde{\gamma}\dot{x}(t) + (t) \tag{3.1}$$

where $\tilde{\gamma}$ is the friction coefficient and the noise obeys the conditions:

$$\langle \tilde{\eta}(t) \rangle = 0; \quad \big\langle \tilde{\eta}(t)\tilde{\eta}(t') \big\rangle = \tilde{\Gamma}\delta(t-t') \tag{3.2}$$

so noise at different times are not correlated, while $\tilde{\Gamma}$ is a measure of the amount of noise[1].

For simplicity we will use the formalism for a discrete state space but we will keep using continuous time (since we're dealing with time derivatives). Let's now state a more general condition for detailed balance with respect the one we have seen yet: under time reversal we need to change the sign of the momentum vector $\vec{p} \overset{\text{time reversal}}{\longrightarrow} -\vec{p}$.

We will refer to:

- state $\alpha \rightarrow (x.p)$ as a state defined by *position* and *momentum*;
- state $\beta \rightarrow (x', p')$ as a state defined by *position* and *momentum*;

but under time reversal we will consider states:

- $\alpha^* = (x, -p)$;
- $\beta^* = (x', -p')$.

---

[1] $\wedge\tilde{\gamma}$ and $\tilde{\Gamma}$ are related through the Einstein relation: $\tilde{\Gamma} = 2\tilde{\gamma}T$.

Then, considering the probability of going from state α to state β in forward dynamics, the detailed balance condition becomes:

$$\boxed{p_\alpha W_{\beta,\alpha} = \rho_{\beta^*} W_{\alpha^*,\beta^*}} \tag{3.3}$$

So the probability of going from state α to state β in forward dynamics must be the same of going back from state β to state α considering backward dynamics. In the context of MC we didn't have velocities or momenta and we didn't have to change the definition of states under time reversal.
For $dt << 1$:

$$\begin{cases} x(t+dt) = x(t) + \frac{p}{m}dt & (3.4) \\ p(t+dt) = p(t) - U'(x)dt - \frac{\tilde{\gamma}}{m}p(t) + dW & (3.5) \end{cases}$$

It's important to observe that the first line of (3.5) is just deterministic, while the stochastic term enters in the second line and it is defined as:

$$dW = \int_t^{t+dt} \tilde{\eta}(t)dt \qquad \textit{Wiener process} \tag{3.6}$$

The only relevant point of a Wiener process is that dW is a gaussian stochastic variable with **zero average and variance $\tilde{\Gamma}dt$**. We will now use this in order to write down an explicit expression for the transition rates.
The *forward transition* $\alpha \to \beta$ is composed by two parts, one for the positions and one for the momenta; the first one is deterministic, while the second is stochastic and sampled from a normal distribution:

$$W_{\beta,\alpha} = \underbrace{\delta(x' - x - \frac{p}{m}dt)}_{\text{Deterministic part}} \cdot \frac{1}{\sqrt{2\pi\tilde{\Gamma}dt}} \exp\left(-\frac{\overbrace{(p' - p + U'(x)dt + \tilde{\gamma}\frac{p}{m}dt)}^{dW \text{ (from (3.5))}}{}^2}{2\tilde{\Gamma}dt} \right) \tag{3.7}$$

Now we want to express a similar equation for the *backward transition* $\beta^* \to \alpha^*$ reversing the sign of the momenta in the equation (the first gaussian part stays the same because we have to invert $p \mapsto p'$ and then change the sign):

$$W_{\alpha^*,\beta^*} = \delta(x - x' + \frac{p'}{m}dt) \cdot \frac{1}{\sqrt{2\pi\tilde{\Gamma}dt}} \exp\left(-\frac{(p' - p + U'(x')dt - \tilde{\gamma}\frac{p'}{m}dt)^2}{2\tilde{\Gamma}dt} \right) \tag{3.8}$$

The differences between positions and momenta in the previous equations are of the order of:

$$x' - x \sim dt; \quad p' - p \sim \sqrt{dt} \ (\sim dW) \tag{3.9}$$

Let's finally write an equation for the following ratio (remember that we want to recover detailed balance condition):

$$\frac{W_{\beta\alpha}}{W_{\alpha^*\beta^*}} \overset{?}{=} \left(\frac{p_{\beta^*}}{p_\alpha}\right) = \exp\left\{\frac{\tilde{\gamma}}{\tilde{\Gamma}}\Bigg(\underbrace{\frac{p^2 - p'^2}{2m}}_{\sim\sqrt{dt}} - \frac{2p}{m}U'(x)dt + \dots\Bigg)\right\} \tag{3.10}$$

In the second term of the exponential we can see an explicit dependence on dt, while the first term scales as $\sqrt{dt}$. We neglect terms of order at least $\mathcal{O}(dt^{\frac{3}{2}})$. We can rewrite the second term as follows:

$$\frac{p}{m}U'(x)dt = \frac{\cancel{p}}{\cancel{m}}\frac{U(x+dx) - U(x)}{\cancel{dx}}\cancel{dt} = U(x') - U(x) \tag{3.11}$$

What is the energy in my state α?

$$E(\alpha) = \frac{p^2}{2m} + U(x) \tag{3.12}$$

We can clearly see that the first term of the ratio (3.10) is related to the kinetic energy difference between the two states and the second term is due to the difference of potential energy, as we can see from (3.11).
Obviously under time reversal the energy of the states don't change and:

$$\begin{cases} E(\alpha^*) = E(\alpha) & (3.13) \\ E(\beta^*) = E(\beta) & (3.14) \end{cases}$$

Eventually what happens is that we can write the ratio between transition rates as:

$$\frac{W_{\beta\alpha}}{W_{\alpha^*\beta^*}} = \exp\left\{\frac{2\tilde{\gamma}}{\tilde{\Gamma}}(E(\alpha) - E(\beta))\right\} = \tag{3.15}$$

and in order to highlight the fact that we derived detailed balance in the context of Langevin equation, related to the invariance under time reversal of the equation of motion, we state that the previous ratio is equal to:

$$= \frac{p_{\beta^*}}{p_\alpha} \tag{3.16}$$

where p_α is the Boltzmann distribution provided the fact that:

$$p_\alpha(x,p) \ \alpha \ \exp\left\{-\frac{E(\alpha)}{k_B T}\right\} \quad \Longleftrightarrow \quad \boxed{k_B T = \frac{2\tilde{\gamma}}{\tilde{\Gamma}}} \tag{3.17}$$

which is again the Einstein equation.

What we saw us that the detailed balance condition is connected to microscopic reversibility and this is relation to the condition of equilibrium of thermodynamic equilibrium, provided the Einstein condition holds.

3.2 Fluctuation - dissipation relations

One key point of this topic is having equations or relations that connect on one side *transport coefficients* and on the other side *current-current equilibrium auto-correlation function*: one has to consider the auto-correlation function between some current flowing in the system at different times and then take the equilibrium average of this AC function. This results in a general way to define/compute transport coefficients.
Some example are:

- diffusion coefficients $\Longleftrightarrow$ particle current;
- thermal conductivity $\Longleftrightarrow$ energy (heat) current;
- magnetic susceptibility $\Longleftrightarrow$ magnetization current;
- viscosity $\Longleftrightarrow$ momentum current.

A general thermodynamic formalism based on Langevin and/or Fokker Plank to describe the fact of *thermal noise*. In particular (very relevant in the context of hydrodynamics) we will deal with *continuity equations*[2] and *conserved quantities.*

The final important point is the general idea behind the *linear response*: in LRT we are considering how our system respond to **small perturbations** (in the limit of vanishing small perturbations).

The idea is to perturb the system in order to become globally out of equilibrium but, since the perturbation is small, locally we can use equilibrium relations.
The central point/main result of LRT is that

the response to small perturbations will be equal related to the response to thermal fluctuations in (thermodynamic) equilibrium

and this allows us to eventually write what are known as fluctuation - dissipation relations because we are able to connect quantities that are defined out of equilibrium (dissipation) and quantities that re defined in equilibrium (equilibrium averages, current-current auto-correlation functions...)

3.2.1 Kubo relation

The Kubo relation is the first simple example FD relation involving a current and - we are in the context of a Brownian particle - involves the diffusion coefficient on one hand and the velocity-velocity auto-correlation function on the other hand.
Starting from the FP equation for a free brownian particle (in 1d):

$$\frac{\partial}{\partial t}p(x,t) = D\frac{\partial^2}{\partial x^2}p(x,t) \tag{3.18}$$

where D is assumed to be constant.

---

[2] ∧We have already seen how to write the FP equation as a continuity equation.

We already saw that the average mean squared distance from the initial point:

$$\left\langle x^2(t)\right\rangle - \left\langle x^2\right\rangle \overset{t\to\infty}{\longrightarrow} 2Dt \tag{3.19}$$

Let's manipulate (3.18) by multiplying it by x^2 and integrating it over dx:

$$\frac{\partial}{\partial t}\int_{-\infty}^{+\infty} x^2 p(x,t)dx = D\int_{-\infty}^{+\infty} x^2\frac{\partial^2}{\partial x^2}p(x,t)dx \tag{3.20}$$

$$\frac{\partial}{\partial t}\left\langle x^2(t)\right\rangle \overset{(b)}{=} 2D\int_{-\infty}^{+\infty} p(x,t)dx \overset{(c)}{=} 2D \tag{3.21}$$

$$\frac{\partial}{\partial t}\left\langle x^2(t)\right\rangle = 2D \tag{3.22}$$

So on the left side of the equation we got an (equilibrium) ensemble average of x^2 and in (b) we used an integration by parts assuming that:

$$x^2\frac{\partial}{\partial t}p \overset{x\to\pm\infty}{\longrightarrow} 0 \quad x^2\frac{\partial^2}{\partial x^2}p \overset{x\to\pm\infty}{\longrightarrow} 0 \tag{3.23}$$

while the passage in (c) is due to the normalization of the probability distribution. This means, by integrating over time (3.22):

$$\left\langle x^2(t)\right\rangle = \left\langle x^2(0)\right\rangle + 2Dt \tag{3.24}$$

i.e. the variance of the initial distribution increases linearly with the increasing of time, only if the initial condition is a delta function then the MSD is equal to $2Dt$.
Let's now rewrite $x(t), x^2(t)$ such that:

$$x(t) = \int_0^t dt'v(t') \qquad \& \qquad x^2(t) = \int_0^t dt'v(t')\int_0^t dt''v(t'') \tag{3.25}$$

Let's now consider:

$$\frac{\partial}{\partial t}x^2(t) = 2\int_0^t dt'v(t')v(t) \tag{3.26}$$

Let's now take the average (where by $\langle . \rangle$ we mean equilibrium thermodynamic average):

$$\frac{\partial}{\partial t}\left\langle x^2(t)\right\rangle = 2\int_0^t dt'\left\langle v(t')v(t)\right\rangle \tag{3.27}$$

$$\overset{(c)}{=} 2\int_0^t dt'\left\langle v(0)v(t-t')\right\rangle \tag{3.28}$$

where in (c) we remind that at equilibrium we have time translation invariance, so we subtract t' to the argument of the mean and, by defining $\tau := t - t'$ we get:

$$\frac{\partial}{\partial t}\left\langle x^2(t)\right\rangle = 2\int_0^t d\tau\left\langle \underbrace{v(\tau)v(0)}_{\text{A-C function}}\right\rangle \tag{3.29}$$

This is a second way in which we can express the time derivative of the average of MSD: comparing it with (3.22) we conclude that

$$D = \int_0^t d\tau \, \langle v(\tau)v(0)\rangle \tag{3.30}$$

In the context of FP this would be and exact equation but more generally it becomes the **Kubo relation**:

$$\boxed{D = \lim_{t\to\infty} \int_0^t d\tau \, \langle v(\tau)v(0)\rangle} \tag{3.31}$$

and in this way it holds not only for FP but also in the context of Langevin equation; in fact with FP we are always describing the diffusion regime whereas in Langevin we get to the diffusive regime only asymptotically (in a short time only ballistic regime).
This is important also in practise because this kind of relation is actually used in numerical simulations to measure the diffusion coefficient starting from the velocity-velocity A-C function.

The Kubo relation provides us a way to estimate the diffusion coefficient using the average of the current-current A-C function at different times (which in the case of particles' currents coincide with velocities).

3.3 Generalized brownian motion

So far, whenever we're dealing with FP of Langevin we were always describing a brownian particle: the point is that, in the same framework, we can describe the time evolution driven by thermal fluctuations of *any* microscopic thermodynamic observable $\mathcal{X}$.
Thermal fluctuations means that we are at (or close to, considering small perturbations) thermal equilibrium at temperature T. This approach can be justified rigorously (we won't do that).
Now we will describe how $\mathcal{X}(t)$ fluctuates in time and if we are at equilibrium, these fluctuations will be centered under some equilibrium value, called $\mathcal{X}^*$.

In general thermal equilibrium is archived in any system because there are interactions with microscopic particles (thermal bath) and the conceptual point is that equilibrium is archived through interactions with a very large number of microscopic degrees of freedom, typically of the order of $N_A \sim 10^{23}$.
The kind of fluctuations that we want to describe (in the generalized brownian motion approach) vanish in the thermodynamic limit:

$$\Delta\mathcal{X} = |\mathcal{X} - \mathcal{X}^*| \sim \frac{1}{\sqrt{N}} \tag{3.32}$$

This is due to central limit theorem because we treat the interactions with microscopic degrees of freedom as originating from independent stochastic variables and therefore there are many of them, allowing us to apply the CLT.

An interesting conclusion is that **generalized brownian motion is possible only for finite systems**: for an infinite size system there are no fluctuations due to thermal noise[3].

(Lesson 8 of 22/10/20) Compiled: January 11, 2021

The idea of generalized brownian motion is to describe the time evolution driven by thermal fluctuations of any microscopic thermodynamic observable X in the framework of FP/Langevin equation.

The fact that we deal with finite size systems is crucial in order to fluctuations to take place: we assume that thermal fluctuations are due to independent interactions with a large number of microscopic degrees of freedom. In this way we can apply the CLT and therefore the fluctuations' amplitude scales with system's size like $1/\sqrt{N}$.

The time evolution for a generic thermodynamic observable X driven by fluctuations is given by Langevin equation:

$$\tilde{\gamma}\frac{dX}{dt} = \mathcal{F}(X) + \tilde{\eta}(t) \tag{3.33}$$

where we are neglecting the mass term (*overdamped Langevin equation*), $\tilde{\gamma}$ is a generalized friction coefficient, $\mathcal{F}(X)$ is a thermodynamic force and $\tilde{\eta}$ is the stochastic noise term:

$$\langle\tilde{\eta}(t)\rangle = 0 \quad \left\langle\tilde{\eta}(t)\tilde{\eta}\left(t'\right)\right\rangle = \tilde{\Gamma}\delta\left(t-t'\right) \tag{3.34}$$

Assuming that noise in uncorrelated at different times implies that our thermodynamic observable is varying on (macroscopic) timescale which are much larger than the microscopic noise correlation time.

Using a FP description (in 1d):

$$\frac{\partial}{\partial t}P(X,t) = -\frac{\partial}{\partial X}J(X,t) \tag{3.35}$$

where P is the probability distribution and J is a generalized current, defined as:

$$J(X,t) := v(X)P(X,t) - \underbrace{\frac{\tilde{\Gamma}}{2\tilde{\gamma}^2}}_{=D}\frac{\partial}{\partial X}P(X,t) \tag{3.36}$$

and the generalized drift velocity is

$$v := \mathcal{F}(X)/\tilde{\gamma} = \frac{1}{\tilde{\gamma}}\frac{\partial}{\partial X}\mathcal{U}(X) \tag{3.37}$$

An important role is played by the thermodynamical potential $\mathcal{U}(X)$ which can be defined as a function of the value taken by our thermodynamical observable. We know that the thermodynamical potential is minimum when the observable takes the equilibrium value $X = X^*$ and $\mathcal{U}(X^*) = F(V,T)$ is the *Helmholtz free energy* (assuming we're in the fixed volume/temperature ensemble).

---

[3] ∧A field that became very popular is the stochastic thermodynamics: the smaller the systems, the larger the effects of stochasticity if we deal with thermodynamics.

Assuming that my observable X can take different values from equilibrium, this allows us to define the function $\mathcal{U}(X)$.

At (local) equilibrium[4] we know that $J = 0$ and as a consequence we can express the drift velocity as:

$$v(X) \overset{\tilde{\Gamma}=2\tilde{\gamma}T}{=} -\frac{2T}{\tilde{\Gamma}}\frac{\partial}{\partial X}\mathcal{U}(X) \tag{3.38}$$

which is different from the definition of drift velocity because we have temperature in the equation using the Einstein relation (we can do that because we're at equilibrium)[5]. Let's now Taylor expand $\mathcal{U}(X)$ around the equilibrium point:

$$\mathcal{U}(X) = F(V,T) + \frac{1}{2}\frac{\partial^2 \mathcal{U}}{\partial X^2}\Big|_{X=X^*}(X-X^*)^2 + \dots \tag{3.39}$$

and if we stop at the second order term this is equivalent to linearize the Langevin equation:

$$\frac{\partial}{\partial t}X = -\frac{2T}{\tilde{\Gamma}}\frac{\partial}{\partial X}\mathcal{U}(X) + \frac{\tilde{\eta}(t)}{\tilde{\gamma}} \simeq \tag{3.40}$$

the force in general is not a linear function of X but we can linearize (3.40) such that:

$$\simeq -\frac{2T}{\tilde{\Gamma}}\chi_X^{-1}(X-X^*) + \frac{\tilde{\eta}(t)}{\tilde{\gamma}} \tag{3.41}$$

where χ_X is known as **thermal (static) susceptibility**:

$$\chi_X := \frac{1}{\frac{d^2\mathcal{U}(X)}{dX^2}|_{X=X^*}} \tag{3.42}$$

Neglecting all the other terms in the Taylor expansion we are linearizing the thermodynamic force and the important parameter in this linearization is χ_X.

Let's consider the case of a very large susceptibility: $\chi_X >> 1$: this means that the second derivative of the potential is very small and therefore we are in a situation like the one represented in Figure 3.1.
Here the curvature is very small and this means that the restoring force is very small: if we think of this as a spring it would be very loose and so we can push the spring very far but the restoring force would be very small, the system is very susceptible to external perturbations.

On the other hand, if $\chi_X << 1$ it means that the potential derivative is very large and so the restoring force is very strong, as we can see from Figure 3.2, where the curvature is very high.
In this case, even if we moved a little away from equilibrium, the restoring force is already very large and therefore the system is not not really susceptible to external perturbations.

---

[4] ∧Implicitly: whenever $X \neq X^*$ we are globally out of equilibrium but we can still assume a local equilibrium by saying that the probability distribution has a form of a Boltzmann distribution (assuming $k_B = 1$): $P(X) = C\exp\{-\mathcal{U}(X)/T\}$.

[5] ∧We aren't writing equations which are different from the ones we already saw, but the context is different.

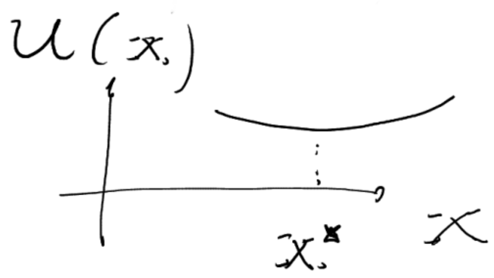


Figure (3.1) – Thermodynamic potential $\mathcal{U}$ in the case of $\chi_X >> 1$.

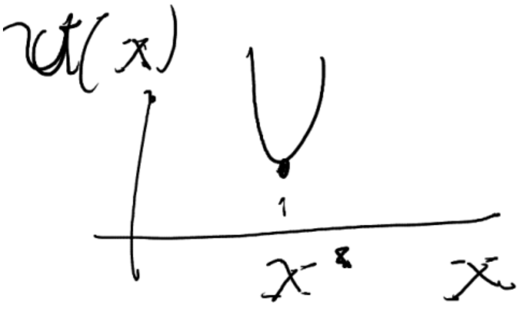


Figure (3.2) – Thermodynamic potential $\mathcal{U}$ in the case of $\chi_X << 1$.

3.4 Linear response theory introduction

In this section we will talk about how one uses microscopic dynamics (in particular Hamilton equations) combined with statistical mechanics (Boltzmann-Gibbs ensemble).

3.4.1 Microscopic dynamics

We want to describe N particles (in d dimensions): we will deal with (generalized) positions $q_i(t)$ and momenta $p_i(t)$ with $i = \{1, \ldots, N \cdot d\}$.
The Hamilton function is $\mathcal{H}(q_i, p_i) = E$ and we assume in general that energy is conserved; for miscroscopic dynamics we can write down Hamilton equation:

$$\begin{cases} \frac{dq_i}{dt} = \frac{\partial \mathcal{H}}{\partial p_i} & (3.43) \\ \frac{dp_i}{dt} = -\frac{\partial \mathcal{H}}{\partial q_i} & (3.44) \end{cases}$$

So far we are dealing with *deterministic dynamics* (microscopic reversibility and therefore time reversal invariance) and the point is that forward and backward trajectories are completely determined by initial conditions.

3.4.2 Statistical mechanics

The Boltzmann-Gibbs probability is defined as ($\beta = T^{-1}$):

$$\pi(q_i, p_i) = \frac{1}{Z} \exp\{-\beta \mathcal{H}(q_i, p_i)\} \tag{3.45}$$

where Z is the canonical partition function, $F(V,T)$ the Helmholtz free energy and ν is the phase space:

$$Z := \int_{\nu} d\nu \exp\{-\beta\mathcal{H}\} = \exp\{-\beta F(V,T)\} \quad d\nu = \frac{1}{N!}\prod_{i=1}^{Nd}(\frac{dq_i dp_i}{2\pi\hbar}) \tag{3.46}$$

Now we have a generic system with its Hamilton function and at what happens at equilibrium is describable either at microscopic level by Hamilton equation or using statistical mechanics with the partition function.

Let's now perturb the Hamiltonian: $\mathcal{H}' := \mathcal{H} - hX$: the perturbation is hX, where h is a perturbation field which is coupled to $X = X(q_i, p_i)$, which is a generic macroscopic thermodynamic observable.
A way to say that X is coupled to h is to state that h, X are conjugate thermodynamic variables where h is intensive, while X extensive (like $P - V, T - E, \mu - N$).

Let's now consider the partition function for the perturbed system:

$$Z_h = \int_{d\nu} \exp\{-\beta\mathcal{H}'\} = \exp\{-\beta F_h\} \tag{3.47}$$

where F_h is the *perturbed free energy.*
So far we've perturbed the system but we are still at equilibrium: if we consider the h dependence of F_h, this allows me to compute average equilibrium values of my observables as a function of h using

$$\frac{\partial}{\partial h}F_h = -\langle X\rangle\,; \quad \chi_X \overset{(**)}{=} \frac{\partial}{\partial h}\langle X\rangle \overset{(*)}{=} -\frac{\partial^2}{\partial h^2}F_h\,(=\frac{1}{\frac{\partial^2}{\partial X^2}\mathcal{U}(X)}) \tag{3.48}$$

as a matter of fact we can go from F_h to $\mathcal{U}(X)$ using a *Legendre transform* in order to express the static susceptibility.
Using (*) to express χ_X we can cast it in this way, relating it to the variance of X:

$$\chi_X = \beta[\langle X^2\rangle - \langle X\rangle^2] \tag{3.49}$$

In (**) we can see directly that the more the average of X changes when I change h, the more the system is susceptible to perturbations but we can already see in (3.49) that, at equilibrium level, this is connected to how much X is fluctuating.

Example: magnetic susceptibility In this example H is the magnetic field and M the macroscopic magnetization:

$$\chi = \frac{\partial}{\partial H}M = -\frac{\partial^2}{\partial H^2}F = \beta[\langle M^2\rangle - \langle M\rangle^2] \tag{3.50}$$

where $\mathcal{H}' = \mathcal{H} - HM$.

3.5 Linear response theory

So far we've just discussed equilibrium properties shifted by a perturbing field; now we will consider the response of a system to a **small** perturbation which is driving the system out-of-equilibrium.
We will start with an easy case, where the specific time dependent variation of the perturbing field h is described in Figure 3.3, essentially:

$$h(t) = \begin{cases} h & -\infty < t < 0 \qquad (3.51) \\ 0 & t > 0 \qquad (3.52) \end{cases}$$

The point is that, at $t = 0$, since the perturbation is active since $-\infty$, the system is at equilibrium in the perturbed situation; then h is switched off, so suddenly the system finds itself out-of-equilibrium and therefore what we are interested in is to describe how the system relaxes back to equilibrium for positive times in the absence of a perturbing field.

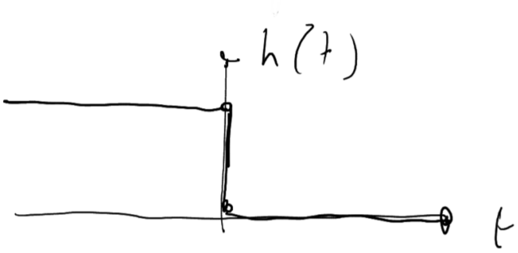


Figure (3.3) – Time dependent variation of the perturbing filed $h(t)$.

The relaxation to equilibrium is driven by the thermal bath (by all the interaction with the microscopic degrees of freedom).

At $t = 0$:

$$\langle X \rangle_h \sim \text{equilibrium average for } \mathcal{H}' \tag{3.53}$$

At $t > 0$:

$$X(t) \text{ relaxes to } \langle X \rangle_0 \tag{3.54}$$

where $\langle X \rangle_0$ is the new equilibrium value, which is the average for the unperturbed Hamiltonian.
To do that we want to 'mix together' the idea of following the microscopic dynamics given by the Hamilton equation using - at the same time - the Boltzmann-Gibbs ensemble.

The crucial point is to follow the behaviour of X as a function of t (which is a non-equilibrium quantity) defining an *out-of-equilibrium average*: not putting the label $_0$ we will consider out-of-equilibrium averages.
The idea is to average over different initial conditions for out-of-equilibrium trajectories: I'm starting in a situation in which I switch off the perturbation and so at $t = 0$ the system is out-of-equilibrium; I'm going to follow the dynamics given by the Hamilton equations (how the system relaxes to equilibrium) but I'm

considering an ensemble of possible initial conditions for the Hamilton equation and in this sense I'm introducing the idea of considering an out-of-equilibrium average.

To sum up, we are averaging over different relaxation trajectories that starts from different initial conditions:

$$\langle X(t)\rangle = \underbrace{\frac{1}{Z_h}\int_\nu \exp\{-\beta\mathcal{H}' d\nu\}}_{I}\underbrace{X(t)}_{II} \tag{3.55}$$

The point is, since I know that at $t = 0$ what happens is determined by the equilibrium with the perturbed Hamiltonian (at that time $\langle X\rangle$ e.g. is determined by the equilibrium value with the perturbed Hamiltonian), I'm going to consider the ensemble of possible initial conditions $q_i(0), p_i(0)$ for the Hamilton equations using the B-G ensemble with $\mathcal{H}'$ (using again the fact that the perturbation was ON and constant for all negative times). This is described by part I of equation (3.55).

In part II we can find the non equilibrium relaxation dynamics implied by the Hamilton equations: formally, when I write this equation

$$X(t) = X(q_i(t), p_i(t)) \tag{3.56}$$

where q, p were obtained by solving the Hamilton equations with initial conditions $q_i(0), p_i(0)$.

What we are doing is considering a given initial condition $q_i(0), p_i(0)$ and then assuming and solving Hamilton equations getting the trajectories $q_i(t), p_i(t)$ and this is defining time evolution of my macroscopic observable $X(t)$. Of course we can't do this in practise and the trick is to average different possible initial conditions, but those are determined by the B-G ensemble of the perturbed Hamiltonian because for all negative times we had the perturbation switched ON at constant value h.

Let's now assume the small perturbation hypotheses $\beta h << 1$: this means that we can expand (only to the first order) the Boltzmann factor where the perturbation enters

$$\exp\{\beta h X\} \simeq 1 + \beta h X \tag{3.57}$$

which allows me to rewrite (3.55) as:

$$\langle x(t)\rangle = \frac{\int_\nu \exp\{-\beta\mathcal{H}(q_i, p_i)\}(1 + \beta h X(0))d\nu \cdot X(t)/Z_0}{\int_\nu d\nu \exp\{-\beta\mathcal{H}(q_i, p_i)\}(1 + \beta h X(0))/Z_0} = \tag{3.58}$$

What we've done is that the Boltzmann factor which is left depends only on the unperturbed Hamiltonian, while in the factor (3.57) we're considering the initial conditions because is the perturbed one.

the trick now is to divide both the numerator and denominator for the unperturbed partition function $Z_{h=0} = Z_0$ such that now we rewrite N and D as equilibrium averages:

$$\langle x(t)\rangle = \frac{\langle (1 + \beta h X(0))X(t)\rangle_0}{\langle 1 + \beta h X(0)\rangle_0} \tag{3.59}$$

N.B.: on the left hand of this equation we have a non-equilibrium average but we manage to express it on the right side using equilibrium averages.
But how are we allowed to conclude that those a re equilibrium averages? Formally $X(t)$ is defined by following the Hamilton equations!
The trick is to change the Boltzmann factor from the perturbed Hamiltonian to the unperturbed one using the small field Taylor expansion.

At equilibrium we have time translation invariance (we can think of this as energy conservation) and this means that:

$$\langle X(t)\rangle_0 = \langle X\rangle_0 \tag{3.60}$$

because it won't depend on time.
Finally, expanding the denominator as a function of h and rearranging terms:

$$\boxed{\langle X(t)\rangle - \langle X\rangle_0 = \beta h[\langle X(t)X(0)\rangle_0 - \langle X\rangle_0^2]} \tag{3.61}$$

This is a first form of a fluctuation-dissipation relations: on the left hand side we find an out-of-equilibrium average and we're describing non-equilibrium relaxation; for infinite time, asymptotically, the left hand side will go to zero (and this is related to dissipation and entropy production).
On the right hand side we see that only equilibrium averages are present and we can see the properties of equilibrium fluctuations encoded in auto-correlation functions.
What this equation is telling us is that both of them decay in the same time and will both go to zero asymptotically. This holds only in the small perturbation limit.
If we have e.g. an exponential decay (and so a characteristic time non equilibrium relaxation or for the decay of the A-C function as a function of time) this equation is telling us that the characteristic time will be the same and so the out-of-equilibrium behaviour is related to the equilibrium behaviour of the A-C function.

(Lesson 9 of 28/10/20) Compiled: January 11, 2021

From now on we will consider $\langle X\rangle_0 = 0$ in order to simplify equations: in this way the relation (3.61) can be rewritten as

$$\langle x(t)\rangle = \beta h[\langle X(t)X(0)\rangle] \tag{3.62}$$

where the relevance of this equation is that on the left hand side we see a non equilibrium relaxation to the final equilibrium value while on the right hand side we see the behaviour of the average auto-correlation function of the observable X. the two quantities decay the same way in the limit of $\beta h << 1$ i.e. when linear response theory is valid.

Now we want to generalize (3.62) in the case of a generic perturbation $h(t)$. We will start by defining a very important quantity, which is the **response function** $\Xi(t,t')$:

$$\langle X(t)\rangle = \int dt' \Xi(t,t')h(t') \tag{3.63}$$

In principle the response function is a function of t, t' but in the context of LRT it can be expressed as a function of $(t - t')$:

$$\Xi(t,t') = \begin{cases} \Xi(t-t') & \text{if } t' < t \qquad (3.64) \\ 0 & \text{if } t' > t \text{ (Because we want causality to hold.)} \qquad (3.65) \end{cases}$$

The response function tells how the system respond to the presence of a perturbation at previous time (so t' needs to be smaller than t).
How do we determine Ξ? The trick is to consider the equation that we already derived for the previous specific case and it will allow us to derive the response function for the generic case: note that the importance of equation (3.63) is given by the fact that when we know the response function then we can compute the non-equilibrium average of the observable X for *any* external perturbation $h(t)$.

In the case represented in Figure 3.3 we get:

$$\int_{-\infty}^{0} dt' \Xi(t-t') \overset{\tau=t-t'}{=} \int_{t}^{+\infty} d\tau \Xi(\tau) \overset{(3.62)}{=} \frac{\langle X(t)\rangle}{h} = \beta \langle X(t)X(0)\rangle_0 \qquad (3.66)$$

$$\int_{t}^{+\infty} \Xi(\tau) d\tau = \beta \langle X(t)X(0)\rangle_0 \qquad (3.67)$$

In this way we are able to express the response function in terms of equilibrium averages (of the A-C function).
Now, if we derive with respect to time, we get an explicit equation for the response function:

$$\Xi(t) = -\beta\theta(t)\frac{d}{dt}\langle X(t)X(0)\rangle_0 \qquad (3.68)$$

where $\theta(t)$ is the Heaviside step function.

From now one we need to play with Fourier Transforms in order to study the properties of $\Xi(\omega)$[6]:

$$\Xi(\omega) = \int_{\mathbb{R}} e^{-i\omega t}\Xi(t)dt \qquad (3.69)$$

To clarify our FT convention we will define the IFT as:

$$\Xi(t) = \int_{\mathbb{R}} \frac{d\omega}{2\pi} e^{i\omega t}\Xi(\omega)d\omega \qquad (3.70)$$

Notice that (3.63) is a convolution so in Fourier space (FS) this expression will be a product of the two functions, therefore:

$$(3.63) \overset{FS}{\longmapsto} \langle X(\omega)\rangle = h(\omega)\cdot\Xi(\omega) \qquad (3.71)$$

and in other words in FS the out-of-equilibrium relaxation is just the product between the perturbation and the response function in FS.

---

[6] ∧We wrote $\Xi = \Xi(\omega)$ because now we are in the frequency domain.

Let's now rewrite equation (3.68), which allows us to express the response function, in FS:

$$(3.68) \xmapsto{FS} \Xi(\omega) = -\beta \int_{\mathbb{R}} \frac{d\omega'}{2\pi} \theta(\omega - \omega') \underbrace{i\omega'}_{=\frac{d}{dt}} C(\omega') \tag{3.72}$$

where $C(t) := \langle X(t)X(0)\rangle_0$ to simply notation.

Properties of $C(\omega)$

The function $C(\omega)$ is known as *power spectrum* and tells as a function of the frequency ω how the auto-correlation function is distributed. 'Power' is related to the power dissipated in the non-equilibrium relaxation.
Let's write the definition of the FT for $C(t)$:

$$C(\omega) = \int_{\mathbb{R}} dt\, e^{-i\omega t} C(t) \overset{(a)}{=} \lim_{T\to\infty} \frac{1}{T} \left\langle |X_T(\omega)|^2 \right\rangle_0 \tag{3.73}$$

Where in (a) we used the **Wiener-Kinchin theorem**, which states that the power spectrum can be expressed as the limit for infinite T of the equilibrium average of the square modulus of a function similar to a FT (in the limit of infinite T), namely:

$$X_T(\omega) = \int_{-\frac{T}{2}}^{+\frac{T}{2}} dt\, e^{-i\omega t} X(t) \tag{3.74}$$

In general the equilibrium average of X_T does not admit a FT ($\langle X(t)\rangle_0 \notin \mathbb{L}^2$) so it diverges for $T \to \infty$ and this is why we have to consider the limit to get a converging quantity.
This expression shows that $C(\omega) \in \mathbb{R}$ and $C(\omega) \geq 0 \,\forall\, \omega$: from the FT definition in (3.73) the A-C function could have been in general a complex number but actually is a real positive number for any frequency.
In order to make an example, let's consider a typical exponential decay (*Lorentzian*), e.g.:

$$C(t) = \frac{1}{\tau} \exp\left\{-\frac{|t|}{\tau}\right\} \,\forall\, t \in \mathbb{R} \tag{3.75}$$

$$C(\omega) = \underbrace{\frac{1}{1+i\omega}}_{\in \mathbb{C}} + \underbrace{\frac{1}{1-i\omega}}_{\in \mathbb{C}} = \underbrace{\frac{2}{1+\omega^2\tau^2}}_{\in \mathbb{R}} \tag{3.76}$$

Another interesting property of the power spectrum is that the A-C function is an even function of time, which implies that the power spectrum is also an even function of frequency: this is due to time translation invariance at equilibrium

$$C(t) = C(-t) \Longleftrightarrow C(\omega) = C(-\omega) \tag{3.77}$$

and due to time translation invariance at equilibrium, subtracting a t term from the A-C function arguments,

$$\langle X(t)X(0)\rangle_0 = \langle X(0)X(-t)\rangle_0 = C(-t) \tag{3.78}$$

The IFT is defined as:

$$\Xi(t) = \frac{1}{2\pi}\int_{\mathbb{R}} \exp\{i\omega t\}\Xi(\omega) \tag{3.79}$$

and the point is that it is useful to analytically extend the response function in the frequency domain to imaginary/complex frequencies: let's add to the frequency $\omega \in \mathbb{R}$ an imaginary part, namely

$$z := \omega - i\epsilon \tag{3.80}$$

In order for the causality to hold i.e. $\Xi(t) = 0$ for $t < 0$, this implies that, extending the response function to a whole complex plain, $\Xi(z)$ needs to be *analytic* $Im(z) < 0$: this is due to the fact that if the response function is analytic then there are no poles in the lower half of the complex plain and therefore we can compute the integral (3.79) in the frequency domain using *residues theorem*. Since there are no poles the exponential factor goes to zero if we are in the lower half of the complex plane (and this happens for negative times).
For negative times (if there are no poles in the lower half of the complex plain) then $\Xi(t) = 0$ and causality holds.
Let's write an expression for the FT of $\theta(t)$:

$$\theta(\omega) = \lim_{\epsilon\to 0^+}\int_0^{+\infty} dt \exp(-(\epsilon + i\omega t)) = \lim_{\epsilon\to 0^+}\frac{1}{\epsilon + i\omega} = \tag{3.81}$$

$$= \pi\delta(\omega) - iPV(\frac{1}{\omega}) \tag{3.82}$$

where PV is the *principal value*, namely:

$$PV(\frac{1}{\omega}) := \lim_{\epsilon\to 0^+}[\int_{-\infty}^{\epsilon}\frac{\phi(\omega)}{\omega}d\omega + \int_{\epsilon}^{+\infty}\frac{\phi(\omega)}{\omega}d\omega] \tag{3.83}$$

Formally the analytic continuation is a regularization and the fact that we see a PV means that all equations we will write are in general valid in the distribution space and they only makes sense only if applied to test functions $\phi(\omega)$ [7].

Thanks to (3.82) we are now able to rewrite the definition of the response function (3.72) as

$$\Xi(\omega) = -\beta[\frac{i\omega}{2}C(\omega) + PV(\int_{-\infty}^{+\infty}\frac{d\omega'}{2\pi}\frac{\omega'}{\omega - \omega'}C(\omega'))] \tag{3.84}$$

using the fact that $C(\omega)$ is a real number: essentially the first term is the imaginary part, namely (remembering that $C(\omega)$ is even but it's multiplied by ω):

$$\boxed{\Xi^{\mathrm{I}}(\omega) = -\beta\frac{\omega}{2}C(\omega)} \longrightarrow \text{odd function of}\,\omega \tag{3.85}$$

while on the other hand the real part is:

$$\boxed{\Xi^{\mathrm{R}}(\omega) = PV[\int_{-\infty}^{+\infty}\frac{d\omega'}{\pi}\frac{1}{\omega - \omega'}\Xi^{\mathrm{I}}(\omega')]} \tag{3.86}$$

---

[7] ∧Appendix F of *Livi and Politi* for more informations about the previous calculation.

In this way we just need to know the imaginary part of the response function (or only the power spectrum) to know the real part (which is clearly an even function).
Written in this general way, equations (3.85) and (3.86) are one of the typical ways to express the *fluctuation-dissipation theorem*, fluctuation because the power spectrum is related to the equilibrium average of the A-C function, while on the other hand the power spectrum is also related to energy dissipation in the non-equilibrium relaxation.

One can also express the fluctuation-dissipation theorem in a different way, called **Kramers-Kronig relation**, by writing the overall response function Xi such that:

$$\boxed{\Xi(\omega) = \lim_{\epsilon \to 0^+} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\Xi^1(\omega')}{\omega - \omega' - i\epsilon}} \tag{3.87}$$

Notice out that this expression is equivalent to the ones written above.

3.5.1 Work done on a system by the perturbation

Since we are out-of-equilibrium, we will talk how to use the previous formalism to compute the dissipation work: we are interested in the system energy $-hX$, which means that the work done by the field on the system comes with a '+' sign.
Formally, given that in general case, h is a function of time we can write that:

$$W = \int_{-\infty}^{+\infty} dt\, h(t) \left\langle \frac{dX(t)}{dt} \right\rangle \tag{3.88}$$

where the average is a *non-equilibrium average*; in the special case of periodic perturbations then the previous integral will be defined over a period of the perturbation.
In order to compute integral (3.88) we have to play with FT and the main point it is to use the Fluctuation - Dissipation theorem:

$$\langle X(t) \rangle = \int_{-\infty}^{+\infty} dt' \Xi(t - t') h(t') \tag{3.89}$$

We now consider the FT of all the quantities in the above expression ($h(t), h(t'), \Xi(t - t')$) and at the end we get (skipping the details of calculations):

$$W = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} i\omega\, \Xi(\omega) |h(\omega)|^2 \tag{3.90}$$

and since the perturbing field is real ($h(t) \in \mathbb{R}$) this implies that $h^*(\omega) = h(-\omega)$. Since the result needs to be real, this implies that the only part that contributes to the integral is just the *imaginary part* of the response function, so the dissipated work becomes:

$$W = -\int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} i\omega \Xi^{\mathrm{I}}(\omega) |h(\omega)|^2 \tag{3.91}$$

and now we use the FD theorem to express the dissipated work such as:

$$W = \frac{\beta}{2} \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \omega^2 C(\omega) |h(\omega)|^2 \tag{3.92}$$

We can see here the relevance of the power spectrum; the contribution to a dissipated work is proportional to the power spectrum and to the square modulus of the FT of ht perturbing field.
the response of a system that results in dissipation is essentially given by the power spectrum: the frequencies contributing most to the dissipated work are the frequencies for which the power spectrum is higher.

Note that the dissipation of a system, under non-equilibrium conditions is related to the power spectrum/imaginary part of a response function in the linear response framework (small perturbations).

3.5.2 Simple applications of LRT

Susceptibility

The basic definition of the response function in the frequency domain, considering the non-equilibrium average of our observable X, can be obtained as:

$$\langle X(\omega) \rangle = \Xi(\omega) h(\omega) \tag{3.93}$$

This tells us that the response function can be as well interpreted as a "dynamic" susceptibility, in the sense that it is *frequency-dependent* and essentially it measures how much the system react to a given perturbation in a way that is depending on frequency.

The usual *Static thermodynamic susceptibility* can be considered as the limiting case of a dynamic susceptibility for zero frequency (which corresponds to an infinite timescale) i.e. an equilibrium situation, namely:

$$\chi = \lim_{\omega \to 0} \Xi(\omega) = \frac{\partial \langle X(\omega) \rangle}{\partial h(\omega)} |_{\omega=0} \tag{3.94}$$

The right hand side of equation (3.94) is correct to define static susceptibility also beyond LRT.
Let's prove that this is consistent with the definition we already gave for Ξ. Using the definition of Ξ, using the FT of the time-dependent response function and taking into account the Heaviside theta function (the integral is defined in $\mathbb{R}_+$):

$$\chi = \lim_{\omega \to 0} \Xi(\omega) = \tag{3.95}$$

$$= \lim_{\omega \longrightarrow 0} -\beta \int_0^{+\infty} dt e^{-i\omega t} \frac{d}{dt} \langle X(t) X(0) \rangle_0 = \tag{3.96}$$

$$\overset{(a)}{=} \lim_{\epsilon \to 0^+} \left\{ \left[-\beta e^{-\epsilon t} \langle X(t) X(0) \rangle_0 \right]_0^{+\infty} - \beta \epsilon \int_0^{+\infty} dt e^{-\epsilon t} \langle X(t) X(0) \rangle_0 \right\} = \tag{3.97}$$

$$= \beta \left\langle X^2(0) \right\rangle_0 = \beta \left\langle X^2 \right\rangle_0 \tag{3.98}$$

where in (a) we introduced a *regularization* $z = \omega - i\epsilon$ extending the frequency ω to the complex plain. the crucial point is that we consider a specific order in the two limits: we first compute the zero frequency limit and then the $\epsilon \to 0$ limit. In (a) the first limit was already computed and we performed a BP integration.

$$\chi = \lim_{\omega \to 0} \Xi(\omega) = \beta \left\langle X^2 \right\rangle_0 \tag{3.99}$$

The equilibrium average (3.99) doesn't depend on time. Let's recall that one of the ways in which we have defined the susceptibility was related to the variance of the observable X, but assuming that the average of X is equal to zero:

$$\chi = \beta[\left\langle X^2 \right\rangle_0 - \cancel{\langle X \rangle_0^2}] \tag{3.100}$$

so we can see indeed that we recovered the correct definition for the static susceptibility.

Another interesting way to express χ is using the Kramer-Kronig relation. By introducing again a regularization and by keeping the order of the two limits the same and (we first set $\omega \to 0$ and then $\epsilon \to 0$):

$$\chi = \lim_{\epsilon \to 0^+} \lim_{\omega \to 0} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\Xi^{\mathrm{I}}(\omega')}{\omega' - \omega - i\epsilon} \tag{3.101}$$

$$= - \lim_{\epsilon \to 0^+} \int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{\Xi^{\mathrm{I}}(\omega')}{\omega' + i\epsilon} = \tag{3.102}$$

Now, recalling that:

$$\Xi^I(\omega) = -\frac{\beta\omega}{2} C(\omega) \tag{3.103}$$

we can compute the limit for $\epsilon \to 0$, substitute the imaginary part of the response function and what we get is just[8]:

$$= \frac{\beta}{2\pi} \int_{\mathbb{R}} d\omega C(\omega) \tag{3.104}$$

We conclude stating that the final relation is:

$$\chi = - \lim_{\epsilon \to 0^+} \int_{\mathbf{R}} \frac{d\omega'}{\pi} \frac{\Xi}{\omega' + i\epsilon} = \frac{\beta}{2\pi} \int_{\mathbb{R}} d\omega C(\omega) > 0 \tag{3.105}$$

In this way we recover (since we were able to express the static susceptibility as an integral of the power spectrum[9]) the fact that the static thermodynamic susceptibility is *positive.*

In general equation (3.105) is called *thermodynamic sum rule*; the one showed previously is an example applied to susceptibility but similar relations can be found for other quantities.

The point is that the thermodynamic equilibrium quantity can in general be written as the integral over frequency of the corresponding dynamic quantity, in this case the response function. This can be useful when one whats to connect the equilibrium quantities (such as χ) to quantities (such as the response functions) that control the non-equilibrium behaviour.

---

[8] ∧The ω' at the denominator cancels the corresponding factor that comes out from the previous relation.

[9] ∧Which is a real appositive number for all possible frequencies.

3.5.3 Damped harmonic oscillator

The dynamics of a damped harmonic oscillator under the action of an external driving linear force $F(t)$ is described by the Hamilton equation

$$m\ddot{x}(t)+\tilde{\gamma}\dot{x}(t)+kx(t)=F(t) \tag{3.106}$$

where x is the position of the oscillator, $\tilde{\gamma}$ is the damping friction term and k is the strength of the linear force due to a spring.
The presence of the external force corresponds to considering an energy term $-x\cdot F$, where F can be interpreted as the perturbing field (intensive quantity), while x is the observable: the formalism of linear response theory can be applied also in this case.

In this example there is no noise term in equation (3.106), which means that we don't have thermodynamics (*no temperature*) nor statistical mechanics.
The fact that the Hamilton equation (3.106) is *linear* implies that the linear response theory is **exact** and it isn't an approximation anymore in the case of an harmonic oscillator! Therefore the response function is the exact Green function of the system:

$$\Xi(t-t')=G(t-t')$$

Let's compute the Green function using the definition of response function: we know that the response is the convolution of the green function with the perturbation and since we don't have thermal noise we don't need to take averages in the equation

$$x(t)=\int_{-\infty}^{+\infty}dt'G\left(t-t'\right)F\left(t'\right) \tag{3.107}$$

and we can also express the Green function as the following IFT:

$$G(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega e^{i\omega t}G(\omega) \tag{3.108}$$

putting (3.107) and (3.108) together we obtain:

$$x(t)=\int_{-\infty}^{+\infty}dt'\frac{1}{2\pi}\int_{-\infty}^{+\infty}d\omega\, e^{i\omega\left(t-t'\right)}G(\omega)F\left(t'\right) \tag{3.109}$$

Going back to the Hamilton equation

$$F(t)=m\ddot{x}(t)+\tilde{\gamma}\dot{x}(t)+kx(t) \tag{3.110}$$

we can substitute the expression of $x(t)$ and of its derivatives that we derived in the previous equation:

$$F(t)=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\int_{-\infty}^{+\infty}dt'\left(-m\omega^2+i\tilde{\gamma}\omega+K\right)e^{i\omega\left(t-t'\right)}G(\omega)F\left(t'\right) \tag{3.111}$$

with this equation we can derive the Green function in the frequency domain and its solution is the following one:

$$G(\omega)=-\frac{1}{m\omega^2-i\tilde{\gamma}\omega-k} \tag{3.112}$$

This is true because essentially we ’cancel’ together the highlighted factors in order to have their product equal to one: therefore when that product it’s equal to one then the remaining terms becomes

$$\int \frac{d\omega}{2\pi} \rightarrow \delta(t-t') \qquad \int dt' \rightarrow F(t)$$

It is common to introduce the *natural frequency* of the undamped oscillator, $\omega_0 = \sqrt{k/m}$, and in this way we can write the Green function as follows:

$$G(\omega) = -\frac{1}{m\left(\omega^2 - i\gamma\omega - \omega_0^2\right)} \tag{3.113}$$

where $\gamma = \tilde{\gamma}/m$.

The susceptibility of the damped and forced harmonic oscillator is

$$\chi = \lim_{\omega\to 0} G(\omega) = \frac{1}{m\omega_0^2} = \frac{1}{k} = \frac{1}{\frac{d^2U}{dx^2}}$$

and so in this way we reconnect to the other definition of static susceptibility: F is the perturbation which is driving the system out of equilibrium position, x is the response of the system and $1/k$ how the response is proportional to the perturbation (and it is the static susceptibility)

$$U(x) = \frac{1}{2}kx^2; \quad F = kx \rightarrow x = \frac{F}{k}$$

The poles of $G(\omega)$ in the complex plane described in (3.113) are:

- $\omega_1 = \Omega + i\frac{\gamma}{2}$
- $\omega_2 = -\Omega + i\frac{\gamma}{2}$

where $\Omega^2 = \omega_0^2 - \frac{\gamma^2}{4}$, so Ω can be either real or complex. Using the poles we can rewrite the Green function as follows:

$$G(\omega) = -\frac{1}{m\left(\omega - \omega_1\right)\left(\omega - \omega_2\right)} \tag{3.114}$$

- If $\Omega \in \mathbb{R} \quad \rightarrow \quad \omega_0^2 > \frac{\gamma^2}{4}$ then both poles have the same real part but opposite real parts and ω_1 is the one with positive real part:

  Underdamped harmonic oscillator

- If $i\Omega \in \mathbb{R} \quad \rightarrow \quad \omega_0^2 < \frac{\gamma^2}{4}$ then the real part is zero for both poles and ω_1 is the one with the largest imaginary part:

  Overdamped harmonic oscillator

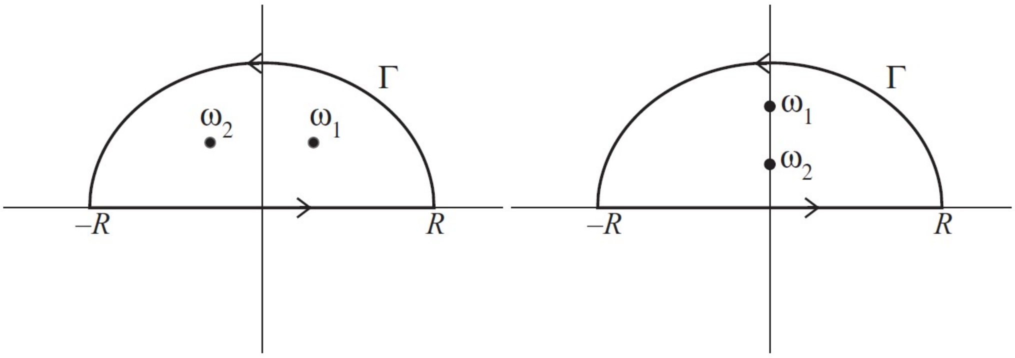


Figure (3.4) – The two poles have a different location in the underdamped case (left) and in the overdamped case (right), but they are always in the upper-half complex plane, therefore preserving causality.

There are no poles in the lower half plane and that has to do with the constraint given by *causality*, which states that $G(t) \overset{!}{=} 0$ for $t < 0$.

We can obtain an explicit expression of $G(t)$ for $t > 0$ by considering the inverse Fourier transform of $G(\omega)$:

$$G(t) = -\frac{1}{2\pi}\int_{-\infty}^{+\infty} d\omega e^{i\omega t}\frac{1}{m\left(\omega-\omega_1\right)\left(\omega-\omega_2\right)} \tag{3.115}$$

Now we will use the residues theorem and we will compute integral (3.115) over the real line using the fact that we can consider an integral over the circuit represented in Figure 3.4:

$$G(t) = -\frac{1}{2\pi m}2\pi i\left[\frac{e^{i\omega_1 t}}{\omega_1-\omega_2}+\frac{e^{i\omega_2 t}}{\omega_2-\omega_1}\right], \quad \text{with } \omega_1-\omega_2 = 2\Omega \tag{3.116}$$

Combining the two exponential factors together in order to obtain a sine function we get:

$$\boxed{G(t) = \frac{\sin(\Omega t)}{m\Omega}e^{-\gamma t/2}} \tag{3.117}$$

This relation is general, even when $\Omega \notin \mathbb{R}$, and we can point out that in the underdamped case that the Green function has an *exponential decay* with characteristic time $\tau = 2/\gamma$ and oscillations with frequency Ω.
In the overdamped case what happes is taht we have no more oscillation because Ω is now imaginary and then $\omega_{1,2}$ are pure imaginary numbers with positive imaginary part (therefore both terms correspond to an exponential decay with two different characteristic time).

In this simple example we realized that the imaginary part of the poles is related to exponential decay, whereas the real part is related to oscillations[10].

---

[10] ∧This is a general feature in the properties of response functions.

3.5.4 Strongly overdamped regime

If we set the inertial term to zero $m = 0$ then the Green function in the frequency domain becomes:

$$G(\omega) \simeq \frac{1}{k + i\tilde{\gamma}\omega} \tag{3.118}$$

and so in this approximation we have just one (imaginary) pole, namely:

$$\omega_1 = \frac{ik}{\tilde{\gamma}}$$

Let's compute the power spectrum in this simple case using the approximation (3.118):

$$C(\omega) = -\frac{2}{\beta\omega} G^I(\omega) \quad = \tfrac{-2}{\beta\omega}\tfrac{-\omega\tilde{\gamma}}{K^2+\tilde{\gamma}^2\omega^2} = \tag{3.119}$$

$$= \tfrac{2}{\beta}\tfrac{\tilde{\gamma}}{k^2+\omega^2\tilde{\gamma}}^{2} \tag{3.120}$$

which is a Lorentzian function with width of $k/\tilde{\omega}$. Our power spectrum for the harmonic oscillator in the overdamped regime can be represented as in Figure (3.5).

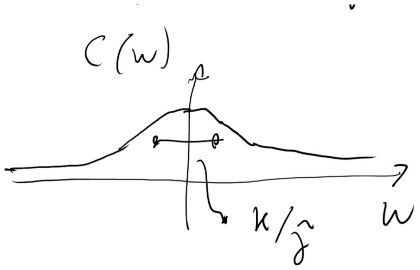


Figure (3.5) – Plot of the overdamped harmonic oscillator power spectrum.

(Lesson 10 of 29/10/20) Compiled: January 11, 2021

3.6 Hydrodynamics and Green-Kubo relation

We already derived the Kubo relation in the previous section: the main difference with respect what we have studied previously is that, when we consider hydrodynamic systems, we consider dependence also on *spatial variables* and not only on time variables: it is the same difference between the Langevin approach (in whose context we derived the Kubo relation) and the FP approach. In one case (L) we follow the trajectory of a single Brownian particle, while in the FP we follow the probability distribution/concentration profile for an ensemble of Brownian particles.

We will be dealing with the case of *free particles.* In the case of hydrodynamics in general we have a conserved quantity a (which could be $N, p, E, \dots$) with the corresponding density $\rho_a = \rho_a(\vec{x}, t)$; let's consider our problem in $3d$.
The current related to ρ_a is called $\vec{J_a} = \vec{J_a}(\vec{x}, t)$.

We know that for a conserved quantity a *continuity equation* holds:

$$\frac{\partial}{\partial t}\rho_a(\vec{x},t) = -\vec{\nabla}\cdot\vec{J}_a(\vec{x},t) \tag{3.121}$$

At this stage the continuity equation (3.121) is an example of an *exact microscopic law*: if the equation of motion (like the Hamilton equation) is such that a given quantity is conserved then (3.121) is an exact microscopic law.

Let's now consider a **phenomenological (approximate) constitutive equation** : this kind of relation holds in general for *weak gradients*, which means that we are in a situation of *local equilibrium*, in a context where we can talk of LRT.
Being a phenomenological equation implies the use of averages:

$$\left\langle \vec{J}_a(\vec{x},t)\right\rangle = -D_a\vec{\nabla}\left\langle \rho_a(\vec{x},t)\right\rangle \tag{3.122}$$

where the proportionality constant is a generalized transport coefficient.
We can simply realize the Eq. (3.122) is nothing but the Fick's law if we are dealing with number of particles as the conserved quantity and in this case the transport coefficient is the usual diffusion coefficient.
Notice that averages are involved when we write down this kind of phenomenological equations and we are dealing with non-equilibrium averages, similarly to what we already discussed.
To sum up we are considering a system mildly driven out-of-equilibrium with weak density gradients and upon this approximation we can state that the corresponding non-equilibrium current is proportional to the opposite of the gradient of the density.
The divergence of a current is zero in general to archive stationarity but at proper thermodynamic equilibrium the current itself needs to be zero: outside equilibrium the current is not zero and this is (for weak gradients) how we can compute the non-zero current in a non-equilibrium condition.

Transport coefficients can be derived also through kinetic theory e.g. for the diffusion coefficient:

$$D = \langle v\rangle \frac{\lambda}{3}$$

where λ is the mean free path. To deppen the connection with kinetic theory see Ch.1 of the *Livi, Politi* book.

Putting together the constitutive equation and the continuity equation we obtain again the FP equation in the case of a free particle for the non-equilibrium average of the density associated to a conserved quantity:

$$\frac{\partial\langle\rho_a(\vec{x},t)\rangle}{\partial t} = D_a\vec{\nabla}^2\langle\rho_a(\vec{x},t)\rangle \tag{3.123}$$

When LRT holds (which is the same approximation thanks to we can write also the constitutive equation) we can say that the no-equilibrium average is proportional to equilibrium averages and in particular we can consider that:

$$\langle\rho_a(\vec{x},t)\rangle \propto \underbrace{\left\langle\rho_a(\vec{x},t')\rho_a(\vec{y},t)\right\rangle_0}_{:=C(\vec{x}-\vec{y},t-t')} \tag{3.124}$$

Essentially we need to consider the A-C function of the density and the difference with what we saw in the previous lessons is that now we don't have only the time dependence but also upon spatial coordinates. The fact that the A-C function C at equilibrium depends on $t-t'$ is depending on time translation invariance (energy conservation) at equilibrium, while the fact that the A-C function depends on $\vec{x}-\vec{y}$ is an *assumption*: we are assuming space homogeneity in our system[11].

It's simple to realize that now we can write a FP equation for $C(\vec{x}-\vec{y},\, t-t')$[12]:

$$\frac{\partial C}{\partial t} = D\vec{\nabla}^2_{\vec{x}}C \tag{3.125}$$

Let's now consider the FT (both in space and in time) starting from the one in space (where $\vec{k}$ is the wavevector and $\int_V$ denotes the integral over the volume$V$ of the system.):

$$C\left(\vec{k}, t-t'\right) = \int_V d\vec{x}e^{-i\vec{k}\cdot(\vec{x}-\vec{y})}C\left(\vec{x}-\vec{y}, t-t'\right) = \tag{3.126}$$

exploiting the spatial homogeneity property the previous expression is independent of $\vec{y}$ and so:

$$C\left(\vec{k}, t-t'\right) = \frac{1}{V}\left\langle \rho(\vec{k},t)\rho\left(-\vec{k},t'\right)\right\rangle_0 \tag{3.127}$$

The main point is that, using the LRT trick, we are now dealing with equilibrium averages.
We can now write how the FP equation looks like in FS with respect to the spatial variables:

$$\frac{\partial C(\vec{k},t)}{\partial t} = -Dk^2C(\vec{k},t) \tag{3.128}$$

whose solution for $t>0$[13] is an exponentially decaying in time, namely:

$$C(\vec{k},t) = \exp\left(-Dk^2t\right)\underbrace{C(\vec{k},0)}_{:=\mathscr{C}} \tag{3.129}$$

The property of time reversal of the (non-equilibrium average of) A-C function holds if we assume that we have invariance under mirror symmetry: $C\left(\vec{x}-\vec{y},t\right) = C\left(\vec{y}-\vec{x},t\right)$. From this we can derive the invariance under time reversal.

Once we have solved the FP equation in FS with respect to the spatial coordinates, now we perform a time FT:

$$C(\vec{k},\omega) = \int_{-\infty}^{+\infty} dte^{-i\omega t}C(\vec{k},t) = \int_{-\infty}^{+\infty} dte^{-i\omega t}\mathscr{C}\exp\left(-Dk^2|t|\right) = \tag{3.130}$$

---

[11] ∧Just to simplify calculations.

[12] ∧From now on we will simplify the notation writing $C(\vec{x}-\vec{y},\, t-t') = C$.

[13] ∧Because we considered the initial solution at $t=0$; for negative times we can use the fact that the A-C function is even under time reversal, namely $C(\vec{k},-t) = C(\vec{k},t)$. For this reason the solution $\forall\, t$ is $C(\vec{k},t) = \mathscr{C}\exp\left(-Dk^2|t|\right)$.

$$\overset{(a)}{=}= \mathscr{C}\int_0^{+\infty} dt e^{-Dk^2 t}\left(e^{-i\omega t}+e^{i\omega t}\right) = \tag{3.131}$$

$$= \mathscr{C}\left[\frac{1}{Dk^2+i\omega}+\frac{1}{Dk^2-i\omega}\right] = \tag{3.132}$$

$$= \mathscr{C}\frac{2Dk^2}{\omega^2+\left(Dk^2\right)^2} \tag{3.133}$$

where in (a) we separated the integral in two contributions, one for positive times and the second for negative times. The result is a Lorentzian function with width Dk^2.
According to LRT this is the typical frequency at which dissipation occurs and it is also the inverse of the relaxation time to equilibrium according to the solution of the FP equation for a given $\vec{k}$ in FS.

At equilibrium, when $\vec{k}=0$ and I'm interested in the value of the conserved quantity averaged over the whole space, we don't have dissipation (the width of the Lorentzian is zero) and the relaxation time is infinite. Computing the limit:

$$\boxed{\lim_{k\to 0}\frac{1}{k^2}C(\vec{k},\omega) = \mathscr{C}\frac{2D}{\omega^2}} \tag{3.134}$$

The whole point is to be able to associate the diffusion coefficient to the current-current A-C function.

Let's now start from the continuity equation and its FT (at first with respect to the spatial coordinates):

$$\frac{\partial \rho(\vec{k},t)}{\partial t} + i\vec{k}\cdot\vec{J}(\vec{k},t) = 0 \tag{3.135}$$

From the equilibrium average of the A-C function (3.127) we compute the derivatives with respect t, t':

$$\frac{\partial}{\partial t}\frac{\partial}{\partial t'}C\left(\vec{k},t-t'\right) = \frac{1}{V}\left\langle \frac{\partial \rho(\vec{k},t)}{\partial t}\frac{\partial \rho\left(-\vec{k},t'\right)}{\partial t'}\right\rangle = \tag{3.136}$$

$$\overset{(b)}{=}\frac{1}{V}\sum_{i,j}k_i k_j\left\langle J_i(\vec{k},t)J_j\left(-\vec{k},t'\right)\right\rangle_0 \tag{3.137}$$

where in (b) we explicitly write the scalar product and because of the fact that there are two such contributions the imaginary unit isn't present anymore.
Let's now consider the time FT:

$$\int_{-\infty}^{+\infty} d\left(t-t'\right)e^{-i\omega\left(t-t'\right)} := (\star) \tag{3.138}$$

Let's apply the FT both to the left and right hand side of (3.137):

$$\omega^2 C(\vec{k},\omega) = \frac{1}{V}\int_{-\infty}^{+\infty} d(t-t')\exp\{-i\omega(t-t')\}\sum_i k_i k_j\left\langle J_i^T(\vec{k},t)J_j^T(-\vec{k},t')\right\rangle_0 \tag{3.139}$$

where in the right hand side I get the correlation function between two quantities that are essentially the *total current*:

$$J_i^T(t) := \lim_{k\to 0} J_i(\vec{k},t) = \int_V d\vec{x} J_i(\vec{x},t) \tag{3.140}$$

which is the integral of the current in the whole space, therefore we call it total current.

Let's now consider the limit of the following quantity:

$$\lim_{\omega\to 0}\lim_{\vec{k}\to 0}\frac{\omega^2}{k^2}C(\vec{k},\omega) = \frac{1}{V}\int_{-\infty}^{+\infty} d(t-t')\lim_{k\to 0}\frac{\sum_{ij}k_i k_j}{k^2}\cdot\left\langle J_i^T(t)J_j^T(t')\right\rangle_0 \tag{3.141}$$

We already assumed that our system is homogeneous in space (invariant under mirror symmetry in any direction) and now we will assume that the system is also *isotropic*, which means that the A-C function us diagonal and so for d dimension holds:

$$\left\langle J_i^T(t)J_j^T(t')\right\rangle_0 = \frac{\delta_{ij}}{d}\left\langle \vec{J}^T(t)\vec{J}_j^T(t')\right\rangle \tag{3.142}$$

using the previous relation we get:

$$\lim_{\omega\to 0}\lim_{\vec{k}\to 0}\frac{\omega^2}{k^2}C(\vec{k},\omega) = \frac{2}{Vd}\int_0^{+\infty} dt\left\langle \vec{J}^T(t)\vec{J}_j^T(t')\right\rangle_0 \tag{3.143}$$

where the yellow factor is due to the fact that we were separating the contribution of positive and negative times and we also used the invariance under time reversal of the total current $\vec{J}^T(t) = \vec{J}_j^T(-t)$ so the contribution from negative times is the same of the positive times.

If we now multiply Eq. (3.134) by ω^2 and then we take the zero frequency limit we get exactly the left hand side of eq. (3.143).
We can conclude, thanks to (3.134) and (3.143), that the transport/diffusion coefficient can be expressed in this way:

$$\boxed{D = \frac{1}{Vd\mathscr{C}}\lim_{\epsilon\to 0^+}\int_0^{+\infty} dt\exp\{-\epsilon t\}\left\langle \vec{J}^T(t)\cdot\vec{J}^T(0)\right\rangle_0} \tag{3.144}$$

where $\mathscr{C} = C(0,0) = \int_V d\vec{x}C(\vec{x},0)$ and this is known as the general *Green-Kubo relation* dealing with a generic conserved quantity. This equation expresses a transport coefficient D, associated with a density $\rho_a(\vec{x},t)$, in terms of the time integral of the auto-correlation function of the total current $\vec{J}^T(t)$.
The importance of this relation is that it can be used practically in numerical simulation computing the A-C function (and so the transport coefficient of the studied system).

Example for $1d$ system of N particles In this example particles of mass m interact through a nearest neighbour potential and so particles are arranged in lattice sites (in $1d$), defined as $V(x_{n+1} - V(x_n))$, where the subscript n labels the lattice site and the variable x_n can be read as the displacement of the nth particle with respect to its equilibrium position, as showed in Figure 3.6. If we consider PBC and if we enforce the constraint that the centre of mass velocity is null $v_{CM} = 0$ one can prove that the bulk viscosity[14] in the system η_B can be computed in this way:

$$\eta_B = \frac{1}{NT} \int_0^{+\infty} dt \, \langle J_p(t) J_p(0) \rangle_0 \tag{3.145}$$

where $J_p(t) := \sum_{n=1}^{N} F_n(t)$ is the *total momentum flux*: the flux in $1d$ is the time variation of the momentum, which is the force.

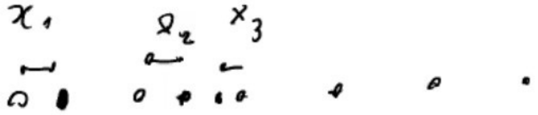


Figure (3.6) – Lattice sites.

In this context the equations of motion are:

$$m\ddot{x}_n = -F_n + F_{n-1} \tag{3.146}$$

$$F_n = -V'(x_{n+1} - x_n) \tag{3.147}$$

One can use the Green-Kubo relation to compute the thermal conductivity k:

$$\kappa = \frac{1}{NT^2} \int_0^{+\infty} dt \, \langle J_E(t) J_E(0) \rangle \tag{3.148}$$

in this case the conserved quantity is energy associated to thermal conductivity as a transport coefficient (for this reason we find the energy-energy current auto-correlation function) and the *total heat flux* can be computed such as:

$$J_E(t) = \frac{1}{2} \sum_{n=1}^{N} F_n(t) \left(\dot{x}_{n+1} + \dot{x}_n \right) \tag{3.149}$$

so the heat flux is the heat times the velocity and one takes into account in this way that there for each particle the two different contributions from the two different neighbours.

3.7 Generalized linear response functions

We have to consider that if $h(t)$ is able to perturb its conjugated macroscopic observable $X(t)$ to which it is directly coupled, it also can influence the dynamical

---

[14] ∧Viscosity is the transport coefficient associated to momentum conservation, so in this example we will be interested in the momentum current-current A-C function

state of other macroscopic observables. More precisely, we can generalize what was discussed by introducing a perturbed Hamiltonian that depends on *a set* of thermodynamic observables $X_k(t)$ and their conjugate (time-dependent) perturbation fields $h_k(t)$: therefore we will introduce different pairs of conjugated variables such that

$$\mathcal{H}' = \mathcal{H} - \sum_k h_k(t) X_k \tag{3.150}$$

The main difference with the case we've seen so far is that a given perturbation $h_j(t)$ can induce a response also in other non conjugated observables X_i with $i \neq j$.
Similarly to what we've done in the previous lectures we will assume that the equilibrium average of all observables is zero, i.e. $\langle X_k \rangle_0 = 0 \, \forall k$ and the definition of the response function is through the following equation, where we are interested in computing thee non-equilibrium average through a convolution of a response function that takes into account the response of the variable X_i to the perturbation $h_j(t)$:

$$\langle X_i(t) \rangle = \int_{-\infty}^{+\infty} dt' \Xi_{ij} \left(t - t'\right) h_j \left(t'\right) \tag{3.151}$$

The order in which we write the indexes in the response function is important because Ξ_{ij} denotes the response of variable X_i to the perturbation $h_j(t)$ and we know, similarly to what we saw in the last lectures, that we can express the response function as:

$$\Xi_{ij}(t) = -\beta \theta(t) \frac{d}{dt} \langle X_i(t) X_j(0) \rangle_0 \tag{3.152}$$

In FS (frequency domain) the definition of response function becomes:

$$\langle X_i(\omega) \rangle = \Xi_{ij}(\omega) h_j(\omega) \tag{3.153}$$

where

$$\Xi_{ij}(\omega) = -\beta \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \theta \left(\omega - \omega'\right) \left(i\omega'\right) C_{ij} \left(\omega'\right) \tag{3.154}$$

and $C_{ij}(\omega)$ is a quantity which is analogous to the power spectrum but for two different observables; it is defined as the FT of the equilibrium average correlation function:

$$\begin{aligned} C_{ij}(\omega) &= \int_{-\infty}^{+\infty} dt \exp\{-i\omega t\} \langle X_i(t) X_j(0) \rangle_0 = && (3.155) \\ &= \lim_{T \to \infty} \frac{1}{T} \left\langle |X_{i,T}^*(\omega) X_{j,T}| \right\rangle_0 && (3.156) \end{aligned}$$

where the order of the indexes is important because in this case the perturbation is j while the responding variable at later time is i and $C_{ij}(\omega) \geq 0$ is a real positive number.

The F-D relation holds in a very similar way to the previous one such that

$$\Xi_{ij}^I(\omega) = -\frac{\beta\omega}{2} C_{ij}(\omega); \quad \Xi_{ij}^R(\omega) = PV \left[\int_{-\infty}^{+\infty} \frac{d\omega'}{\pi} \frac{1}{\omega' - \omega} \Xi_{ij}^I \left(\omega'\right)\right] \tag{3.157}$$

In this way we extended what we have learnt in the previous lessons extending it to the case of the action of a perturbation inducing a response for a variable that is not the variable conjugated to it (in a thermodynamic sense).

If we chose, going back to the simplest case, the step-wise perturbation which is switched off instantaneously at $t = 0$ (which is represented in Figure 3.7), namely

$$h_i(t) = h\theta(-t) \tag{3.158}$$

we recover a simple way to express the non-equilibrium average related to an equilibrium correlation function between the two variables X_i, X_j

$$\langle X_i(t)\rangle = \beta h \langle X_i(t)X_j(0)\rangle_0 \tag{3.159}$$

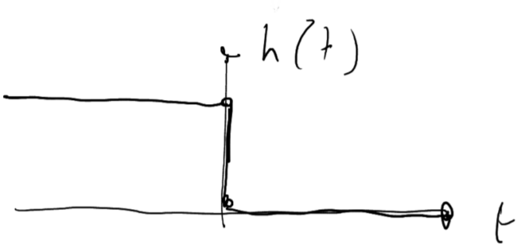


Figure (3.7) – Step-wise perturbation $h(t)$.

where on the left hand side we can find the non-equilibrium relaxation to the equilibrium value while on the right hand side we find the equilibrium decay of the correlation function.
Again, how a given observable X_i relaxes to equilibrium after a perturbation induced by the field coupled conjugated a to different observable X_j is essentially controlled by the properties of the equilibrium auto-correlation function between the two variables X_i, X_j, *always in the limit of small perturbation.*

It is important to observe that historically relation (3.159) was proposed first by Onsager and it is actually known as the **Onsager regression relation**.
Regression because it is not obvious the point that, if we perturb the field conjugated to some observable X_j, also another observable like X_i will respond to this perturbation.
Another way to state the properties encoded in equation (3.159) is to say that if we observe some fluctuations/decay with time in a system we cannot tell whether it is a non-equilibrium relaxation or it is just the decay of some equilibrium fluctuations when the perturbations are small.

Time reversal properties of $\Xi_{ij}(t)$

Let's introduce a time-reversal operator $\mathcal{T}$ whose action applies to the phase–space points $\{q_k(t), p_k(t)\}_{t=0,T}$ [15] as:

---

[15] ∧Which are trajectories solving the Hamilton equations with initial conditions given by the values at zero time $(q_k(0), p_k(0))$.

$$\mathcal{T}\left(q_k(t), p_k(t)\right) = \left(q_k(t), -p_k(t)\right) \tag{3.160}$$

The point about reversibility property (which corresponds to detailed balance in stochastic processes) is that if $(q_k(t), p_k(t))$ is a trajectory with initial conditions $(q_k(0), p_k(0))$ then the time-reversed trajectory, which can be formally archived by using the time-reversal operator, it is also a solution with initial conditions $\mathcal{T}(q_k(0), p_k(0))$.

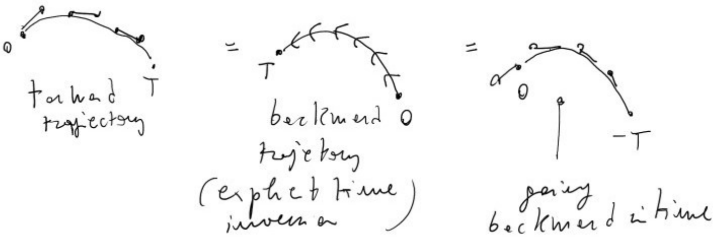


Figure (3.8) – Differences between forward, backward and time-reversed trajectories. The arrows indicate the momenta's direction.

So with *time-reversed trajectory* we mean that the trajectory starts from the same coordinate as the forward trajectory but then going backwards in time. This fact is important because we will now assume that my observables X_i are eigenfunctions of the time-reversal operator $\mathcal{T}$: which are the eigenvalues?
Considering a time reversed trajectory it's like going backwards in time and in general our observable X_i is a function of the coordinates, so applying $\mathcal{T}$ to X_i or to its coordinates is the same:

$$\begin{aligned} X_i(-t) = \mathcal{T}X_i(t) &= X_i(\mathcal{T}(q_k(t), p_k(t))) = \\ &= X_i(q_k(t), -p_k(t)) = \\ &= \tau_i X_i(t) \end{aligned} \tag{3.161–3.163}$$

where τ_i is the eigenvalue of our observable X_i with respect to time reversal operator and we can have *even* or *odd* observables upon time reversal, $\tau_i = \pm 1$. On the other hand, applying the time-reversal operator to the Hamiltonian (which is invariant under time reversal, $\mathcal{H} = \mathcal{T}\mathcal{H}$) it means that at equilibrium the Boltzmann distribution $\exp\{-\beta\mathcal{H}\}$ is the same for the forward and time-reversed trajectories.

Let's now compute the equilibrium correlation function between two different observables $\langle X_i(t)X_j(0)\rangle_0$.
We consider this correlation function having in mind the forward trajectories, meaning that we sample the forward trajectories according to Boltzmann distribution: we will switch considering time-reversed trajectories but since the Boltzmann distribution is the same we can state that an equilibrium average performed over a Boltzmann distribution for the time-reversed trajectory needs to give the same result. Using the action of the $\mathcal{T}$ operator:

$$\langle X_i(t)X_j(0)\rangle_0 = \langle \mathcal{T}X_i(-t)\mathcal{T}X_j(0)\rangle_0 = \tag{3.164}$$

$$\overset{(a)}{=} \tau_i \tau_j \left\langle X_i(-t) X_j(0) \right\rangle_0 = \tag{3.165}$$

$$\overset{(b)}{=} \tau_i \tau_j \left\langle X_j(t) X_i(0) \right\rangle_0 \tag{3.166}$$

where we can state that the two averages are the same because we are considering on the left hand side an average over forward trajectories using the Boltzmann distribution and on the right hand side an average over time-reversed trajectories using the Boltzmann distribution again and which is invariant under time reversal. In (a) then we used the fact that X_i, X_j are eigenfunctions of the time-reversal operator, while in (b) the time translation invariance adding t to both arguments.

We can conclude that the correlation functions of observables with the same parity with respect to time reversal are even functions of time, while those of observables with different parity are odd functions of time. This result has important consequences for the properties of the response function, that, for $t > 0$, can be rewritten as (switching i with j):

$$\Xi_{ij}(t) = -\beta\theta(t)\frac{d}{dt}\left\langle X_i(t) X_j(0) \right\rangle_0 = -\beta\tau_i\tau_j\theta(t)\frac{d}{dt}\left\langle X_j(t) X_i(0) \right\rangle_0 \tag{3.167}$$

We said at the beginning of this part that the order in which I write the indexes in the response function is important: for example $\Xi_{ij}(t)$ is the response of i to j but are there any relations with the response function describing how j response to i? The connection is related to the time-reversal invariance properties of the two observables:

$$\boxed{\Xi_{ij}(t) = \tau_i\tau_j\Xi_{ji}(t)} \tag{3.168}$$

Equation (3.168) tells us that the response function may be symmetric in the case we are dealing with two observables with the same parity under time reversal or may be anti-symmetric in the case we are dealing with two observables with different parities under time reversal.

3.8 Entropy Production, Fluxes, and Thermodynamic Forces (Affinities)

In this section we will start to introduce how we can merge the Onsager theory used to describe how a given observable respond to the perturbation coupled to another observable and the context of entropy production.

Let's start recalling the **second law of thermodynamics**: *for isolated systems entropy always increases* ($dS \geq 0$) *and in particular, in out-of-equilibrium (or irreversible) processes* $dS > 0$ *and so entropy is produced, whereas in equilibrium the entropy of an isolated system doesn't change* ($dS = 0$) *and* S *is maximum at equilibrium.*[16]

Let's now consider the whole system (the *universe*) as divided in two subsystems:

---

[16] ∧Remember that entropy is an extensive variable.

$$\text{universe} = \text{system} + \text{reservoir}$$

We will refer to the total variation of entropy of the universe with $d\mathbb{S}$ and we will assume that in this universe the total variation of entropy can be written as:

$$d\mathbb{S} = dS + dS_r \tag{3.169}$$

i.e., it is the sum of the variation of entropy in the system, dS, and in the reservoir, dS_r.
The second law implies then that $d\mathbb{S} \geq 0$: the other two variations dS, dS_r could be negative by themselves (but not all of them at the same time). For example we can deal with an *adiabatic process* where, by definition, the system doesn't exchange heat with the reservoir such that $dS_r = 0$ (and $dQ = 0$) and the second law can be stated as $dS = d\mathbb{S} \geq 0$ and the entropy of the universe increases as the entropy of the system.
A second example can be explained with an *isothermal process*: in this case some heat $dQ > 0$ is exchanged[17] between the system and the reservoir. In this case the entropy variation in the reservoir is:

$$dS_r = -\frac{dQ}{dt} \tag{3.170}$$

where the '-' sign is due to the fact that the heat is *lost* by the reservoir and according to the second laww we can state that:

$$dS = d\mathbb{S} - dS_r \overset{(3.170)}{\geq} 0 + \frac{dQ}{dt} \qquad \Longrightarrow \qquad \boxed{dS \geq \frac{dQ}{dt}} \tag{3.171}$$

Again, if we are dealing with equilibrium processes then $dS = dQ/dt$, where Q is the heat absorbed by the system.

The key point is that we have a relation between *entropy production* and *thermodynamic forces*, which cause entropy production.
Essentially, saying that the system is out-of-equilibrium implies to say that there is a non zero thermodynamic force acting into the system that will try to restore the equilibrium in the system and in doing so it will produce entropy.
Let's say that our (system) entropy is a function of several extensive thermodynamic observables X_i, namely

$$S = S(\{X_i\}) \tag{3.172}$$

Due to their extensive character, we can assume that a given value $\mathbb{X}_i$ taken in our universe by one of these observables has to be the sum of the values taken by this observable in the system, X_i, and in the reservoir, $X_i^{(r)}$, that is,

$$\mathbb{X}_i = X_i + X_i^{(r)} \tag{3.173}$$

---

[17] ∧We will use the sign convention according to which dQ is positive when the heat is absorbed by the system and lost by the reservoir.

An important point is that X_i is a *conserved quantity* and this implies that the variation in the universe is zero and therefore $d\mathbb{X}_i = 0 \quad \Longrightarrow \quad dX_i = -dX_i^{(r)}$. On the other hand the *thermodynamic force* for the universe is defined in the following way:

$$\mathbb{F}_i \equiv \left(\frac{\partial \mathbb{S}}{\partial X_i} \right) \bigg|_{X_i = \mathbb{X}_i} = \frac{\partial S}{\partial X_i} - \frac{\partial S_r}{\partial X_i^{(r)}} := F_i - F_i^{(r)} \tag{3.174}$$

We are allowed to use this definition because (-)entropy is the thermodynamic potential for an isolated system and therefore if we know how the universe entropy depends on the system variables X_i then we can define a thermodynamic force. The '-' sign is due to the fact that we are using the highlighted relation, while F_i is the thermodynamic force in the system and $F_i^{(r)}$ is the force contribution coming from the reservoir. The thermodynamic force of the universe $\mathbb{F}$ is also called *affinity*.

What happens at equilibrium is that $d\mathbb{S} = 0$ and so $\mathbb{S}$ is at its maximum value. Therefore this implies that the corresponding affinity $\mathbb{F} = 0 \; \forall \, i$. Let us assume for simplicity that the values of different observables at equilibrium (denoted with a *) are all equal to zero, $X_i^* = 0 \; \forall \, i$. On the other hand if $\mathbb{F}_i \neq 0$ then we deal with irreversible processes that set up in order to restore equilibrium.

We can exemplify our previous considerations about a system in out-of-equilibrium conditions by first recalling that typical examples of extensive thermodynamic observables are the internal energy U, the volume V, and the number of particles N_j of the species j contained in the system. The Gibbs relation

$$TdS = dU + PdV - \sum_j \mu_j dN_j \tag{3.175}$$

provides us with the functional dependence of S on these extensive observables, where T is the absolute temperature, P is the pressure, andμ_j is the chemical potential of particles of species j.
Using relation (3.175) implies the assumption of *local equilibrium*: we are trying to describe a situation in which there is globally no equilibrium (because we have some thermodynamic forces different from zero) but the fact that we are using this relation assuming that at least locally we can define the variation of entropy, this implies that at least locally we are assuming equilibrium (or we are dealing, in the thermodynamic language, with *quasi-reversible processes*[18]). We assume that such a functional dependence is valid also for the above described out-of-equilibrium conditions. For instance, we can still define the absolute temperature of the system and of the reservoir (or of the two subsystems) by the expression

$$\left(\frac{\partial S}{\partial U} \right)_{V,N_j} = \frac{1}{T} \tag{3.176}$$

---

[18] ∧Which is more correct because talking about local equilibrium implies the presence of space (variation with space) and in what we will do now there is no spatial variables, therefore the correct statement is talking about quasi-reversible processes.

and, analogously, the pressure and chemical potentials by the

$$\left(\frac{\partial S}{\partial V}\right)_{U,N_j} = \frac{P}{T}, \quad \left(\frac{\partial S}{\partial N_j}\right)_{U,V} = -\frac{\mu_j}{T} \tag{3.177}$$

At this point let's compute the affinities with respect the variation of a quantity:

$$\mathbb{F}_U = \frac{1}{T} - \frac{1}{T_r}, \quad \mathbb{F}_V = \frac{P}{T} - \frac{P_r}{T_r}, \quad \mathbb{F}_{N_j} = -\frac{\mu_j}{T} + \frac{\mu_j^{(r)}}{T_r} \tag{3.178}$$

At equilibrium we get the well known result for which $\mathbb{F}_U = \mathbb{F}_V = \mathbb{F}_{N_j} = 0 \implies T, P, \mu_i$ needs to be the same in the system and in the reservoir.
If e.g. $T_r \neq T$ we have that heat flows from/to the reservoir, to/from the system in order to restore an equilibrium situation in which the two temperatures are the same; this implies also that U changes in the system.
In general we introduce the concept of *flux* when we deal with the change in time of some observables:

$$J_i = \frac{dX_i}{dt} \tag{3.179}$$

The presence of a non-zero flux is related to a non-equilibrium situation in which there is a non-zero affinity: $\mathbb{F}_i \neq 0 \implies J_i \neq 0$ (which is a non-equilibrium situation).
This it will start an entropy production and if we consider the previous equation we can define the rate of entropy as:

$$\frac{d\mathbb{S}}{dt} = \sum_i \left(\frac{\partial S}{\partial X_i} - \frac{\partial S_r}{\partial X_i^{(r)}} \right) \frac{dX_i}{dt} = \sum_i \mathbb{F}_i \, J_i \geq 0 \tag{3.180}$$

In the end Equation (3.180) is the universe production rate. At equilibrium $J_i = 0, \mathbb{F}_i = 0$ and $d\mathbb{S}/dt = 0$: entropy doesn't change; on the other hand at non-equilibrium $\mathbb{F}_i, J_i \neq 0, d\mathbb{S} > 0$.
There real condition for equilibrium is having zero affinities and there may be particular situations in which non-zero fluxed may be present at equilibrium. From the equation for the entropy production rate we just need that affinity be zero in order for the entropy production to be zero.

Since our universe is isolated, the second principle of thermodynamics states that in out-of-equilibrium conditions the total entropy has to increase, namely,

$$\frac{d\mathbb{S}}{dt} = \sum_i \mathbb{F}_i J_i \geq 0$$

and it vanishes only when all affinities and the corresponding fluxes vanish, i.e., at thermodynamic equilibrium.[19]

(Lesson 11 of 04/11/20) Compiled: January 11, 2021

---

[19] ∧There are peculiar situations in coupled transport processes, where, as a consequence of symmetries, a flux can be made to vanish by applying suitable, non-vanishing affinities, although the system is kept in stationary out-of-equilibrium conditions.

3.9 Non-equilibrium Conditions in a Continuous System

Summary: in the previous lecture we introduced the idea of *generalized response function* in the context of LRT (weak perturbations) $\Xi_{ij}(t)$, which describes the response of observable i to the perturbation provided by the field conjugated to observable j.
What we have shown is that, upon time reversal, we can exchange the two indexes of the response function and what we get is:

$$\Xi_{ij}(t) = \tau_i \tau_j \Xi_{ji}(t) \tag{3.181}$$

where τ_i, τ_j are the eigenvalues of the corresponding observables for the time reversal operator $\mathcal{T}$, $\mathcal{T} X_i = \tau_i X_i$; if $\tau = +1$ the observable is even upon time reversal, if $\tau = -1$ it's odd.
In the simplest case in which our perturbation is just step-wise, as shown in Figure 3.3, then we can deduce the so called *Onsager regression relation*:

$$\langle X_i(t) \rangle = \beta h \left\langle X_i(t) X_j(0) \right\rangle_0 \tag{3.182}$$

The main point is that on the left hand side we have a non-equilibrium average, while on the right hand side we have an equilibrium average of the correlation function between the two different observables.

We moved then in the context of *entropy production rate*, where the entropy of the universe can be written as:

$$d\mathbb{S} = dS + dS_r; \qquad d\mathbb{S} \geq 0 \tag{3.183}$$

Our variable X_i is an *extensive thermodynamic observable* and we can define an *affinity* $\mathbb{F}_i$ just deriving the overall entropy with respect to X_i, which is the system's observable:

$$\mathbb{F}_i = \frac{\partial \mathbb{S}}{\partial X_i} = F_i - F_i^{(r)} \tag{3.184}$$

where (-) entropy is a thermodynamic potential for the system that, at equilibrium, takes a minimum (?) value.

We can consider an example introducing the so called (μ, T, P) ensemble in which we allow the exchange of energy, particles and variation in volume with the reservoir: in this case we can compute the entropy change dS as

$$TdS = dU + PdV - \sum_j \mu_j dN_j \tag{3.185}$$

where P is the absolute pressure and μ_j is the chemical potential for the particle subspecies j.
The point is that the affinity related to the energy/volume/number of particles of species j ($\mathbb{F}_{U,V,N_j}$, here we are considering energy/volume/number of particles of species j as my extensive observable) then we get that

$$\mathbb{F}_U = \frac{1}{T} - \frac{1}{T_r}, \quad \mathbb{F}_V = \frac{P}{T} - \frac{P_r}{T_r}, \quad \mathbb{F}_{N_j} = -\frac{\mu_j}{T} + \frac{\mu_j^{(r)}}{T_r} \tag{3.186}$$

At equilibrium we want affinities to be zero (because we are in the minimum of the entropy and the derivative of entropy with respect to (?) must be zero) and then (T, P, μ_j) needs to be the same in the system as in the reservoir.

Out-of-equilibrium we characterized the situation by using *fluxes*, so the variation in time of the observables we are interested in is expressed as $J_i = dX_i/dt$ and in the end the *entropy production rate* (how the entropy is increasing in time) can be written as

$$\frac{d\mathbb{S}}{dt} = \sum_i \mathbb{F}_i J_i \geq 0 \quad \text{for the } 2^{nd} \text{ law of TD} \tag{3.187}$$

Let's now extend the formalism we've presented to the case of *two* reservoir (a, b): with $\mathbf{X}_i$ we describe our observable in the universe and it is defined as

$$\mathbb{X}_i = X_i + X_i^{(a)} + X_i^{(b)} \tag{3.188}$$

We will consider in general our extensible observables which are conserved at least in the universe (e.g. $U, V, N \dots$) which implies that $d\mathbb{X}_i = 0 = dX_i + dX_i^{(a)} + dX_i^{(b)}$. It's important to point out that the reservoir in general is bigger than the system, so we will assume that we can neglect the variation in the system, $dX_i \simeq 0$ and so:

$$d\mathbb{X}_i = 0 = \cancel{dX_i} + dX_i^{(a)} + dX_i^{(b)} \simeq dX_i^{(a)} + dX_i^{(b)} \implies dX_i^{(a)} \overset{(*)}{=} -dX_i^{(b)} \tag{3.189}$$

and so the entropy production rate can be written as

$$\frac{d\mathbb{S}}{dt} \approx \sum_i \left[\underbrace{\frac{\partial S_a}{dX_i^{(a)}} - \frac{\partial S_b}{dX_i^{(b)}}}_{\mathbb{F}_i} \right] J_i^{(a)} \tag{3.190}$$

because from (*) we can state that $J_i^{(a)} = -J_i^{(b)}$ and we can express (3.190) using only one flux. Obviously this is an approximation because we are neglecting what is happening in the system.

To make this example more specific let's consider a situation (represented in Figure 3.9) with two reservoirs at different temperatures $T^{(a)}, T^{(b)}$ with $T^{(a)} < T^{(b)}$: in this situation the heat flux goes from (b) to (a).
For this reason, considering as unique extensive observable the energy U (which implies that the affinity is T^{-1}), the entropy rate can be written as:

$$\frac{d\mathbb{S}}{dt} \approx \left(\underbrace{\frac{1}{T^{(a)}} - \frac{1}{T^{(b)}}}_{\mathbb{F}_U > 0} \right) J_U^{(a)} \overset{(3.187)}{\geq} 0 \implies J_U^{(a)} > 0 \tag{3.191}$$

which means that reservoir (a) is absorbing energy (which is correct because is the coldest reservoir) whereas the flux for reservoir (b) is the opposite and it's negative for (*) because it's giving out energy.

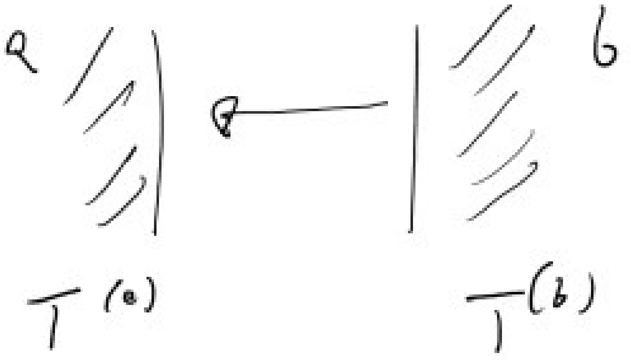


Figure (3.9) – Example using two reservoirs at different temperatures $T^{(a)}, T^{(b)}$, where $T^{(a)} < T^{(b)}$.

How can we generalize then the equation for entropy production rate in the case of continuous systems?

So far we have talked about a system referring to it with its energy and about the system as a whole: introducing some space variables in the system we are now allowed to talk about *local energy/entropy density* as a function of the position in the system. We will now deal with entropy and observables functions like $S(\vec{r}); X_i(\vec{r})$: this is not obvious because when we write entropy as a function of the position we are implicitly assuming *local equilibrium* (as in the context of LRT) but it is not granted at all in general.
Assuming we can talk about local equilibrium and knowing that $F_i = \partial S/\partial X_i$ we can write that (switching from extensive to *intensive* quantities $s := S/V; x := X/V$[20]):

$$ds = \sum_i F_i dx_i \tag{3.192}$$

A similar relation applies to the corresponding current densities: to entropy density and observable density we can associate a current density $\vec{j}_s$, namely

$$\vec{j}_s = \sum_i F_i \vec{j}_i \tag{3.193}$$

where $\vec{j}_i$ is the current density for x_i and $\vec{j}_s$ is the current density for entropy. The main point is that entropy is not conserved (entropy out-of-equilibrium can increase) and so in a region of a continuous system we can say that the rate of local production of entropy is given by the entropy entering/leaving this region (surface term) plus the rate of increase of entropy within this region (volume term), as

$$\frac{ds}{dt} = \underbrace{\frac{\partial s}{\partial t}}_{\text{Volume term}} + \underbrace{\vec{\nabla} \cdot \vec{j}_s}_{\text{Surface term}} \tag{3.194}$$

---

[20] ∧Affinities stay the same, $F_i = \partial s/\partial x_i$.

which is generally not zero because entropy is not conserved.
On the other hand the other observables x_i are conserved and so the overall variation can be written as:

$$\frac{dx_i}{dt} = \frac{\partial x_i}{\partial t} + \vec{\nabla} \cdot \vec{j}_i = 0 \tag{3.195}$$

which is the well-known continuity equation. The goal now is to write an equation for the entropy production rate.
Considering now the (partial) time derivative of (3.193):

$$\frac{\partial s}{\partial t} = \sum_i F_i \frac{\partial x_i}{\partial t} \tag{3.196}$$

while computing the divergence of the entropy current density

$$\vec{\nabla} \cdot \vec{j}_s \overset{(3.194)}{=} \vec{\nabla} \cdot (\sum_i F_i \vec{j}_i) = \sum_i (\vec{\nabla} F_i \cdot \vec{j}_i + F_i \vec{\nabla} \cdot \vec{j}_i) \tag{3.197}$$

so finally

$$\frac{ds}{dt} = \frac{\partial s}{\partial t} + \vec{\nabla} \cdot \vec{j}_s = \sum_i F_i \left(\underbrace{\frac{\partial x_i}{\partial t} + \vec{\nabla} \cdot \vec{j}_i}_{=0} \right) + \sum_i \vec{\nabla} F_i \cdot \vec{j}_i \tag{3.198}$$

where the yellow term is null because x_i is conserved.
In the end the final equation describing the overall entropy production rate for a continuous system is:

$$\boxed{\frac{ds}{dt} = \sum_i \vec{\nabla} F_i \cdot \vec{j}_i} \tag{3.199}$$

which is the continuous analogue for $dS/dt \overset{(*)}{=} \sum_i \mathbb{F}_i J_i$, where instead of fluxes we have current densities and we have the gradient of the affinities.

The relation with the non-continuos case can be seen in the affinities: in (3.199) we can think of them as the difference between the affinities computed into nearby positions ($\vec{\mathbb{F}}_i = \vec{\nabla} F_i(\vec{r})$), while in (*) $\mathbb{F}_i = F_i - F_i^{(r)}$.

3.10 Phenomenological equations involving transport kinetic coefficient

After having identified the affinities, we can proceed to the main goal of the thermodynamics of irreversible processes, i.e., finding a relation between affinities and fluxes. For this purpose, always in the framework of LRT (weak perturbations), we will introduce two sets of empirical phenomenological coefficients, called $\mathcal{M}_{ij}$ and L_{ij} where the second ones are called *Onsager kinetic coefficients*.

We suppose that fluctuating macroscopic observables[21] $X_i(t)$ evolve in time according to linear equations of the form[22]

$$\boxed{\langle J_i \rangle = \frac{d}{dt}\langle X_i(t)\rangle := -\sum_k \mathcal{M}_{ik}\langle X_k(t)\rangle} \tag{3.200}$$

So the $\mathcal{M}$ coefficients describe how the time variation of the X_i observable (i.e. the flux J_i) is connected to the values of all other observables, including the same observable of course.
In this approach we are describing the coupling between two different observables out-of-equilibrium and we will assume that $\langle X_i\rangle_0 = 0$.
In the case of one observable we get that

$$\frac{d}{dt}\langle X_i(t)\rangle := -\mathcal{M}_{ii}\langle X_k(t)\rangle \implies \text{exponential decay of} \,\langle X_i(t)\rangle \tag{3.201}$$

In other words this diagonal coefficient (if there is no coupling) is telling us how the non-equilibrium average is decaying to the equilibrium value.

Using the Onsager regression relation $\langle X_i(t)\rangle \propto \langle X_i(t)X_j(0)\rangle_0$ and applying it to equation (3.200) , which defines the $\mathcal{M}$ coefficients, we can replace the non-equilibrium averages on both sides with equilibrium ones:

$$(3.200) \implies \frac{d}{dt}\langle X_i(t)X_j(0)\rangle_0 = -\sum_k \mathcal{M}_{ik}\langle X_k(t)X_j(0)\rangle_0 \tag{3.202}$$

Let's remember that the Onsager regression relation holds in the case of constant perturbation which is then switched off instantaneously at some point.

Let's assume now that all our observables are even under time reversal:

$$\text{If } \tau_i = \tau_j = 1 \implies \langle X_i(t)X_j(0)\rangle_0 = \langle X_j(t)X_i(t)\rangle_0 \tag{3.203}$$

Considering now the time derivative of (3.203) for both sides and using (3.202) we obtain (neglecting the '-' sign at both sides)

$$\sum_k \mathcal{M}_{ik}\langle X_k(t)X_j(0)\rangle_0 = \sum_k \mathcal{M}_{jk}\langle X_k(t)X_i(0)\rangle_0 \tag{3.204}$$

At this point now we define the Onsager kinetic coefficients L_{ij} such that

$$L_{ij} = \sum_k \mathcal{M}_{ij}\langle X_k X_j\rangle_0 \tag{3.205}$$

where the highlighted term is the average of the product of the two observables at the same time, more formally is $\langle X_k(0)X_j(0)\rangle_0$ and therefore there is time dependence no more.

---

[21] ∧No spatial dependence is assumed.

[22] ∧Because of the fact that we are dealing with empirical coefficients/relations we are in general dealing also with (**non-equilibrium**) averages: sometimes they can be omitted, pay attention. Since we are out-of-equilibrium we ha a non-zero current.

Evaluating (3.204) at $t = 0$ tells us that the matrix of the Onsager coefficients is *symmetric*[23]:

$$L_{ij} = L_{ij} \tag{3.206}$$

Because of the definition given in (3.205) for the L_{ij} coefficients we can state that the fluxes

$$\boxed{\langle J_i \rangle = \frac{d}{dt} \langle X_i \rangle = \sum_k L_{ik} \langle \mathbb{F}_k \rangle} \tag{3.207}$$

The main difference with the $\mathcal{M}_{ij}$ coefficients in (3.200) is that we express the fluxes as a linear combination of the average of all observables, while the L_{ij} coefficients allow us to write the fluxes as a linear combination of the *affinities* (corresponding to all possible observables). Remember that the previous equation is a phenomenological equation which holds only for weak perturbations; for non LRT we should add $\mathcal{O}(\mathbb{F}^2)$ terms.

Actually one can provide a general definition for the Onsager coefficients L_{ij}:

$$L_{ik} = \left. \frac{\partial \langle J_i \rangle}{\partial \mathbb{F}_j} \right|_{\mathbb{F}_k = 0 \, \forall \, k} \tag{3.208}$$

i.e., the matrix L of the linear kinetic coefficients contains elements that are computed at equilibrium conditions (crucial), i.e., when all affinities $\mathbb{F}_k$ vanish.

We will now prove the consistency of the definitions of $\mathcal{M}$ and L starting from (3.207) and using the previous equation in order to recover (3.205): using Onsager regression relation we can write (3.207) such that

$$\frac{d}{dt} \langle X_i(t) X_j(0) \rangle_0 = \sum_k L_{ik} \langle \mathbb{F}_k(t) X_j(0) \rangle_0 \tag{3.209}$$

$$- \sum_k \mathcal{M}_{ik} \langle X_k(t) X_j(0) \rangle_0 \overset{(3.202)}{=} \tag{3.210}$$

and changing signs:

$$\sum_k \mathcal{M}_{ik} \langle X_k(t) X_j(0) \rangle_0 = - \sum_k L_{ik} \langle \mathbb{F}_k(t) X_j(0) \rangle_0 \tag{3.211}$$

In the end one can prove that the following average value is[24]:

$$\langle \mathbb{F}_k(t) X_j(0) \rangle_0 = -\delta_{kj} \tag{3.212}$$

i.e. the correlation equilibrium average of the product of affinity and observable is either -1 if $k = j$ of it is zero.
If (3.212) is true than it implies that we can recover the original definition of L coefficients (3.205):

$$\sum_k \mathcal{M}_{ik} \langle X_k X_j \rangle_0 = L_{ij} \tag{3.213}$$

---

[23] ∧Always assuming that all observables are even under time reversal $\tau_i = \tau_j = 1$.

[24] ∧Proof in the following appendix.

Let's use now equation (3.207) to go back to the equation for the entropy production rate:

$$\frac{d\mathbb{S}}{dt} = \sum_i J_i \mathbb{F}_i \overset{(3.207)}{=} \sum_{ij} L_{ij} \mathbb{F}_i \mathbb{F}_j \tag{3.214}$$

which is a *biliniear (quadratic) form* in the affinities $\mathbb{F}_i, \mathbb{F}_j$. This implies that, since from the second law of thermodynamics we know that the entropy production rate needs to be strictly positive ($dS/dt > 0$) if we are out-of-equilibrium (i.e. having at least one affinity $\mathbf{\mathbb{F}_i > 0}$ for one i), the diagonal Onsager coefficients have to be stricly positive $\mathbf{L_{ii} > 0}$ and that $\mathbf{det(L) > 0}$.

From now on we won't use averages but remember that the first line of the previous equation is an exact thermodynamic equation, while the second passage is an empirical phenomenological equation that is true only in the limit of very small perturbation (and so **very small affinities**[25]).

We can also compute the time derivative of the entropy production rate (the two factor is due to the fact that we can do this calculation in both ways),

$$\frac{d^2\mathbb{S}}{dt^2} = 2\sum_{ij} L_{ij} \underbrace{\sum_k \frac{\partial \mathbb{F}_i}{\partial X_k} \overbrace{\frac{dX_k}{dt}}^{J_k}}_{d\mathbb{F}_i/dt} \mathbb{F}_j = \tag{3.215}$$

$$\overset{(a)}{=} 2\sum_{ik} \frac{\partial \mathbb{F}_i}{\partial X_k} J_k J_i = \tag{3.216}$$

$$\overset{(b)}{=} 2\sum_{ik} \frac{\partial^2 \mathbb{S}}{\partial X_k \partial X_i} J_k J_i \tag{3.217}$$

where in (a) we used the fact that L is a symmetric matrix and the fact that $J_i = \sum_j L_{ij}\mathbb{F}_j$. We finally remember that $\mathbb{F} = \partial\mathbb{S}/\partial X_i$ in (b).
In this way we can deduce that, since the overall entropy needs to have a maximum at equilibrium (more precisely the entropy $\mathbb{S}(\{X_i\})$ is a concave function of the observables $\{X_i\}$) and this means that the form defined by the second derivatives of the entropy with respect to variables X_i, X_j is a *negative form.*
This implies that

$$\frac{d^2\mathbb{S}}{dt^2} \leq 0 \implies \frac{d\mathbb{S}}{dt} \quad \text{always decreases} \tag{3.218}$$

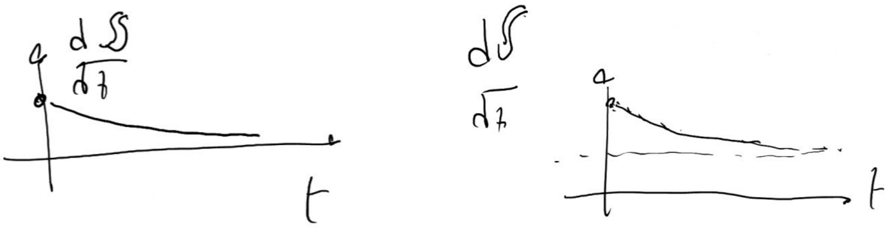
We can actually deal with two different scenarios: we can have

- *relaxation at equilibrium*: asymptotically for infinite time the entropy production rate goes to zero (which is the equilibrium situation) as represented in Figure 3.10a;

---

[25] ∧In our context the thermodynamic quantity which is conjugate to the observable is the affinity.

- *relaxation to a stationary non-equilibrium state*: NESS (non-equilibrium steady-state) in which the entropy production rate asymptotically converges to a finite strictly positive value (as represented in Figure 3.10b)



(a) **(b)**

Figure (3.10) – Graphical representation of EPR in the case of relaxation at equilibrium (a) and NESS (b).

Let us use this formalism to see some examples:

Mechanothermal effect (coupled transport) Let's consider a system made of two (fixed) volumes kept at different temperatures $T, T^{(r)}$ containing the same gas that are in contact through a wall, where a small hole allows for a slow exchange of particles. The exchanged particles also carry their (internal) energy from one gas to the other. Energy and particles can be exchanged between the two systems (energy and particles fluxes are involved and they will be *coupled*) and in this sense, this geometry represents the simplest example of coupled transport.
We are dealing with two relevant observables (U, N) and the entropy change is defined as

$$dS = \frac{dU}{T} - \frac{\mu}{T}dN \tag{3.219}$$

The affinities in this simple example are:

$$\begin{aligned} \mathbb{F}_U &= \tfrac{1}{T} - \tfrac{1}{T_r} \\ \mathbb{F}_N &= -\tfrac{\mu}{T} + \tfrac{\mu_r}{T_r} \end{aligned}$$

while the correspondent fluxes are

$$J_U = \frac{dU}{dt} \quad \text{and} \quad J_N = \frac{dN}{dt} \tag{3.220}$$

Expressing the fluxes using the matrix of the Onsager kinetic coefficients e splitting them in diagonal and off-diagonal contributions we get that

$$\begin{aligned} J_U &= L_{UU}\mathbb{F}_U + L_{UN}\mathbb{F}_N \\ J_N &= L_{NU}\mathbb{F}_U + L_{NN}\mathbb{F}_N(*) \end{aligned} \tag{3.221}$$

(A) Considering the system at *thermal equilibrium* we know that $\mathbb{F}_U = 0(\implies T = T_r$ and even at equilibrium we still have a non-zero energy current associated to the number of particles (for $\mathbb{F}_N \neq 0$):

$$J_U = L_{UN}\left(-\frac{\mu}{T}+\frac{\mu_r}{T}\right) \tag{3.222}$$

the presence of different chemical potentials in the system and in the reservoir the presence of a non-zero off-diagonal Onsager coefficient makes sure that we can find an energy current associated to this situation. For the particles number:

$$J_N = L_{NN}\left(-\frac{\mu}{T}+\frac{\mu_r}{T}\right) \tag{3.223}$$

thus yielding the relation

$$\frac{J_U}{J_N} = \frac{L_{UN}}{L_{NN}} \tag{3.224}$$

In this situation we have coupled transport of particles and heat by a purely mechanical effect even in thermal equilibrium conditions.

(B) Considering a *thermomechanical effect* we have to deal with a stationary state with zero particle flux $J_N = 0$ (we want to archive a zero particle flux and we let just the energy flux survive).
The phenomenological relation (*) reduces to

$$\frac{\mathbb{F}_N}{\mathbb{F}_U} = -\frac{L_{UN}}{L_{NN}};\ J_U = \mathbb{F}_U\left[L_{UU} - \frac{L_{UN}^2}{L_{NN}}\right] = \frac{det(L)}{L_{NN}}\mathbb{F}_U \tag{3.225}$$

and in this case we have both affinities that are different to zero and both of them contributes in driving the system out-of-equilibrium but we are in a special situation in which the particle flux zero (the energy flux is not zero and is determined by both affinities because all the Onsager coefficients contributes to the determinant to establish a non zero energy flux).
Notice also that the ratio between the fluxes in the first case (i.e., the mechanothermal effect) is equal to minus the ratio of affinities in the second case (i.e., the thermomechanical effect). This shows that Onsager relations establish interesting phenomenological similarities among quite different physical phenomena.

(Lesson 12 of 05/11/20) Compiled: January 11, 2021

Summary:
Some keywords we have seen so far are:

- **coupling**: the presence of a non-zero affinity which drives the system out-of-equilibrium implies that different observables respond to this non-zero affinity, non just the observable which is thermodynamically conjugated to that affinity;

- **linear response**: we are working always in the context of linear response i.e. the regime in which affinities are supposed to be small and we are dealing with phenomenological empirical laws;

- **non-equilibrium steady states (NESS)**: we are in a situation in which the system is in a stationary state but the entropy production rate is strictly positive.

3.11 Coupled Transport in Linear Continuous Systems involving charged particles

How we can revisit the following two empirical laws (which hold only in a LR regime), namely the

- **Fourier's law** for transport of heat: the energy/heat flux is just proportional to the temperature gradient $\vec{j}_u = -k\vec{\nabla}T$ where k is an example of transport coefficient and it's known as *thermal conductivity.*

  We can rewrite the Fourier's law using the Onsager formalism such that

  $$\vec{j}_u = -\kappa\vec{\nabla}T = \kappa T^2\vec{\nabla}\left(\frac{1}{T}\right) \quad (\sim L_{uu}\mathbb{F}_u) \tag{3.226}$$

  where the gradient of T^{-1} is the affinity of the system related to energy density.

- **Fick's law** for the particle current (ρ is the number particles concentration) $\vec{j}_\rho = -D\vec{\nabla}\rho$ where the transport coefficient is the *diffusion coefficient* D.

  We can rewrite the Fick's law using the Onsager formalism using the fact that in the context of a linear regime the concentration $\rho(\vec{r})$ can be expressed as $\rho(\vec{r})$=$\mu(\vec{r})/T$[26]:

  $$\vec{j}_\rho = -D\vec{\nabla}\rho = D\vec{\nabla}\left(-\frac{\mu}{T}\right) \quad (\sim L_{\rho\rho}\mathbb{F}_\rho) \tag{3.227}$$

  where the affinity related to the concentration of particles is the gradient of $-\mu/T$.

Now we want to consider the situation of a continuous thermodynamic system made of a single species of particles contained in a fixed volume V, where stationary energy and matter current densities are present at the same time. In this case the Gibbs relation for intensive observables specializes to:

$$du = Tds + \mu d\rho$$

where u, s, and ρ are the densities of internal energy, entropy, and number of particles, respectively. Taking into account the previous phenomenological considerations, we can write the linear coupled transport equations (3.207) in the form

$$\vec{j}_u = L_{uu}\vec{\nabla}\left(\frac{1}{T}\right) + L_{u\rho}\vec{\nabla}\left(\frac{-\mu}{T}\right) \tag{3.228}$$

---

[26] ∧Actually the correct way to express the concentration is the following but when the difference in the equilibrium situation is small, $|\mu(\vec{r}) - \mu_0| << 1$:

$$\rho(\vec{r}) = \rho_0 \exp\left\{-\frac{\mu(\vec{r}) - \mu_0}{T}\right\} \simeq \rho_0 - \left(1 - \frac{\mu(\vec{r}) - \mu_0)}{T}\right) \implies \rho(\vec{r}) \propto \mu(\vec{r})/T$$

considering equilibrium averages equal to zero.

$$\vec{j}_\rho = L_{\rho u}\vec{\nabla}\left(\frac{1}{T}\right) + L_{\rho\rho}\vec{\nabla}\left(\frac{-\mu}{T}\right) \tag{3.229}$$

where $\vec{j}_u$ and $\vec{j}_\rho$ are the current densities. Note that, even if not explicitly indicated, all the physical quantities appearing in these equations are functions of the coordinate vector $\vec{r}$. The symmetric structure of Onsager matrix of linear coefficients yields the relation $L_{u\rho} = L_{\rho u}$, while the affinities are

$$\vec{F}_u = \vec{\nabla}\left(\frac{1}{T}\right); \qquad \vec{F}_\rho = \vec{\nabla}\left(\frac{-\mu}{T}\right)$$

The entropy density production rate in the system is given then by the expression

$$\frac{ds}{dt} = \vec{j}_u \cdot \vec{\nabla}\left(\frac{1}{T}\right) + \vec{j}_\rho \cdot \vec{\nabla}\left(\frac{-\mu}{T}\right) \tag{3.230}$$

We will use these equations to describe transport phenomena for charged particles, in particular in the presence of electric field (*thermoelectric effect*): the presence of an electric field (and so of an electrostatic potential) implies that there are affinities related to the charged particle.

We won't talk about the *magneto-thermoelectric effect* but let's state the *Onsager theorem*, which takes into account the time-reversal properties that comes about in the presence of a magnetic field $\vec{B}$:

Onsager theorem: *In the presence of a magnetic field $\vec{B}$ we can exchange the two indexes of the Onsager's coefficient provided the fact we reverse the direction of the magnetic field:*

$$L_{ij}(\vec{B}) = L_{ji}(-\vec{B})$$

3.11.1 Thermoelectric effects

These physical phenomena concern coupled transport of electric and heat currents **in the absence of a magnetic field**. They result from the mutual interference of heat flow and electric current. In this situation we are dealing with $1d$ metal/semiconductor wires and we adopt here the description of the conductor as a continuous system and we specialize the Gibbs relation to:

$$ds = \frac{1}{T}du - \frac{\mu}{T}dn \tag{3.231}$$

where T is the temperature, s is the local entropy density, u is the local energy density, n is the number of electrons per unit volume (particle density), and, accordingly, μ is the chemical potential per particle.
The two relevant thermodynamical observables are u and n, the affinities are T^{-1} (related to the energy) and $-\mu/T$ (related to the particle density), while the equation for the current densities is:

$$j_s = \frac{1}{T}j_u - \frac{\mu}{T}j_n \tag{3.232}$$

Let's think about our particles as electrons, so the electric current is ej_n (where $e < 0$) and the entropy production rate can be written as:

$$\frac{ds}{dt} = j_u \partial_x \left(\frac{1}{T}\right) - j_n\, \partial_x \left(\frac{\mu}{T}\right) \tag{3.233}$$

The point here is that it's not practical to deal with the yellow derivative because in general we would like to discuss a situation in which possibly both of the chemical potential and temperature depends on x: to solve this let's perform a 'change of variables' in which we switch from the energy flux[27] to the so called *heat flux* j_q:

$$j_u \mapsto j_q := T j_s \overset{(3.232)}{=} j_u - \mu j_n \tag{3.234}$$

We can now rewrite the EPR, separating the yellow gradient in two contributions and rearranging the terms together, as:

$$\frac{ds}{dt} = j_q \partial_x \left(\frac{1}{T}\right) - \frac{j_n}{T} \partial_x \left(\mu\right) \tag{3.235}$$

so now we have the gradient of T and μ split and the relevant quantities are heat and the number of particles.
In this way we can now rewrite the equation that uses that the Onsager matrix in the *heat representation*[28]:

$$\begin{aligned} -j_n &= L_{nn} \frac{1}{T} \partial_x \mu + L_{nq} \partial_x \frac{1}{T} \qquad && (a) \\ j_q &= L_{qn} \frac{1}{T} \partial_x \mu + L_{qq} \partial_x \frac{1}{T} \qquad && (b) \end{aligned} \tag{3.236}$$

The Onsager matrix is symmetric again because we don't have magnetic field ($L_{nq} = L_{qn}$) and now the interesting question is how we relate the Onsager coefficients to physically relevant quantities (that can be measured)? What is the physical representation of the Onsager coefficients?

We have to deal with three independent coefficients: the two diagonal ones and the off-diagonal one, namely L_{nn}, L_{qq}, L_{qn} and so we need three independent parameters that can be measured.

1. Let's start with a situation where the temperature is uniform ($\partial_x T = 0$) and so we just have an electric field providing an electrostatic potential, which is varying along the wire, and an electric current.

   In this context we should call μ *electrochemical potential* because it can be split in two different contributions, one taking into account the electrostatic potential and one coming from the chemical potential. In our context we

---

[27] ∧In $1d$ energy currents are actually fluxes because we don't have the area.

[28] ∧Energy is not equivalent to heat because we have a contribution from the electric field as we can see from (3.234). We will discuss about how the electric fields enters in the chemical potential later.

are going to say that the actual chemical potential is zero because we are dealing with homogeneous materials

$$\mu = \mu_e + \cancel{\mu_c}$$

while the electrostatic potential component of the electrochemical potential is defined as:

$$\mu_e = e\phi$$

where ϕ is the actual electrostatic potential.

On the other hand, μ_c is a function of T and of the electronic concentration. In other words, the electrochemical potential per unit charge $(1/e)\mu$ is such that its gradient $(1/e)\partial_x\mu$ is the sum of the electric field $(1/e)\partial_x\mu_e$ and of an effective driving force $(1/e)\partial_x\mu_c$ associated with the presence of a concentration gradient of electrons. If we assume that the conductor is made of a homogeneous isothermal material, $\partial_x\mu_c = 0$ and $\partial_x\mu = \partial_x\mu_e$, while the electric conductivity σ is defined as the electric current density ej_n per unit potential gradient $(1/e)\partial_x\mu$, i.e., the electromotive force. Thus the *electric conductivity* is defined as the electric current density over the electric field:

$$\sigma = \frac{ej_n}{-\partial_x\phi} = -\frac{e^2 j_n}{\partial_x\mu} \tag{3.237}$$

For $\partial_x T = 0$ (isothermal condition) using (3.236.a) the first diagonal Onsager coefficient is

$$\boxed{L_{nn} = -\frac{Tj_n}{\partial_x\mu} = \frac{\sigma T}{e^2}} \tag{3.238}$$

so in this way we got a first relation of one of the Onsager coefficients with the electric conductivity.

Notice out that the definition of σ is nothing but the Ohm's law.

2. Now we want also to consider the Fourier's law: to consider this law let's consider the case in which $j_n = 0$ (no electric currents flowing in the system, we just have energy or heat flux[29]).

   The parameter we are interested in is the thermal conductivity κ defined as:

   $$\kappa = -\frac{j_q}{\partial_x T} \tag{3.239}$$

   Having constrain of $j_n = 0$ in equation (3.236.a) tells us that:

   $$\partial_x\mu = -T\frac{L_{nq}}{L_{nn}}\partial_x\left(\frac{1}{T}\right) = \frac{L_{nq}}{TL_{nn}}\partial_x T \tag{3.240}$$

   while we can substitute the gradient of the electrochemical potential of the previous expression in equation (3.236.b)

   $$j_q = \frac{1}{T^2}\frac{L_{nq}^2}{L_{nn}}\partial_x T = \frac{L_{qq}}{T^2}\partial_x T \tag{3.241}$$

---

[29] ∧In this case energy and heat flux are the same because $j_n = 0$.

and so we can rearrange this whole equation such that

$$j_q = \frac{1}{T^2}\frac{det(L)}{L_{nn}}\partial_x T \tag{3.242}$$

Comparing this equation with the Fourier's law we can get a relation for the thermal conductivity as a function of the coefficients of the Onsager matrix:

$$\boxed{\kappa = \frac{det(L)}{T^2 L_{nn}}} \tag{3.243}$$

So far we got two equations (3.238) and (3.243) that allow us to relate the Onsager coefficients to physical quantities, such as the electric and thermal conductivity. We need a third one to finish.

When we want to recover the Ohm's law we impose that there is no temperature gradient and equation (3.238) tells us that that the diagonal Onsager coefficient L_{nn} is essentially the electric conductivity.

On the other hand thermal conductivity involves all the coefficients in the Onsager matrix (through the determinant) because the presence of the off-diagonal Onsager coefficients, both in (3.238) and (3.243), tells us that in order to have zero current - since we have a non-diagonal Onsager coefficient - L_{nq} in the first line of (3.240), the presence of a temperature gradient would imply the flow of a current and in order to have zero current we need to have a gradient in the electrochemical potential. Here is where the coupling of transport phenomena comes in and this is essentially why at the end the thermal conductivity is actually depending on all the Onsager coefficients and not by L_{qq} only.

3. In order to derive the third and last relation connecting the Onsager coefficient to physical parameters we need to consider tow peculiar effects due to the coupling between different affinities, the *Seebeck effect* (1821) and the *Peltier effect* (1834)

3.11.2 Seebeck effect

In the Seebeck effect we are dealing with two different kind of metals (e.g. Iron and Copper) or two differently doped semiconductors and with a *temperature gradient* at the two junctions $T_2 > T_1$: the solid line in Figure 3.11 represent one conductor (A - Iron), while the lighter one the second (B - Copper).

We can have a setup in which we close the circuit (as represented in Figure 3.11) and in this setup (without external electric fields initially) there is a so called *thermoelectric power* for which a current flows in this circuit.

To discuss in detail the effect we will use the setup pf the *thermocouple*: a thermocouple is a device that allows to measure temperature differ-

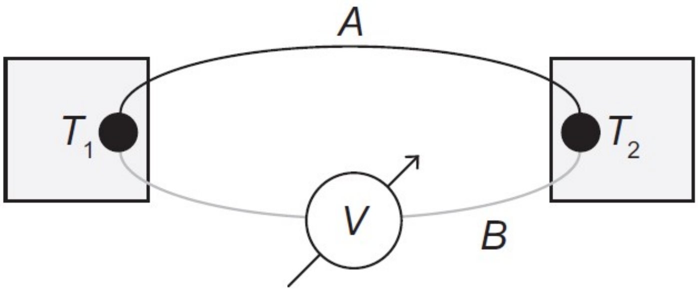


Figure (3.11) – Sketch of the experimental apparatus to observe the Seebeck effect. Two different conducting (or semiconducting) wires, A and B, are joined at their ends (black dots), which are kept at different temperatures T_1, T_2. This temperature gradient induces a difference of electric potential (electromotive force) at the inputs of the voltmeter V.

ences just reading the potential difference, so the actual instrument is a voltmeter[30].

The raw idea behind a thermocouple is that the voltage difference read in the voltmeter is related to the temperature difference between the two junctions.

The presence of the voltmeter is fundamental: is missing we have to deal with a *stationary* current and with NESS which is surprising: we don't need an external field to maintain a constant current flowing in the circuit.

In the thermocouple setup ($j_n = 0$), in order to write fluxes as function of affinities using the Onsager coefficients, from equation (3.236.a) we get a relation between the variation of the electrochemical potential and the variation of temperature (going from $d(T^-1) \mapsto dT/T$ again):

$$d\mu = \frac{L_{nq}}{TL_{nn}} dT \tag{3.244}$$

Our aim is to compute the voltage measured by the voltmeter, where the index r is referred to the point to the right of the voltmeter and l the one to the left.

Let's compute the voltage[31] measured by the voltmeter. Integrating the previous expression over the two wires we can compute the electrochemical potential:

$$\mu_r - \mu_l = \int_{①}^{②} \left[\frac{L^A_{nq}}{L^A_{nn}} - \frac{L^B_{nq}}{L^B_{nn}} \right] \frac{dT}{T} \tag{3.245}$$

Since we are dealing with different materials the values of the Onsager coefficients are different from each other while the '-' sign is due to the fact that we are integrating from the wire ① to the wire ② .

---

[30] ∧We assume the voltmeter to be **ideal**: no measurement perturbation and no current flowing $j_n = 0$.

[31] ∧Sign convention: the point to the right has an higher voltage than the one to the left.

Finally, the measured voltage V is given by the expression:

$$V = \frac{\mu_r - \mu_l}{e} \tag{3.246}$$

The *(relative) thermoelectric power of a thermocouple*, ε_{AB}, is defined as the increment of voltage per unit temperature difference, while its sign is conventionally said to be positive if the increment of voltage drives the current from A to B at the hot junction, T_2. In practice, if $T_1 = T$ and $T_2 = T + \Delta T$, in the limit of small ΔT

$$\varepsilon_{AB} := \varepsilon_B - \varepsilon_A = \lim_{\Delta T \to 0} \underbrace{\frac{\mu_r - \mu_l}{e}}_{\text{V}} \frac{1}{\Delta T} \tag{3.247}$$

In practise the effect can be measured only when you join two different conductors and practically we will always measure the relative power coming from the different properties of the two conductors materials but it is useful to define the coefficient

$$\boxed{\varepsilon_X = -\frac{L^X_{nq}}{eTL^X_{nn}}, \qquad X = A, B} \tag{3.248}$$

which defines the *absolute thermoelectric power* of a single electric conductor and is our last relation. Equation (3.248) is the third relation that we needed to express all coefficients of Onsager matrix using physically measurable quantities.

Considering the definition we gave of absolute thermoelectric powers and we compare it to the way we expressed the electrochemical potential difference then in the limit of $\Delta T \to 0$ we can get rid of the integral and we can read the definition of absolute thermoelectric power from the argument of the integral.

Let's now rearrange (3.238), (3.243), (3.248):

$$L_{nn} \overset{(3.238)}{=} \frac{T\sigma}{e^2}; \quad L_{nq} = L_{qn} \overset{(3.248)}{=} -\varepsilon e T L_{nn} \overset{(3.238)}{=} \frac{-T^2\sigma\varepsilon}{e} \tag{3.249}$$

where the last relation holds for any material. now our aim is to explicitly write each of the Onsager coefficients as a function of $\sigma, \kappa, \varepsilon$.
From equation (3.243) we get that:

$$L_{qq} = \kappa T^2 + \varepsilon^2 \sigma T^3 \tag{3.250}$$

and so eventually we can rewrite the coupled transport equation expressing the Onsager coefficients in this way, in order to read immediately the physically relevant parameters:

$$
\begin{aligned}
&(a) \qquad -j_n = \left(\frac{\sigma}{e^2}\right)\partial_x\mu - \left(\frac{T^2\sigma\varepsilon}{e}\right)\partial_x\frac{1}{T} \\
&(b) \qquad j_q = -\left(\frac{T^2\sigma\varepsilon}{e}\right)\partial_x\mu + \left(T^3\sigma\varepsilon^2 + T^2\kappa\right)\partial_x\frac{1}{T}
\end{aligned}
\tag{3.251}
$$

This is everything we need to know to describe all possible phenomena related to coupled transport of heat and electricity current.

For example, taking into account (3.251.a), the electric field is zero the first term is missing and we can see that - thanks to the Seebeck effect (ε is present) - we observe a particle flux/current due to a temperature gradient.
On the other hand, if $j_n = 0$ we can observe a voltage difference related to the presence of a temperature gradient.

Noticing out that the first two terms of (3.251).b are proportional to the particle current let's rewrite the heat flux j_q such that:

$$
j_q = T\varepsilon e j_n + \kappa T^2\partial_x\left(\frac{1}{T}\right) \tag{3.252}
$$

which is a more transparent way because we isolate the contribution from thermal conductivity and then we can see that the Seebeck contribution ε is really related to the fact that an electric current j_n is coupled to an heat current. This allows us to provide this expression (remembering that the heat current is proportional to the entropy current):

$$
j_s = \frac{j_q}{T} = \varepsilon e j_n + T\kappa\partial_x\frac{1}{T} \tag{3.253}
$$

which is a clear interpretation of what it's going on: entropy is produced by a temperature gradient through a thermal conductivity (Fourier's law) but then if we have charged particles moving they carry with themselves entropy and we can reinterpret ε as the *entropy transported per unit charge.* If a charged particle is moving, is carrying some entropy.

3.11.3 Peltier effect

We can think of the Peltier effect as a 'reversed Seebeck': in this setup we have one junction (between two different conductors) at constant temperature T. The solid line of Figure 3.12 represent conductor A, while the lighter one conductor B.
In the Seebeck effect, in the thermopower setup, a heat flows implies a heat current; here it's reversed in the sense that it's the other way round and what's happening is that we have a discontinuity in the electric current at the junction due to the fact that we are dealing with two different materials and this is implying a discontinuity also in the heat fluxes. For instance, in a situation like this (where the arrows in Figure 3.12 refer to heat currents), energy needs to be conserved, so if the the currents are higher in B than in A and are flowing in the direction showed in Figure 3.12 what happens is that heat is released from the

junction to the system: the discontinuity due to the junction implies that heat needs to be transferred to the system and this effect is used in heaters/heat pumps for this reason.

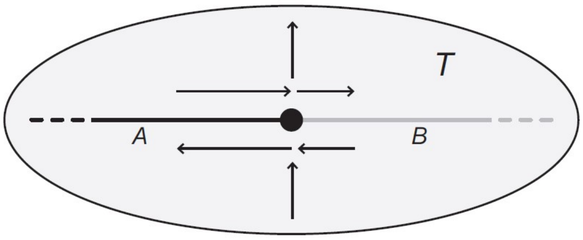


Figure (3.12) – The diagram of the Peltier effect. A junction (black dot) of two different conductors A and B, when kept at constant temperature T, must exchange heat with the reservoir in order to sustain a constant electric current. The horizontal arrows correspond to j_q^A and j_q^B: their difference amounts to the heat exchanged with the environment at temperature T, which may be either positive or negative; see the two cases above and below the junction.

A different situation can be presented when we reverse the direction of the currents (top arrows in Figure 3.12) and in this case we need to *absorbed* heat into the junction in order to conserve energy: this is a way to extract heat from the environment and this setup is used for refrigerators.

Let's consider the heater setup: it's very different from the *Joule effect* because the Peltier effect is due to the presence of a junction and the heat can be either taken or absorbed by the junction and we can control whether it's a heater or a cooler.
In this setup we are in a situation where temperature is constant ($\partial_x T = 0$) and therefore, using (3.251.a) for the particle flux:

$$j_n = -\frac{\sigma}{e^2}\partial_x \mu \tag{3.254}$$

while using (3.251.b) for the heat flux:

$$j_q = -\frac{T\sigma\varepsilon}{e}\partial_x \mu \tag{3.255}$$

Considering the ratio between the two previous equations we get that the heat flux is proportional to the electric current:

$$j_q = T\varepsilon \quad \cdot \quad \underbrace{(ej_n)}_{\text{electric current}} \tag{3.256}$$

From the Seebeck effect we have learnt that for two different materials ε is different which implies that at the junction we have a discontinuity in the heat flux:

$$j_q^B - j_q^A = T(\varepsilon_B - \varepsilon_A)(ej_n) \tag{3.257}$$

So the electric current is **continuous** but the discontinuity arises because the Seebeck coefficients ε are different (due to the presence of a junction) and therefore we have a discontinuity in the heat flux, as described by (3.257).

We can quantify the effect defining the *Peltier coefficients* Π_{AB}

$$\boxed{\Pi_{AB} := T\left(\varepsilon_B - \varepsilon_A\right)} \tag{3.258}$$

which is the heat supplied to the junction per unit electric current (as we can read from (3.257)).
The sign convention in this case is such that positive ($\Pi_{AB} > 0$) means that heat is supplied to the junction.

Let's now assume that $\varepsilon_B > \varepsilon_A$ and let's discuss the two possible situation (heater/cooler setup):

- *Heater setup*: if $j_n > 0$ then electrons are flowing from left to right and so current (remember that $e < 0$) and therefore the heat flux (which is proportional to the current through a positive Peltier coefficient) are instead negative: $ej_n, j_q < 0$ and $j_q^B < j_q^A$ consistently with the bottom sketch of Figure 3.12;

- *Cooler setup*: if $j_n < 0$ then electrons are flowing from right to left and so current (remember that $e < 0$) and therefore the heat flux (which is proportional to the current through a positive Peltier coefficient) are instead positive: $ej_n, j_q > 0$ and $j_q^B > j_q^A$ consistently with the bottom sketch of Figure 3.12.

See Chapter 5, Appendix B for more details.

Chapter 4

Non-equilibrium Phase Transitions

(Lesson 13 of 11/11/20) Compiled: January 11, 2021

What's the difference between *equilibrium states* and *(non-equilibrium) stationary states* NESS?
The tool that we will use in order to describe a NESS in the context of Master equations/Markov Chains is (in continuous time and discrete set of microstates $\{s_i\}$):

$$\frac{\partial p(s,t)}{\partial t} = \sum_{s'} \left[p\left(s',t\right) w_{s,s'} - p(s,t) w_{s',s} \right] \tag{4.1}$$

which is a differential equation for the probability $p(s,t)$ of being in state s at time t. The w are transition rates in continuous time: $w_{s,s'}$ is the transition rate from state s' to s and the yellow term is called *gain term*, while the green one is the *loss term*.
At stationarity we want that:

$$\frac{\partial}{\partial t} p = 0 \qquad \Longrightarrow \qquad \sum_{s'} \left[p(s')^s w_{s',s} - p(s)^s w_{s's} \right] \overset{!}{=} 0 \tag{4.2}$$

which is a relation connecting the rates of our system with stationary probability p^s. If (4.2) holds we are dealing with **steady stationary states**.
Actually we know that there is a stronger condition for equilibrium i.e. *detailed balance*, where essentially every single term in the sum is equal to zero: this condition is connecting the rates of the system with the *equilibrium probability* p^{eq}

$$p(s')^{eq} w_{s',s} = p(s)^{eq} w_{s's} \;\; \forall\, s, s' \text{ couple of states} \tag{4.3}$$

and if (4.3) holds we are dealing with **equilibrium states**. Equilibrium states imply stationarity but not the other way round.

But what are the conditions for NESS? NESS are stationary states for which condition (4.2) holds but without detailed balance (4.3).
If we are in equilibrium a typical approach at fixed T would be to use the Boltzmann distribution at thermodynamic equilibrium $p^{eq}(s) = \exp\{-\beta E(s)/Z\}$ with Z known partition function in order to find the transition rates that satisfy

detailed balance with the equilibrium Boltzmann distribution that we already know $p^{eq}(s)$. Practically we want to find transition rates such that:

$$\frac{w_{s',s}}{w_{s,s'}} = \frac{p^{eq}(s')}{p^{eq}(s)} = \exp\{-\beta[E(s') - E(s)]\} \tag{4.4}$$

An approach used to find the transition rates are Montecarlo simulations, which define rates $w_{s,s'}$ to sample the equilibrium distribution $p^{eq}(s)$: the concept is that we know the equilibrium distribution and we want to find some rates that satisfy DB and allow us to implement a numerical strategy to sample the known equilibrium distribution. The Monte Carlo method creates a trajectory in phase space that does not correspond to real dynamics (as is the case for molecular dynamics), but the resulting visiting probability of each microstate must equal the ensemble probability. The fictitious trajectory is defined assigning the transition rates. For instance, according to the popular Metropolis algorithm, we can adopt the transition rates

$$w_{s',s} = \min\left\{1, e^{-\beta\Delta E}\right\} \tag{4.5}$$

Using this rates DB is satisfied for the Boltzmann distribution.

On the other hand, if we want to deal with NESS we don't have 'a prior' knowledge of the stationary probability distribution $p^{s}(s)$ and we don't have general principles like Boltzmann but what we know typically (if we want to study NESS) is that we have to assign the rates $w_{s',s}$ to define the model.
We can use for example a MC model and then we can use the stationarity condition (knowing the rates) in order to find the stationary distribution.

Let's deal with the following problem now:
given a set of rates $\{w_{s',s}\}$ can we decide, looking at the rates and without knowing the possible equilibrium distribution $p^{eq}(s)$, whether they are compatible with DB? Let's state a theorem which provides a sufficient and necessary condition under which a given set of rates satisfies DB (obviously specifying the equilibrium distribution):

Theorem *The transition rates $w_{s',s}$ satisfy the detailed balance condition*

$$\frac{w_{s',s}}{w_{s,s'}} = \frac{p^{\mathrm{eq}}(s')}{p^{\mathrm{eq}}(s)} \quad \boxed{\forall s, s'}$$

if and only if they satisfy the condition

$$\prod_{i=1}^{N} w_{s_{i+1},s_i} = \prod_{i=1}^{N} w_{s_{i-1},s_i} \tag{4.6}$$

for any set $(s_1, \ldots, s_N)$ of N microstates (with the definition $s_0 = s_N$ and $s_{N+1} = s_1$).

Essentially the idea is that the condition of the theorem is a sort of reversibility condition on a *cycle*: we can arrange our set of N microstates in a circle (PBC) and the left hand side of th. 4 is the probability of going from state 1 to state 2 . . . state s_i to s_{i+1}, whereas on the right hand side the we follow a clockwise order, as visualized in Figure 4.1a.

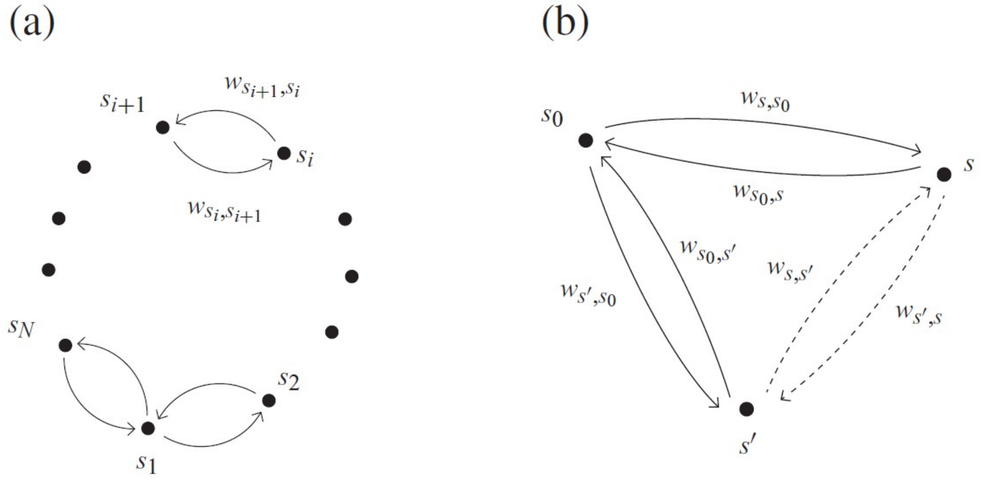


Figure (4.1) – Graphical representation of the transition rates appearing in the proof of Theorem 4.

In other words we are stating that DB holds if for cycles in our system our rates satisfy a reversibility condition.
Intuitively, when such a reversibility condition holds, that implies that we have *no (probability) currents* in the system: a current would be present if the reversibility condition wasn't satisfied[1].

Proof of Theorem 4

$\boxed{\Longrightarrow}$ trivial: let's take a set of N microstates

$$\prod_{i=1}^{N} \frac{w_{s_{i+1},s_i}}{w_{s_i,s_{i+1}}} \overset{DB}{=} \prod_{i=1}^{N} \frac{p^{eq}(s_{i+1})}{p^{eq}(s_i)} = 1$$

because since we are dealing with a cycle $p^{eq}(s_{i+1}) = p^{eq}(s_i)$ and in this way we proved that the reversibility condition is satisfied.

$\boxed{\Longleftarrow}$ given that, for any cycle, we have the reversibility condition let's derive DB: let's define the equilibrium distribution from the rates (it's possible to recover $p^{eq}(s)$ from normalization), such that:

$$\boxed{p^{\mathrm{eq}}(s) = p^{\mathrm{eq}}(s_0)\frac{w_{s,s_0}}{w_{s_0,s}}} \quad \forall s \tag{4.7}$$

Notice that we chose a given 'reference state s_0' and this is equivalent to say that DB holds for $s, s_0\ \forall\, s$. In this case DB holds only for pairs containing s_0 but we can say that always: our aim is to show is that DB holds for *any*

---

[1] ∧If currents are present we are in an out-of-equilibrium situation but we could be in a stationary state.

possible choice s, s'.

Let's choose $s, s' \neq s_0$ choosing a cycle with three different states s_0, s', s as shown in Figure 4.1b: let's write the reversibility condition for this cycle

$$w_{s,s_0} w_{s',s} w_{s_0,s'} = w_{s',s_0} w_{s,s'} w_{s_0,s},$$

which must be satisfied because the theorem condition (reversibility for any cycle) is assumed to be true. We can rewrite it as

$$\left(\frac{w_{s,s_0}}{w_{s_0,s}}\right) w_{s',s} = \left(\frac{w_{s',s_0}}{w_{s_0,s'}}\right) w_{s,s'}$$

and let us evaluate the two fractions between parentheses using our definition of $p^{eq}(s)$

$$\frac{p^{\mathrm{eq}}(s)}{p^{\mathrm{eq}}\left(s_0\right)} w_{s',s} = \frac{p^{\mathrm{eq}}\left(s'\right)}{p^{\mathrm{eq}}\left(s_0\right)} w_{s,s'} \Longrightarrow \frac{w_{s',s}}{w_{s,s'}} = \frac{p^{eq}(s')}{p^{eq}(s)}$$

Once we cancel $p^{\mathrm{cq}}\left(s_0\right)$ from both sides, the above equation proves that detailed balance between s and s' is valid.
In conclusion, we have given an alternative formulation of detailed balance that involves transition rates only, so we can test if detailed balance is broken or not by checking Eq. (4.6). □

4.1 Non-equilibrium phase transitions

We will talk about two different classes of non-equilibrium phase transitions:

- *Transitions with absorbing states*;
- *Transitions in driven systems*

4.1.1 Systems with absorbing states

We call a state s absorbing if we are in state s and my only choice is to remain in state s: $w_{s,s} = 1$.
If my transition rates are normalized this implies that the rate of going from s to any other state s' needs to be zero, $w_{s',s} = 0 \, \forall s' \neq s$ and also means that DB would then imply that a possible equilibrium distribution need to be zero if we are in state s': $p^{eq}(s') = 0 \, \forall s' \neq s$.
In general if we talk about a phase transition of an absorbing state we are referring to a situation in which, by varying a control parameter, for some values of the control parameter our system is not going to the absorbing phase whereas for other values the system is actually going to the absorbing phase.
There is also a very specific value of the control parameter for which these transitions happens (from absorbing/*inactive* to not absorbing/*active*).
If we want to study these transitions it's clear that we can't describe them in the context of an equilibrium situation: we can describe in equilibrium only the inactive state, when the system is always in the absorbing state while the

transitions to absorbing (inactive) phase take place out-of-equilibrium.

The typical example of phase transitions with an absorbing phase is the **directed percolation**.

Isotropic percolation

Percolation is a very interesting problem and the original inspiration used to study it explain how fluid percolates through porous mediums. Take as example the way in which American coffee is prepared, using filtered coffee: in this way the boiled water is percolating through the filter. Another example is how oil percolates through rocks in the oil extraction process or the flowing of electric currents through heterogeneous conductors.
The common point in these example is that we are dealing with heterogeneous mediums and therefore in all the modeling we are dealing with stochastic activation of *percolation channel* with some probability $p, 0 < p < 1$.

Let's start discussing *isotropic percolation*: we are dealing in our model with a squared lattice and each site can be either *wet/active* or *dry/inactive*.
The point is that wet sites can activate/wet neighbouring sites through *active bonds*. We can think of active bonds as modeling pores in our heterogeneous medium. Some pores are present connecting nearby sites, while in other situations nearby sites are not connected by a pore/active bond.
The bonds are active with probability p, which is our external control parameter of the percolation: what we have described until now is called **bond percolation**, because the external parameter p is controlling the activation of bonds and all sites are 'potentially' active.

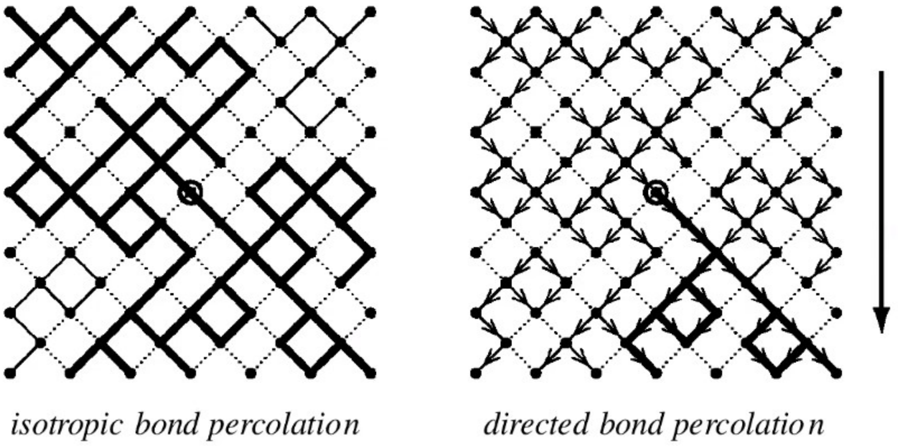


Figure (4.2) – Schematic of isotropic (left) and directed (right) bond percolation. The circled point in the center is the site where percolation originates; i.e., it is the only wet site when dynamics starts. Each bond may be active (solid line) or inactive (dashed line) and a site becomes wet if it is linked to a wet site via an active bond. Active bonds between dry sites (open circles) are thin, while active bonds between wet sites are thick. In isotropic percolation (left) the spread of wet sites proceeds isotropically, while in directed percolation (right) wetting proceeds only in the direction of the arrow. The thicker lines represent the spanning cluster.

We can also deal with **sites percolation** where sites are active with probability p whereas all bonds are 'potentially' active.

What we want to do is to find out if there is a percolating *spanning*[2] *cluster*: typically we will call N the size of the largest active cluster and its definition is different for bond and sites percolation. It is important to stress that this definition holds for fixed system size. For bond percolation *cluster size* is defined as the number of sites connected by active bonds.
Let's now consider the ratio N/L, where L is the system size (number of sites in my lattice): when we are dealing with phase transitions is important what happens in the thermodynamic limit of system size going to infinite and therefore this is why it's relevant to consider the ratio of the size of the largest cluster over system size. Considering the thermodynamic limit what happens (ratio can't be greater than unity) is represented in Figure 4.3:

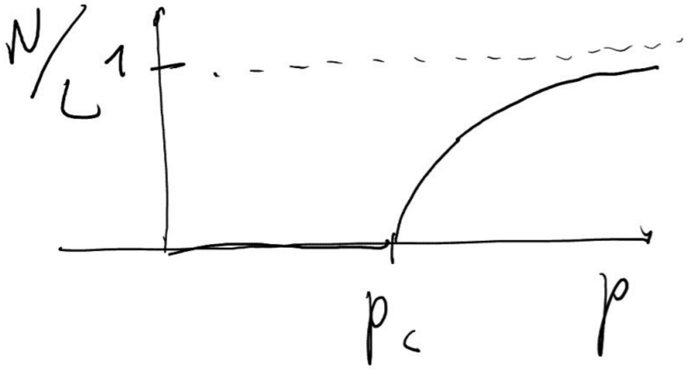


Figure (4.3) – Thermodynamic limit of N/L; p_c is the percolation threshold.

where p_c is a threshold parameter, a critical value of the probability that is known as *percolation threshold* below which the size of the largest active cluster does not scale linearly with the system size and above which it does.
Figure 4.3 is telling us that infinite size clusters appear for $p \geq p_c$ (if $L \to \infty$) and at the percolation threshold (which is an example of a critical point) the percolating cluster is *fractal* (has fractal properties).
So far we've discussed isotropic percolation so we are still dealing with equilibrium phase transitions.

Directed percolation

In DP the preferred /allowed flow direction can be interpreted as time direction and therefore the $d+1$ dimension[3] are meant to represent the non-equilibrium process in dimension d: one dimension is different from the others and it's the preferred dimension (which can be interpreted as a time).
When we talk about DP in this context we refer to it as a phase transition from a fluctuating active phase ($p > p_c$) to an inactive/absorbing phase ($p < p_c$) i.e. all sites are dry/inactive and no other sites can get wet.

---

[2] ∧Spanning through the whole system, from one site to the other.

[3] ∧We interpret the time direction as another dimension.

Looking at Figure 4.4 we can state that at $t = 0$ all sites are active and we can see what happens when times flows: when a row will be full of white dots then the system will be trapped in the absorbing phase.

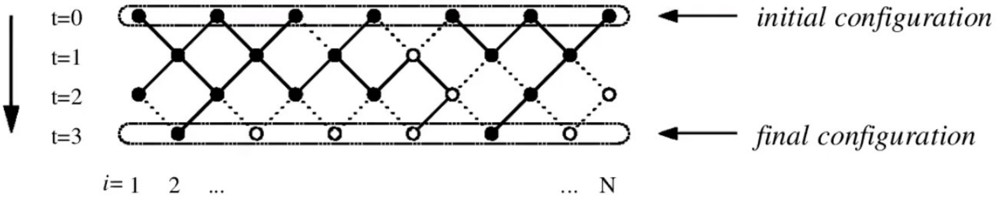


Figure (4.4) – Directed bond percolation in $1+1$ dimensions interpreted as a time-dependent stochastic process. Open (closed) bonds are indicated by solid (dashed) lines. Filled (hollow) circles denote active (inactive) sites. The configuration of the horizontal row at $t = 0$ is the initial state. Starting from a fully occupied initial state the model 'evolves' through intermediate configurations and reaches a final state at $t = 3$.

Stochastic rules

Let's now talk about the possible dynamical processes i.e. the **stochastic rules**: we want to describe in detail how we can go from time t to time $t + 1$.
We have to give probabilities for the following transitions: what is happening at a given site at time $t + 1$ is determined by the two sites that are above it at time t. We will use empty sites as inactive sites, full circles as active sites, dashed lines are inactive bonds, solid lines are active bonds.

If we have two empty sites (first image of Figure 4.5) the site below at $t + 1$ will always be empty with probability 1, it's the absorbing state. The next possible situation is the one in which a site is active and the other one inactive, with two possible outcomes: the site at $t + 1$ can be either active or inactive whether the bond on the left (as represented in Figure 4.5) is active or not. The control parameter p is actually the probability of the bond being active.
The last possible configuration is the one in which both sites are active at time t: if both bonds are not active the site at time $t + 1$ will be not active and this happens with probability $(1 - p)^2$. On the other hand the site at $t + 1$ can be active with probability (which can be derived through normalization) $1 - (1 - p)^2$ for both three sub-cases.

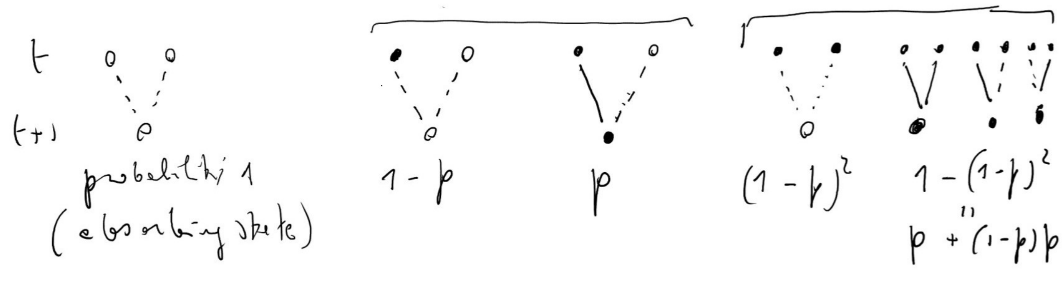


Figure (4.5) – Stochastic rules that follow the time evolution of the percolated system.

The rules we've just described are stochastic so in general we will talk about different realizations of the system and so given some initial conditions we can repeat the evolution several times each time choosing whether a bond is active or not with probability p: the outcome of different realizations could be different and then we will need to take averages over different realizations.

A typical order parameter is based on a Boolean variable that can be defined for each site $s_i(t)$. The index i is labeling the position of different sites on the same row for a given time $1 \leq i \leq L$ with L system size (# sites in a row):

$$s_i(t) = \begin{cases} 1 & \text{site } i \text{ is active at time } t \qquad (4.8) \\ 0 & \text{site } i \text{ is inactive at time } t \qquad (4.9) \end{cases}$$

Let's now define $N(t)$ as the number of active sites at time t:[4]

$$N(t) = \sum_i s_i(t) \tag{4.10}$$

One typical choice for initial conditions is to have just one site being active $s_i(0) = \delta_{i,i_0}$: knowing that the number of active sites is limited to $0 \leq N(t) \leq t+1$ and so at time t the number of active sites must be at most $t+1$ we can use a similar approach to the one we saw in isotropic percolation in which p_c is the critical percolation threshold and for[5]

$$\begin{cases} p < p_c \implies \langle N(t) \rangle \overset{t>>1}{\sim} \exp\left\{-t/\xi_{||}\right\} \overset{t\to\infty}{\longrightarrow} 0 & \text{subcritical inactive phase} \quad (4.11) \\ p > p_c \implies \langle N(t) \rangle \overset{t>>1}{\sim} t & \text{supercritical active phase} \quad (4.12) \\ p = p_c \implies \langle N(t) \rangle \overset{t>>1}{\sim} t^{\theta} & \text{critical phase} \quad (4.13) \end{cases}$$

In the *subcritical inactive phase* the number of active sites (asymptotically) decays exponentially in time and we will see that this allows us to define a correlation time and for infinite times it goes to zero: we can start with some active sites but sooner or later on average no active sites survives and the system gets trapped in the inactive phase. No infinite clusters are present[6].
In the *supercritical active phase* infinite clusters[7] exists with finite probability and the number of active sites grows linearly with time: if we think to an initial condition with just one active site what's going on is that $N(t)$ grows with time linearly and we see a cone. The opening angle of this cone depends on $p - p_c$, on how much we are above the percolation threshold. For a finite size system what we can state is that we have a finite density of active sites, as shown in figure 4.6
In this plot we recover the same behaviour shown in Figure 4.3 but here we are referring to a non-equilibrium process.

Finally at the percolation threshold we recover a typical situation of the critical points: asymptotically the number of active sites follows a power law in time with a critical exponent θ. Power laws implies that there is no characteristic

---

[4] ∧Shouldn't be averaged over different realizations???

[5] ∧$\langle . \rangle$ means average over different realizations of the stochastic process.

[6] ∧With this term we are referring to 2D percolation, a spanning cluster going from top to bottom where the active sites are surviving at infinite time.

[7] ∧Holds if the systems' size is infinite, when the number of active sites can grow indefinitely. Read on for finite sites.

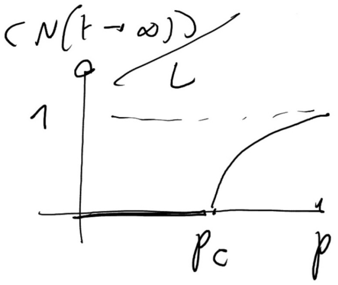


Figure (4.6) – Infinite time limit of the number of active sites over the system' size as a function of the percolation.

length or time an essentially we can observe clusters of all sizes (or *fractal clusters*) and we have scale-free behaviour.
The behaviour $\langle N(t)\rangle \sim t^{\theta}$ holds for infinite size systems.

Directed percolation is the analogous of the Ising model in the case of non-equilibrium phase transitions. While for $d = 1, 2$ we do have an analytic solution for the Ising model, for direct percolation we don't have yet an exact analytic solution, even in 1+1 (one space and one time) i.e. $d = 1$: the only knowledge we have about DP is coming from numerical simulations/evidences. The critical percolation threshold is known as $p_c \simeq 0.645$ and $\theta \simeq 0.302$ and the values of the exponents are universal: we will make examples of other systems which belong to the same universality class as directed percolation implies that they show power law behaviour with the same exponent (like θ) whereas the values of the control parameter at which we have a phase transition are typically non-universal (e.g. critical temperature in the Ising model).

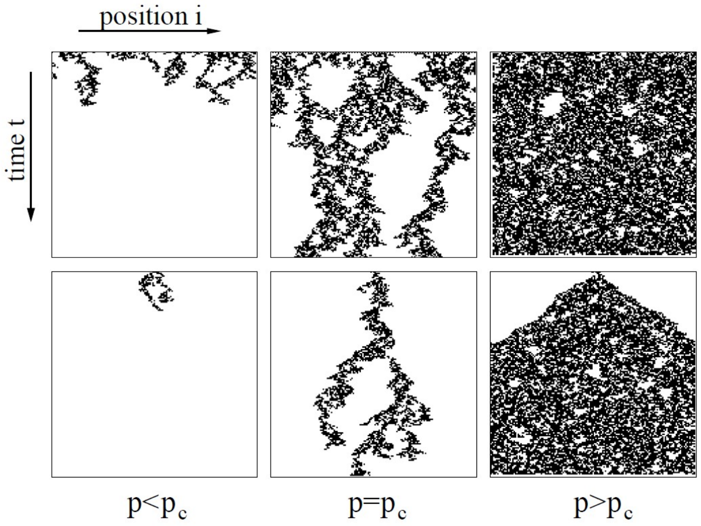


Figure (4.7) – Directed bond percolation in 1+1 dimensions starting from random initial conditions (top) and from a single active seed (bottom). Each horizontal row of pixels represents four updates. As can be seen, critical DP is a reaction-limited process.

Figure 4.7 shows specific realizations of the system for two different types of initial conditions in the three different phases (below/at/above the transition), where i labels different sites along any given row (and along a fixed time) and the time direction is the vertical one. Another typical initial condition choice (along the single initial active site at zero time, shown in the bottom row of Figure 4.7) is to start with a (random) fixed non-zero density of initial active sites (top row of Figure 4.7).

We can clearly see the behaviour previously described: in the first column active sites survive for some time but they eventually die out (no matter what the initial conditions are), above the transition we can see that the whole system is full of active sites (starting with a fixed fraction of active sites) or - starting with a single active site - we can recognize the characteristic conic shape (for a finite system) which depends on $p - p_c$ and eventually the number of active sites broads until reaches system's size L. The holes present in the third column of Figure 4.7 are not fractals: at any given time we have a finite density of active sites and holes are creating and disappearing but the density of active sites is asymptotically constant.

The interesting point is at $p = p_c$ where, starting with one site or with a fraction of them, in the end we are able to get to the bottom and the active site survives at infinite time. In addition the clusters look fractalic, they look self-similar at different scales.

(Lesson 14 of 12/11/20)
Compiled: January 11, 2021

4.1.2 Reaction-diffusion model

Let's highlight the connection of DP with a very used and popular model, called *reaction-diffusion*, whose name is due to the fact that it combines diffusion (the fact that particles in the model are moving around diffusing) and reaction (the number of entities in the model can change).

This kind of model is used to describe the combination of chemical reactions with the diffusion of the chemical species involved in the reaction.

In the context of DP we can show some examples in Figure 4.8: in the first sketch we can show two examples of diffusion: the active site is moving either to the left or to the right (like a unbiased random walk in $2d$). Another possibility is the case of a 'death' process in which all the active sites are disappearing all together or one more active site can appear. like in the 'offspring' generation. Another typical case is the 'coalescence' in which two active sites becomes just one at $t + 1$.

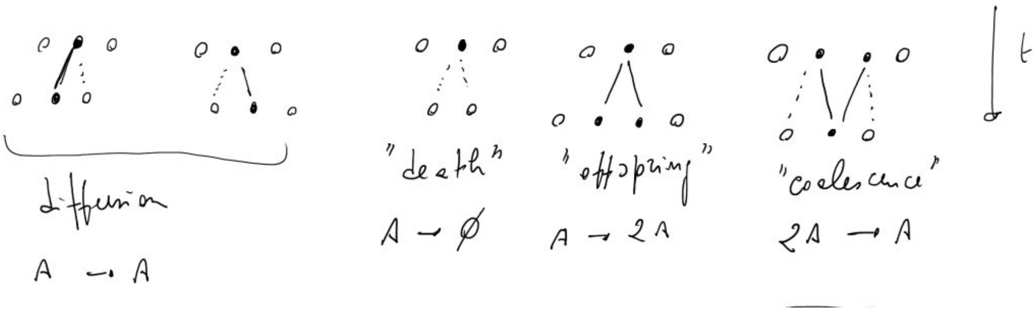


Figure (4.8) – Examples of directed percolation in different contexts. A stands for '#active site'.

We can realize from Figure 4.8 that in order to define those events (which are not really stochastic update rules) we had to put together different nearby sites to properly describe those events but the point is that DP can be seen at a very simple level as a reaction of a model which combines reactive and diffusive events.

4.2 Generalization of DP: The Domany–Kinzel Model of Cellular Automata

Many basic models of non-equilibrium phase transitions can be formulated as dynamical processes of interacting particles moving on a lattice. When a lattice site can be either occupied by a single particle or empty (exclusion process) and the evolution rule is local, synchronous, and Markovian, the model at hand is just a cellular automaton (CA).
In other words cellular automata (CA) is a binary model based on a lattice, so the sites of the lattice can be either *active* or *inactive* (**exclusion process**: there cannot be double occupancy of the sites). CA is also characterized by

- *Local evolution rules*: the evolution rules depend only on neighbouring sites;
- *Synchronicity*: sites can be updated in parallel (DP is an example);
- *Markovianicity*: what happens at $t + 1$ depends only on the history at the previous time t.

In addition CA can be either *deterministic* (with deterministic evolution update rules) or *stochastic* (stochastic update rules): DP and the DK model are examples of stochastic cellular automata.
The stochastic update rules in the Domany-Kinzel model are the ones presented in Figure 4.9:

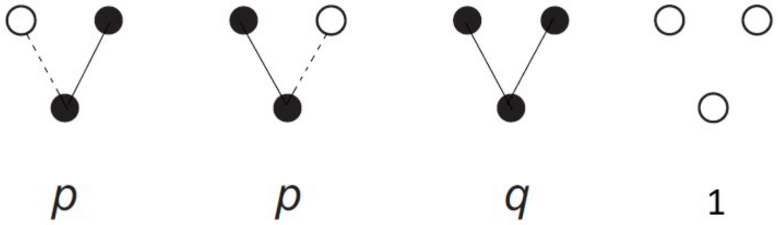


Figure (4.9) – Probabilistic evolution rules. The cases in which the final site is inactive can be recovered through normalization.

The third event of Figure 4.9 is associated to a probability q, so in the DK model we are dealing with two different parameters, p, q: p is the probability of diffusive event, while q is the probability of the coalescence event.

The phase diagram in the (p, q) plane is the one represented in Figure 4.10: we can see a transition line (the solid one) such that on the right of it we have the active phase while on the left the inactive phase.
The main point is that we have a critical line $p_c(q)$ (for any value of q we have a percolation threshold as a function of q) and for all q strictly less than unity $(0 \leq q < 1)$ we are in the same universality class of DP and only for $q = 1$ the universality class is changed and we move to another kind of non-equilibrium phase transitions called *compact directed percolation (CDP)*.
For $q = 1$ the corresponding percolation threshold is $1/2$ and we will discuss later why is that true.

We can now choose different examples of directed percolation in order to see how they are realized in the context of the DK model:

Bond directed percolation

We already saw that the event called 'coalescence', to which a probability q is associated in the DK model, for BDP q is just related to the following function:

$$q = p(2 - p) \tag{4.14}$$

which is a parabola in the (q, p) plane, as represented in Figure 4.10.

Site directed percolation

Looking closer to the coalescence event in site percolation p is the probability of a site being active, so the probability that the site below two active sites is active is just p: we don't have to look to bond activation but only to site activation, so $q = p$, represented in Figure 4.10 as the diagonal of the square.

Bond and site percolation share the same universality class but the percolation threshold is different.

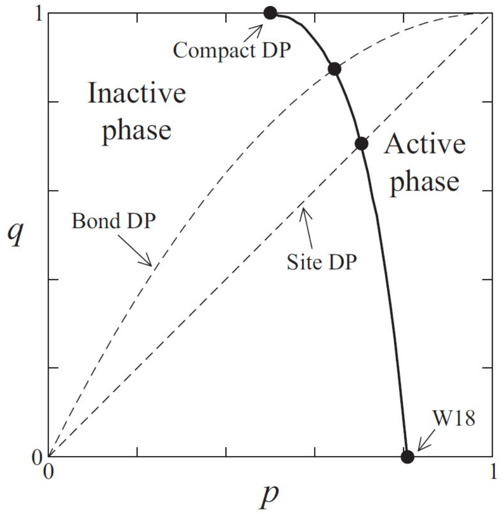


Figure (4.10) – Phase diagram of the DK model. The thick solid line is the curve $p_c(q)$, separating the absorbing (inactive) phase from the active one. The dashed lines correspond to the bond DP $(q = p(2 - p))$ and to the site DP percolation $(q = p)$.

Another example is $q = 0$: in this case the site below two active sites is always inactive and essentially there is no coalescence, called **W18** because it's a stochastic version of an update rule listed as Wolfram classification.
The last peculiar example is at $q = 1$: this is a different universality class, called *compact DP*, with $p_c = 1/2$ due to a 'symmetry' between active and inactive sites: when $q = 1$ we can also see the situation in which all the sites are active becomes an absorbing phase in the system, having two possible absorbing states[8] in the system (all sites empty and they keep being empty or all sites active and they keep staying active because $q = 1$).

It is also interesting how the percolating clusters look like at the percolation transition: in Figure 4.11 we see, as a function of p, the fractal nature of the percolating clusters right at the transition.
The quantity on the y axis is the average size of active spots which are stretches of active sites without holes in between: in a given time we can have different stretches and we can take the average of their size.
The higher is p the clusters presents several holes, which corresponds to low values of the $\langle S_{act} \rangle$ parameter. If we increase q then the corresponding percolation threshold is increasing and we can see e.g. BDP the holes are decreasing and $\langle S_{act} \rangle$ increasing.
In the limit of $q \to 1$ and therefore the percolation threshold going to 1/2 what happens is that holes disappear and essentially this is why the CPD are called in this way: the cluster are not fractal objects anymore.

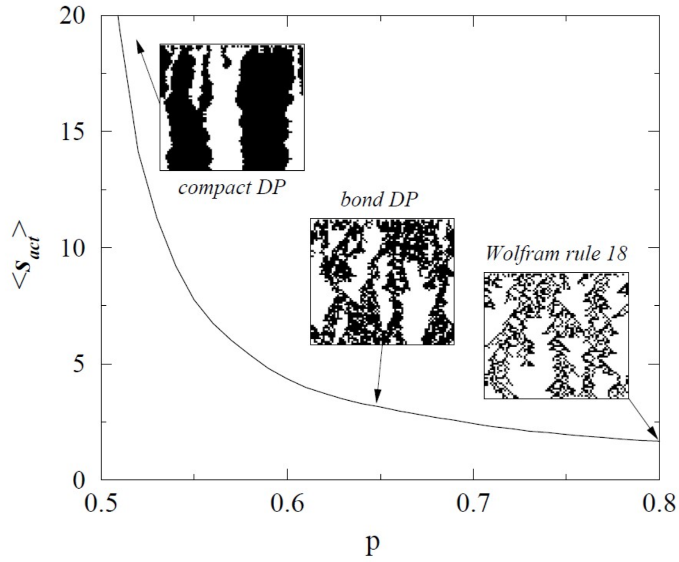


Figure (4.11) – Numerical estimates for the average size of active spots $\langle S_{act} \rangle$ in the Domany-Kinzel model measured along the phase transition line. The insets show typical clusters for three special cases discussed in the text.

Figure 4.12 is reported in order to clarify what 'active spots' means: to the right wee ave two different active spots, one of size 2 and one of size 3

---

[8] ∧This is why the universality class changes for $q = 1$.

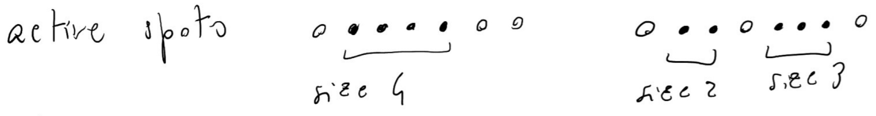


Figure (4.12) – Active spots' graphical interpretation.

4.3 The Phase Transition in DP-like Systems

4.3.1 Order Parameters, Correlation lengths and Critical Exponents

We define as *control parameter* the probability p (comparable to)
The DP class of non-equilibrium phase transitions to one single absorbing state is characterized by typical scaling properties at the transition point that are widely reminiscent of critical phenomena in the equilibrium case. For instance, the ferromagnetic transition in the Ising model (which will be used as a comparison) is found to occur at a critical temperature T_{c}, where the magnetization vanishes as $M \sim (T_{\mathrm{c}} - T)^{\beta}$. The temperature T and the magnetization M are the control and the order parameter of this phase transition, respectively. The divergence of the correlation length as $\xi \sim |T - T_{\mathrm{c}}|^{-\nu}$ implies that very close to T_{c} there is no typical macroscopic length scale; i.e., the physical system is invariant under scale transformations. From the discussion in the previous section, one can easily infer that in the DP class the natural control parameter, analogous to the temperature T in the equilibrium case, is some probability p, e.g., the probability of an open channel in bond DP/site activation, the parameter $p(q)$ in the DK model or the ratio (λ/r) in the contact process. As in equilibrium phenomena, the critical value of the control parameter[9], p_c, is a model-dependent quantity. As for the order parameter, in DP-like systems there are two possible ways to define it: (i) we can count the active sites and evaluate asymptotically in time their number (or their density), which must vanish in the inactive phase or (ii) we can evaluate the probability of not yet having reached the absorbing phase at time t (and, again, taking the limit $t \to \infty$). More precisely, the first choice depends on the initial conditions, which may be characterized by a vanishing or a finite density of active sites. In the former case (think of the limiting case of one single active site at $t = 0$) the morphology does not scale with the size of the system and we must simply count the number of active sites,

$$N(t) = \left\langle \sum_i s_i(t) \right\rangle$$

where the ensemble average $\langle \bullet \rangle$ is performed over many realizations of the stochastic evolution. For homogeneous initial conditions, instead, we should

---

[9] ∧The value of the control parameter is not universal: the critical value of the control parameter is non-universal, in a similar way of what happens in equilibrium phase transitions.

use the density of active sites[10]

$$\rho(t) = \frac{1}{L}\sum_i \langle s_i(t)\rangle = \frac{N(t)}{L}$$

where L is the total number of sites. The second choice for the order parameter is the survival probability for a trajectory whose initial state has one active site only, $s_i(0) = \delta_{i,k}$. It can be formally defined as

$$P(t) = \left\langle 1 - \prod_i (1 - s_i(t)) \right\rangle$$

where $P(t)$ is the ensemble average of an observable that is equal to 1 until an active site is present, while it vanishes only when the system evolves into the fully inactive absorbing state. In other words, $P(t)$ is the fraction of the ensemble of stochastic evolutions that at time t have not yet reached the absorbing state. Comparing DP with Ising model what we get is:

- *Control parameter*: the control parameter is the bond/site activation p

$$T \longleftrightarrow p \text{ or } (p, q) \text{ in DK}$$

- *Order parameter*: in the Ising model the magnetization density is used (average spin value): In the context of DP we can have different possible order parameters and it may depend for example on the kind of initial conditions that one is using: for example for one initially active site we can use (4.10) while for homogeneous initial conditions (fixed fraction of initially active sites) we can use $\rho(t) := N(t)/L$

$$m := \frac{\langle \sum_i S_i \rangle}{L} \longleftrightarrow \begin{cases} N(t) := \left\langle \sum_i s_i(t) \right\rangle & \text{1 IAS} \quad (4.15) \\ \rho(t) := N(t)/L & \text{F.F. of IAS} \quad (4.16) \\ P(t) := \left\langle 1 - \prod_{i=1}^{L} (1 - s_i(t)) \right\rangle & \text{S.P.} \quad (4.17) \end{cases}$$

It is important to state that the first average us over different realizations of a stochastic process, while the Ising one is just the thermodynamic ensemble average.

The last possible order parameter for a trajectory with one initially active state is called *survival probability*, defined as the average over different realizations of (4.17). The factors in the product are either 0 when the site is active or 1 when the site is inactive so the whole product is 1 $\iff$ all sites are empty or zero otherwise: this means that the yellow quantity is 0 for all empty/inactive sites or 1 for any other state with at

---

[10] ∧The density of active sites can actually be evaluated even for a single, initial active site if we normalize $N(t)$ with respect to t, which is the maximal possible number of active sites at time t, starting from a single active site.

least one active site. Taking then the average over all realizations of this quantity the survival probability is the fraction of survived trajectories, so $0 \leq P(t) \leq 1$ and 0 means that all trajectories at time t eventually end up in the absorbing phase, where all sites are empty. On the other hand $P(t) = 1$ means that all trajectories survived and none of the trajectories reached the absorbing phase;

- *Order with limits*: dealing with non-equilibrium phase transitions we also have time and we are interested in what is going on asymptotically at infinite time, therefore we have two limits: $t \to \infty$ and $L \to \infty$. The order in which these two limits are taken is very important: the correct order is first (for fixed time) taking the thermodynamic limit of infinite size system and then infinite time limit. This is the correct order to describe asymptotic behaviour in the thermodynamic limit.

  Doing the way around what we get is the asymptotic behaviour for a finite system, no matter how big it is: to study the property of an infinite size system the right limit order is the latter one.

The three order parameters that we introduced are zero in the inactive phase and they're greater than zero in the active phase: in this sense they are good order parameters.

- *Critical exponents*: In the limit $t \to \infty$ - in analogy to equilibrium phase transitions - these order parameters can be associated to critical exponents as:

$$m \sim (T_C - T)^{\beta} \longleftrightarrow \begin{cases} \rho(\infty) \sim (p - p_c)^{\beta} & (4.18) \\ P(\infty) \sim (p - p_c)^{\beta'} & (4.19) \end{cases}$$

  where the behaviour of the order parameter is similar to the curve represented in Figure 4.6 and the behaviour very close to the transition point is a power law and it defines the critical exponent β (as the exponent used in equilibrium phase transitions).

  These relations indicate that when approaching the critical point p_c from the active phase, $p > p_c$, both order parameters vanish according to a power law. It is customary to associate the survival probability with the annihilation process and the density of active sites with the creation process, so $\rho(t)$ and $P(t)$ are sometimes referred to as creation and annihilation order parameters, respectively.

  It is not obvious to say a priori if β and β' should be equal or not[11]: in general $\beta \neq \beta'$ and for $q = 1$ in the case of the DK model with Compact DP $\beta \neq \beta'$ whereas for $q < 1$ the DK model (DP) belongs to the bond DP universality class, has only one absorbing state and $\beta = \beta' \simeq 0.276$ in $1d$.

---

[11] ∧A primary criterion seems to be related to the number of absorbing states, as shown by the DK model.

> Let's now justify the fact that in DP $\beta = \beta'$ in the special case of Bond DP: we can actually show that the two order parameters are indeed the same quantity
>
> $$P(t) = \rho(t) \tag{4.20}$$
>
> because of time reversal symmetry, which holds only in the BDP case.

Let's now compute the survival probability $P(t)$: in Figure 4.13 we are drawing a trajectory where some branches die and some other survive until time t. Let's now take the bottom row and consider the time reversal (we have a full time reversal symmetry only in the case of BDP also because of the fact that we chose this tilted square lattice): let's consider all sites initially active and then let's consider all trajectories after reversing time.

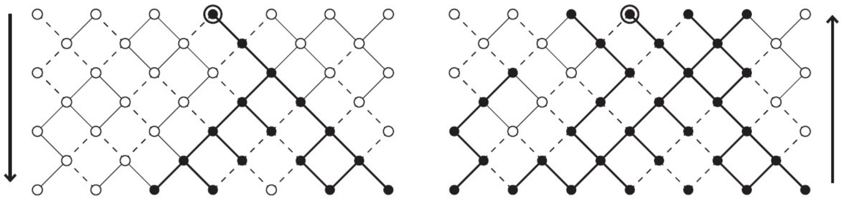


Figure (4.13) – Left: Directed percolation process starting from a single active site. Right: Time-reversed process of the left one, starting from a fully active state. If there is one directed path from top to bottom (left), there must be a directed path from bottom to top (right).

The point is that if we consider the fraction of active sites on top of the right of Figure 4.13 having started with all initially active sites on bottom is equal to the fraction of survived trajectories from top, because if we can go from bottom to the top and we see something acting to the top this means (due to time reversal symmetry) that we can start from that site active in the top and then reach back to the bottom.
When we say 'fraction of survived trajectories' it is a fraction in which we average over the different possible location/positions of the initially active sites, but in the definition of S.P. we need to average over different realizations of the system.
It turns out that those two kinds of averages (average over different initial conditions and average over different realizations of a stochastic process) provide the same result under the so called *self-averaging condition*: in general dealing with heterogeneous systems or with stochastic processes one has to perform an average over different realizations of the system and in this case over different possible trajectories or in a spin-glass over different samples of material for example.
The point is that, if a quantity is self-averaging what happens we can average over different subsets of the system: formally self-averaging holds only in the thermodynamic limit and instead of choosing always the same site as initially active and then to run the stochastic process at different times we can choose the same site as initially active and then try a trajectory various times (average over different realizations) we can average over different positions of the initially

active site and if the system is big enough the sampling of different trajectories is the same as sampling different realizations starting from the same point. The only rigorous proof that $\beta = \beta'$ is for BDP but numerically it can hold also for other examples of DP because $P(t) \overset{t>>1}{\sim} \rho(t)$.

From the book: The equivalence between the exponents β and β' in DP is a consequence of a special symmetry of this model, which amounts to a sort of time-reversal symmetry. A heuristic explanation can be given in the case of bond DP, considering a configuration of open and closed bonds as the one shown in Figure 4.13. The quantity $P(t)$ is evaluated in direct time (left panel) activating a single site and determining if there is a directed path through active bonds, leading to the opposite (bottom) side. If we are in the thermodynamic limit, the average over disorder realizations can be replaced, using self-averaging, by an average over the starting site, so $P(t)$ is just the fraction of initial sites that are connected to the opposite side. Now we revert the time arrow, as shown in the right panel of the same figure: we start from all active sites and evaluate the density of active sites at time $t, \rho(t)$ It is clear that a "top" site is now active if and only if there is a directed path connecting it to the bottom side, which is exactly the condition because, in direct time, it contributes to $P(t)$. In conclusion, if we average over disorder or we take the limit $L \to \infty$, we expect that

$$P(t) = \rho(t)$$

Accordingly, in the active phase both order parameters $P(\infty)$ and $\rho(\infty)$ have to saturate to the same value and have to exhibit the same critical behavior at p_c; i.e., β and β' have to be the same critical exponent. This equivalence holds also for other kinds of DP processes such as site DP or the contact process, although the same argument based on the exact time-reversal symmetry typical of bond DP does not apply. Nonetheless, there is numerical evidence that this symmetry still holds asymptotically, while $P(t)$ and $\rho(t)$ become proportional to each other in the long time limit and $\beta = \beta'$.

Let's now discuss the *correlation lenght*: the main feature that makes non-equilibrium critical phenomena different from equilibrium ones is the presence of independent spatial $(\xi_\perp)$ and time $\left(\xi_\|\right)$ correlation lengths, where the $\perp$ and $\|$ symbols refer to the time arrow. These quantities are associated with the asymptotic behavior of the space and (positive) time correlation functions

$$c_{|i-j|} := \left\langle \lim_{t\to\infty} \frac{1}{t} \sum_{\tau=0}^{t} \left(s_i(\tau) - \bar{s}\right)\left(s_j(\tau) - \bar{s}\right) \right\rangle \sim e^{-|i-j|/\xi_\perp} \tag{4.21}$$

$$c(t) = \left\langle \lim_{L\to\infty} \frac{1}{L} \sum_{i=1}^{L} \left(s_i(0) - \bar{s}\right)\left(s_i(t) - \bar{s}\right) \right\rangle \sim e^{-t/\xi_\|} \tag{4.22}$$

where i, j are the position of two different sites (and they refer to spatial coordinates) and the average (over different realizations) value

$$\bar{s} = \lim_{t\to\infty} \frac{1}{t} \sum_{\tau=0}^{t} \langle s_i(\tau) \rangle$$

does not depend on the site index (the limit of infinite time is crucial).

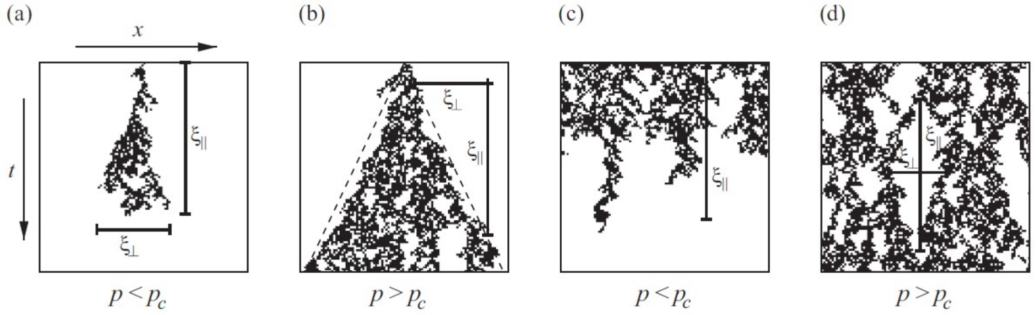


Figure (4.14) – Pictorial description of the correlation lengths $\xi_{||}$ and $\xi_{\perp}$ in a DP process for different initial conditions, below and above criticality. The explanation for part labels (a)–(d) are discussed in the text.

The physical interpretation of the temporal and spatial correlation lenghts $\xi_{||}$ and $\xi_{\perp}$ is represented in Figure 4.14. In the subcritical phase (a) $p < p_c$, $\xi_{\perp}$ is the typical size of a cluster and $\xi_{||}$ is the typical time of clusters before they disappear: in the inactive phase eventually all active sites disappear and so the correlation time is the typical survival time of the cluster.
On the other hand in the supercritical phase $p > p_c$ (b) $\xi_{\perp}$ is the typical size while $\xi_{||}$ is the typical duration time of islands of empty sites within clusters: in phase (b) we have a spanning cluster going from top to bottom, as big as the system' size but we have holes in it (*islands of empty sites*) that appear and disappear (it's a fluctuating phase). In the supercritical phase one can see that the ratio $\xi_{\perp}/\xi_{||}$ is related to the cone opening: if we start with one initially active site the cluster will grow and the opening of the cone is related to the previous ratio.

Of course when we are approaching the percolation threshold both the two correlation length diverges, so in this way we can define two more critical exponents: very close to p_c both correlation lengths are found to diverge as

$$\xi_{\perp} \sim |p - p_c|^{-\nu_{\perp}} \tag{4.23}$$

$$\xi_{||} \sim |p - p_c|^{-\nu_{||}} \tag{4.24}$$

for $p \to p_c$. A very important quantity used in describing non-equilibrium phase-transitions is the *dynamical exponent* z:

$$z := \frac{\nu_{||}}{\nu \perp} \tag{4.25}$$

From a practical point of view, the most efficient order parameter for determining the critical point of DP processes by numerical simulation is the average cluster mass which is found to grow algebraically at p_c as

$$N(t) \sim t^{\theta} \quad \text{for } p = p_c \tag{4.26}$$

It can be shown, also in out-of-equilibrium phase transitions, that one deals

Scaling laws

with **scaling laws** between different critical exponents :

$$\theta = \frac{d\nu_\perp - \beta - \beta'}{\nu_\|} \tag{4.27}$$

where d is the spatial dimension.
Let's show that scaling theory can be used also for non-equilibrium phase transitions.

4.3.2 Phenomenological Scaling Theory

As in equilibrium critical phenomena, we can work out a phenomenological scaling theory by making explicit the scale invariance engendered by the divergence of space and time correlation lengths close to p_c. Let's define the distance from the critical point as

$$\Delta := |p - p_c| \tag{4.28}$$

In practice, we can assume that close to the critical point the macroscopic properties of DP processes are invariant under scaling transformations of the following form

$$\Delta \to \Lambda\Delta \implies x \to \Lambda^{-\nu_\perp}x,\ t \to \Lambda^{-\nu\|}t,\ \rho \to \Lambda^{\beta}\rho,\ P \to \Lambda^{\beta'}P \tag{4.29}$$

This means that if we rescale the distance from the critical point by an arbitrary scaling factor , we can recover the same macroscopic properties of the original DP process by rescaling all other physical quantities.
To understand what does it mean, let's suppose that $\Delta < 1$, so we are approaching the critical point and in this case a typical length, like x, is expected to diverge.
We can use this scaling assumption to find how the order parameter behaves as a function of time $\rho(t)$ at the critical point: we can do this computing the order parameter at the rescaled time

$$\rho(\Lambda^{-\nu_\|}t) \overset{!}{=} \Lambda^{\beta}\rho(t) \tag{4.30}$$

i.e. if we either rescale time or rescale ρ we need to get the same result.
Choosing $\Lambda^{-\nu_\|}t = 1$:

$$\Lambda^{-\nu_\|}t = 1 \implies \Lambda = t^{\frac{1}{\nu_\|}} \tag{4.31}$$

$$\rho(t) = \Lambda^{-\beta}\rho(1) = \tag{4.32}$$

$$= t^{\frac{-\beta}{\nu_\|}}\rho(1) \tag{4.33}$$

$$\text{and so } \rho(t) \overset{t\to\infty}{\sim} t^{-\delta},\ \text{with } \delta = \frac{\beta}{\nu_\|} \tag{4.34}$$

The analogy with the Ising model is (for $T = T_c$) that $m \sim H^{1/\delta}$ with H magnetic field. In this view we can see time as an 'external field' because we have to send $t \to \infty$ to see the critical behaviour.

We can do the same trick for $P(t)$:

$$\text{for } p = p_c \implies P(t) \sim t^{-\delta'}, \text{ with } \delta' := \frac{\beta'}{\nu_\parallel} \tag{4.35}$$

In general $\beta \neq \beta'$ and $\delta \neq \delta'$ but for DP $\beta \neq \beta' \implies \delta \neq \delta'$ and the scaling law (4.27) becomes:

$$\theta = \frac{d\nu_\perp - 2\beta}{\nu_\parallel} \tag{4.36}$$

Finite size scaling

Similarly to equilibrium phase transitions it is important to point out that the knowledge of the critical exponents provides relevant information about the behavior of the order parameters close to the critical point and in a finite-size system.
For $t >> 1$, $\Delta << 1$ and for very large systems $V >> 1$ (volume, in $d = 1$ then $V = L$) ρ and P depend on these parameters. On the other hand, the property of scale invariance implies that one of these parameters can be expressed in terms of the others, thus yielding the expressions

$$\rho(t, \Delta, V) \sim t^{-\beta/\nu_\parallel} f\left(\Delta t^{1/\nu_\parallel}, t^{-d/z} V\right) \tag{4.37}$$

$$P(t, \Delta, V) \sim t^{-\beta'/\nu_\parallel} g\left(\Delta t^{1/\nu_\parallel}, t^{-d/z} V\right) \tag{4.38}$$

where f and g are suitable scaling functions whose explicit expression is unknown and the yellow argument is $\Delta\Lambda$ while the green one is $V\Lambda^{-d\nu_\perp}$ (which is the way how Δ and V are rescaled): the idea is to say that the system is invariant under a scaling transformation (4.29) and doing the previous trick we can fix Λ as

$$\Lambda = t^{\frac{1}{\nu_\parallel}} \tag{4.39}$$

(Lesson 15 of 18/11/20) Compiled: January 11, 2021

4.3.3 Mean-field theory

In analogy with equilibrium phase transitions, it has been conjectured that the notion of universality applies also to continuous non-equilibrium phase transitions. This means that scaling properties characterizing the behavior close to the critical point depend on basic properties only and are independent of the details of the model at hand. It is worth pointing out that such a conjecture has been successfully checked in many cases by careful numerical studies, but a rigorous mathematical proof is still unknown, because the dynamical renormalization group method encounters more serious technical difficulties to be worked out than the static one.

What we will do is writing a phenomenological Langevin equation for a quantity called $\rho(\vec{x}, t)$ which is the density of active sites at position $\vec{x}$ and at time t. This quantity has to be understood as a space-time coarse-grained average.

Mean-field treatement of contact processes

Let's start with a further approximation in which we consider a uniform density of active sites $\rho(\vec{x}, t)$ with a *contact process*, which is actually a very simple example to model epidemic spreading. The fact of talking about contact processes is to emphasize the concept of 'universality': the detail of the model that we will preset will be different from DP but it belongs to the same class of universality.

Let's call active sites *infected individuals* and empty becomes *healthy individuals*: if all individuals stay healthy (empty) then the others will be healthy too but if we have a single initially infected individual (*patient zero*).

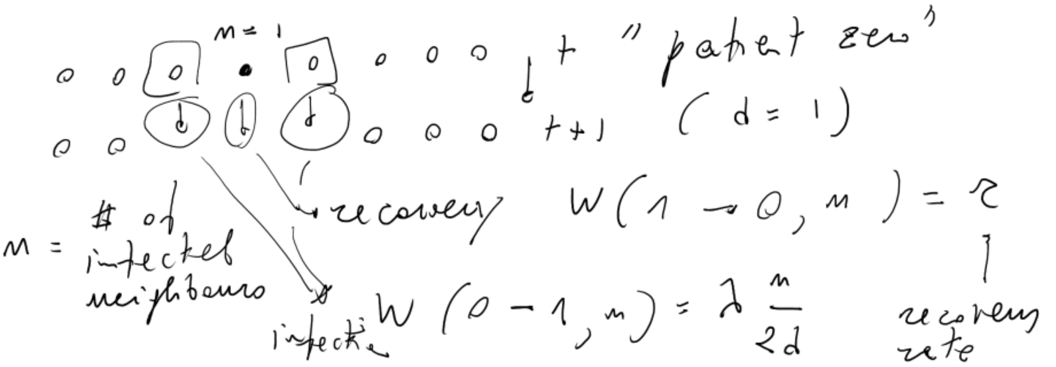


Figure (4.15) – Contact process: epidemic spreading example, where 0 corresponds to empty/healthy while 1 corresponds to active/infected.

A first difference with DP can be seen in Figure 4.15: in this example we are not using a tilted lattice and we can recognize two different processes going on, *infection* and *recovery*.

People who were infected can recover and the probability that describes this event is defined as the *recovery rate* $r := w(1 \to 0, n)$. In principle this rate[12] could depend on n i.e. on the number of infected neighbours: for example in Figure 4.15 for the squared sites n corresponds to one because they both have an infected neighbour.

In the simplest case recovery does not depend on the number of infected neighbours and is a given probability r.

For what concerns infection we can decide whether an infected site stay infected or get healthy just depending on the recovery rate but we also must have a rule for infection: one possible rule is $w(0 \to 1, n) = \lambda n/2d$, where λ is the *infection rate* i.e. the probability of being infected by a neighbour in one timestep and in the sketch (which is in $d = 1$ but we are formulating it in d dimensions) $n/2d$ is the fraction of infected neighbours (because $2d$ is the number of nearest neighbours).

This model belongs to the **same universality class of DP** and numerically[13] we can show that the critical ratio of the transition threshold $(\lambda/r)_c \simeq 3.29785$. In this very simple model *reinfection* is allowed: one a given individual is recovered it can be infected again.

---

[12] ∧Not so precise: we are describing a discrete time model defining rates as if the time was continuous.

[13] ∧No analytic solutions even for $d = 1$.

Mean-field

Let's now introduce the mean-field approach with uniform density of infected sites $\rho(t)$. The mean-field evolution equation, switching to continuous time, is:

$$\frac{\partial \rho}{\partial t} = \underbrace{\lambda\rho(1-\rho)}_{\text{gain term}} - \underbrace{r \cdot \rho}_{\text{loss term}} := a\rho - \lambda\rho^2 \tag{4.40}$$

where the yellow term is the healthy one, while the green term is the infected one and the linear term is defined as $a := \lambda - r$; this is a mean-field approach because we are losing the fact that we have neighbours and everything is uniform. Factorizing ρ and looking for stationary solutions ρ^*:

$$\frac{\partial \rho}{\partial t} = \rho(a - \lambda\rho) \quad s.t. \quad \frac{\partial \rho}{\partial t}|_{\rho=\rho^*} = 0 \tag{4.41}$$

then

$$\partial_t \rho|_{\rho^*} = 0 \quad \Longleftrightarrow \quad \begin{cases} \rho_1^* = 0 & (4.42) \\ \rho_2^* = \dfrac{a}{\lambda} = \dfrac{\lambda - r}{\lambda} = 1 - \dfrac{r}{\lambda} & (4.43) \end{cases}$$

when are $\rho_{1,2}^*$ stable or unstable? Let's compute the second derivative:

$$\frac{\partial^2}{\partial t^2}\rho = a - 2\lambda\rho \quad \Longrightarrow \quad \frac{\partial^2}{\partial t^2}\rho|_{\rho=\rho_1^*} = a; \quad \frac{\partial^2}{\partial t^2}\rho|_{\rho=\rho_2^*} = -a; \tag{4.44}$$

and so

$$\text{if} \begin{cases} a > 0 \longrightarrow \rho_2^* & \text{is stable and } \rho_1^* \text{ is unstable;} \quad (4.45) \\ a < 0 \longrightarrow \rho_2^* & \text{is unstable and } \rho_1^* \text{ is stable;} \quad (4.46) \end{cases}$$

the solution $\rho_1^* = 0$ is the inactive phase (all sites healthy), $\rho_2^* = a/\lambda$ is the active phase (epidemic spreading) and so even if we go to the thermodynamic limit a finite fraction of all sites are infected.
To conclude we've found that the critical point -in the uniform approach - is given by $a_c = 0$ i.e. $(\lambda/r)_c = 1$ (which is clearly different from 3.298): the mean-field approach under estimates the exact value of the critical threshold.n

Non-uniform density of active sites

Let's now consider a non-uniform density $\rho(\vec{x}, t)$ of active sites: mean-field means that stochastic fluctuations are neglected.
The overall aim is to get a mean-field calculation of a critical exponent: essentially we will write a Langevin-like equation for ρ, adding a diffusion term due to the fact that ρ isn't uniform anymore and a stochastic noise η

$$\frac{\partial \rho(\vec{x}, t)}{\partial t} = a\rho(\vec{x}, t) - \lambda\rho^2(\vec{x}, t) + D\nabla^2\rho(\vec{x}, t) + \eta(\vec{x}, t) \tag{4.47}$$

we will define the noise in a different way with respect to the Langevin equations used so far for the presence of the blue term (but it's still uncorrelated in space and time):

$$\langle \eta(\vec{x}, t) \rangle = 0; \qquad \left\langle \eta(\vec{x}, t)\eta(\vec{x}', t') \right\rangle = \Gamma\, \rho(\vec{x}, t)\, \delta(\vec{x} - \vec{x}')\delta(t - t') \tag{4.48}$$

Multiplicative noise

This is an example of *multiplicative noise* and we need to consider noise in such

a way because noise is present only in the active phase. In the active phase, in which all sites are healthy/empty, there is no fluctuation/ noise and $\rho = 0$ everywhere.
Looking at physical dimensions we can realize that the strength $\Gamma = [s^{-1}]$.
In general the noise correlation tells us that

$$\eta(\vec{x}, t) \sim \sqrt{\rho(\vec{x}, t)} \tag{4.49}$$

Let's now deduce the values of the critical exponents in the mean-field approach: the trick is to use *scaling invariance* close to the critical point $a_c = 0$ (we already found it in the context of uniform density).
In the last lecture we saw an example of scaling transformation with scaling factor Λ that we chose to be equal to the distance from the critical point, which can say it's equal to a because the critical point is $a = 0$:

$$\Lambda = \Delta = a \tag{4.50}$$

Now we will write a rescaled Langevin equation applying (4.29) to (4.47) taking into account that the distance Δ from the critical point is now equal to $a = \lambda - r$ because the critical point is defined precisely by the condition $a = 0$. With the condition $\Lambda = a$ in mind (the yellow $(\beta) + 1$ is due to this fact), the rescaled equation is

$$\begin{aligned}
\Lambda^{\beta+\nu_\parallel} \frac{\partial \rho(\mathbf{x}, t)}{\partial t} &= \Lambda^{\beta+1} \rho(\mathbf{x}, t) - \lambda \Lambda^{2\beta} \rho^2(\mathbf{x}, t) + \qquad (4.51)\\
&+ D \Lambda^{\beta + 2\nu_\perp} \nabla^2 \rho(\mathbf{x}, t) + \Lambda^{\gamma} \eta(\mathbf{x}, t) \qquad (4.52)
\end{aligned}$$

where the exponent[14] $\gamma = \left(\beta + d\nu_\perp + \nu_\parallel\right)/2$ while taking into account the property of the Dirac delta distribution $\delta(cx) = \frac{1}{|c|}\delta(x)$.
Dividing all terms by $\Lambda^{\beta+\nu_\parallel}$ we obtain

$$\begin{aligned}
\frac{\partial \rho(\mathbf{x}, t)}{\partial t} &= \Lambda^{1-\nu_\parallel} \rho(\mathbf{x}, t) - \lambda \Lambda^{\beta-\nu_\parallel} \rho^2(\mathbf{x}, t) + \qquad (4.53)\\
&+ D \Lambda^{2\nu_\perp - \nu_\parallel} \nabla^2 \rho(\mathbf{x}, t) + \Lambda^{\gamma - \beta - \nu_\parallel} \eta(\mathbf{x}, t) \qquad (4.54)
\end{aligned}$$

If we impose that the deterministic part of the Langevin equation is invariant under scale transformations, we must impose the vanishing of the relative scaling exponents, which allows us to obtain

$$\beta = \nu_\parallel = 1, \quad \nu_\perp = \frac{1}{2}, \quad \nu_\parallel = 1 \implies z = \frac{\nu_\parallel}{\nu_\perp} = 2$$

So far we've asked that the deterministic terms in the Langevin equation stay the same and we didn't consider yet the stochastic term: let's look at the stochastic term to determine the upper critical dimension.

---

[14] ∧Riguarda 11.33 pt 2, non ho ben capito il perchè.

When dealing with mean-field a limit in which we are sure mean-field treatment becomes exact is the limit of infinite dimension: in general what happens for any system is that there is an *upper critical dimension* such that above that dimension the mean-field treatment provides exact results, so the exact results are the same of mean-field.

The point is that mean-field exponents are exact when the stochastic term is **irrelevant** i.e. disappears in our scaling transformation (which implies that the yellow term of (4.54) must be positive because getting closer to the critical point means that Λ is small) if $\gamma - \beta - \nu_\parallel > 0$:

$$\Lambda^{\gamma-\beta-\nu_\parallel} \overset{\Lambda \to 0}{\longrightarrow} 0 \tag{4.55}$$

Substituting the value of γ found in (4.52) in the previous expression we can find a condition on the dimension d:

$$d\nu_\perp - \beta\nu_\parallel > 0 \implies \boxed{d > \frac{\beta + \nu_\parallel}{\nu_\perp} = 4} \tag{4.56}$$

and in this way we were able to find the upper critical dimension, namely $d_c = 4$, as in the Ising model, for instance.
This idea to check when mean-fields are exact by looking at the relevance of the stochastic term is known as *Ginzburg criterion.* In mean-field we can also show that $\beta = \beta'$.

Ginzburg criterion

Recovering the scaling law for the θ exponent (which we didn't prove because it's difficult in the out-of-equilibrium phase transitions context)

$$\theta = \frac{d\nu_\perp - 2\beta}{\nu_\parallel} \overset{d=4}{=} 0 \tag{4.57}$$

this relation holds only for $d \leq 4$ and inn the context of mean-field: when we are at the upper critical dimension $d_c = 4$ the mean-field exponents are also correct but with logarithmic corrections to the power law, therefore we can use the scaling law for θ only with $d = 4$ and if we do it we get as result zero.

4.3.4 Different universality class (from DP)

We again talking about non-equilibrium phase transitions and in particular the ones with absorbing states. We will show different examples on models where we move away from DP universality class.
An overall aim of this section will be to emphasize the similarity and the differences with respect to the case of equilibrium phase transitions. In general, if we have in the model more absorbing phases, then we have a different universality class.
A way to change universality class can be expressed through a contact process example i.e. epidemic spreading: the reason why the following model belongs to another universality class is because it has more absorbing phases.

In DP we have only 1 absorbing phase: all sites are empty and the same was holding in the example of contact process with reinfection: all the individuals are healthy (unique absorbing state in the system if reinfection with the same probability $p_2 = \lambda n/(2d)$ is possible[15]).

Let's complicate the model introducing the *immunization*, which means that the idea that the reinfection probability p_2 is less than p_1. We can talk about *partial immunization* if still $p_2 > 0$.
We can have a complete immunization if we say that $p_2 = 0$ and this implies the use of a model called SIR, i.e. a given individual can be in 3 different states:

- **S**usceptible (somebody who is originally healthy but never got the decease)
- **I**nfected
- **R**ecover

Once the individual recovers can't be infected again because $p_2 = 0$.
In the perspective of non-equilibrium phase transitions with absorbing phases we can have more absorbing phases; in the previous example we have a n infinite number of possible absorbing phases/states. Any combination of S,R individuals will just say the same: the crucial thing to have an absorbing state is not have any infected individuals.

This is a way to change universality class: if $p_2 = 0$ and for small enough $p_2 > 0$ we can simulate the system at the critical point (based on the ratio of infection/recovery rate) finding that the critical exponent value are different from the DP case.

This universality class is called *dynamical percolation*.
If $p_2 = 0$ the only parameter is p_1 and when $p_1 > p_{1,c}$ where $p_{1,c}$ is a threshold value, we are in the active phase in which we have the propagation of a percolation front and not clusters anymore, while in the other case we are in the inactive phase

4.4 SIR model

It is a sort of mean-field approach with uniform ρ (no spatial structure, time is the only parameters).
N is the total number of individuals which is constant. The partition of our system is based on 3 classes:

$$S(t) + I(t) + R(t) = N \tag{4.58}$$

and we have to deal with two parameters: λ and r.

$$\lambda = \frac{\textit{\#infected people by one infected individual}}{\textit{unit time}} \iff \text{transition} S \to I \tag{4.59}$$

---

[15] ^Infection probability will be called p_1.

$$r = \frac{\textit{recover probability}}{\textit{unittime}} = \frac{1}{t_r} \Longleftrightarrow \text{transition} I \to R \tag{4.60}$$

where t_r is the typical recovery time.
The equation for the SIR model is:

$$\frac{dS}{dt} = -\lambda \frac{S}{N} I \tag{4.61}$$

$$\frac{dI}{dt} = \lambda \frac{S}{N} I - rI \tag{4.62}$$

$$\frac{dR}{dt} = rI \tag{4.63}$$

At epidemic start $S(t) \lesssim N$ and $I << N$ and so we can approximate that $S/N = 1$ and so the time evolution equation for the infected individuals becomes a close equation

$$\frac{dI}{dt} = (\lambda - r)I \tag{4.64}$$

whose solution is

$$I(t) = \exp\{(\lambda - r)t\} = \exp(r(\lambda/r - 1)t) \tag{4.65}$$

where $R_0 := \lambda/r$ and it is called *reproduction number* and it is the number of people infected by an individual before recovery. If $R_0 = 1$ critical threshold: $R_0 > 1$ active phase with exponential increase, $R_0 < 1$ exponential decrease.

Chapter 5

Appendix

Appendix A: proof of (3.212)

In this appendix we want to prove that

$$\langle \mathbb{F}_k X_j \rangle = -\delta_{kj} \tag{5.1}$$

holds and it was used in order to show the consistency between the two ways to introduce the Onsager coefficients (one way is (3.205)), the other one is (3.207)). Let's prove this equation emphasising the fact that we are working in the LR regime (very small affinities).

Formally we can write
da finire 04-11

Appendix B: Thomson-Joule effect

da finire 05-11
The Thomson-Joule effect appears when an electric current flows through a conductor with an applied temperature gradient. We consider first a conductor through which a heat current flows in the absence of an electric one. This implies that a temperature gradient sets in the conductor, where the temperature field $T(x)$ along the conductor is determined by the dependence on temperature of its kinetic coefficients. We can now perform an idealized setup, where the conductor is put in contact at each point x with a heat reservoir at temperature $T(x)$. In such conditions there is no heat exchanged between the conductor and the reservoirs. Then, we switch on a stationary electric current j_n flowing through the conductor, thus producing a heat exchange with the reservoirs, in such a way that any variation of the energy current through the conductor has to be supplied by the reservoirs. Before switching on the electric current we know that the energy current must be conserved, i.e., $\partial_x j_u = 0$. After the electric current is switched on, according to (2.267) we can write

$$\partial_x j_u = \partial_x j_q + j_n \partial_x \mu$$

because j_n is a constant current. Using (2.265) and (2.263) we can rewrite this equation as

$$\partial_x j_u = \partial_x \left(T\varepsilon e j_n + T^2 \kappa \partial_x \frac{1}{T} \right) + \left(-\frac{e^2}{\sigma} j_n + T^2 \varepsilon e \partial_x \frac{1}{T} \right) j_n$$

In the adopted setup the only quantities[1] that depend on the space coordinate x are T and ε, and we can simplify (2.275), obtaining

$$\partial_x j_u = T \left(\partial_x \varepsilon \right) e j_n - \kappa \partial_x T - \frac{e^2}{\sigma} j_n^2$$

since in the absence of an electric current, i.e., $j_n = 0$, we must have $\partial_x j_u = 0$; the temperature field must be such that the second addendum on the right-hand side must vanish, i.e.,

$$\kappa \partial_{xx} T = 0$$

This means that the temperature field $T(x)$ is expected to exhibit a linear dependence on the space coordinate x, consistently with the Fourier's law. Thus, assuming as a first approximation that the temperature profile does not change when $j_n \neq 0$, we can simplify Eq. (2.276) as

$$\partial_x j_u = T \left(\partial_x \varepsilon \right) e j_n - \frac{e^2}{\sigma} j_n^2$$

On the other hand, the thermoelectric power depends on x because it is a function of temperature, so we can write

$$\partial_x \varepsilon = \frac{d\varepsilon}{dT} \partial_x T$$

from which

$$\partial_x j_u = T \frac{d\varepsilon}{dT} \partial_x T e j_n - \frac{e^2}{\sigma} j_n^2$$

The second term on the right-hand side is the so-called Joule heat, which is produced even in the absence of a temperature gradient. The first term is the so-called Thomson heat, which has to be absorbed by the reservoirs to maintain the temperature gradient, $\partial_x T$, when the electric current flows through the conductor. We can define the Thomson coefficient, τ, as the amount of Thomson heat absorbed per unit electric current $(e j_n)$ and per unit temperature gradient $(\partial_x T)$, obtaining

$$\tau = T \frac{d\varepsilon}{dT}$$

Making use of this definition and of Eq. (2.273) we can establish a relation between the Peltier and Thomson coefficients with the thermoelectric power,

$$\frac{d\Pi_{AB}}{dT} = \left(\tau_B - \tau_A \right) + \left(\varepsilon_B - \varepsilon_A \right)$$

which can be interpreted as a consequence of the energy conservation. In fact, the thermoelectric power of a junction is the result of the contributions of the heat per unit temperature and per unit electric current supplied to the junction by the Peltier and by the Thomson effects.

---

[1] ∧In principle κ should also depend on T and, accordingly, on x, but for sufficiently small temperature gradients, it can be assumed to be constant.