

Lecture Notes on Non-equilibrium Statistical Physics

B. Fourcade

Bertrand.Fourcade@univ-grenoble-alpes.fr,
Laboratoire interdisciplinaire de physique,

Lecture notes available at :

[http://liphy-annuaire.univ-grenoble-
alpes.fr/pages_personnelles/bertrand_fourcade](http://liphy-annuaire.univ-grenoble-alpes.fr/pages_personnelles/bertrand_fourcade)

Things to do :

- Send me an e-mail, so I know your address;
- Download this document (no need to print because it will be upgraded).

CONTENTS

Chapter 1. Introduction: Equilibrium and non-equilibrium statistical mechanics with some examples, general overview	7
1. Some questions and useful references	7
2. Equilibrium and non-equilibrium systems	8
3. Thermodynamics	9
4. Can fluctuations beat the second principle ?	10
5. The principle of detailed balance	11
6. Phase space	13
7. The Liouville equation	14
Chapter 2. Stochastic variables	17
1. Fundamental definitions	17
2. Bayesian Statistics	17
3. Average, moments and cumulants	18
4. Characteristic functions-Cumulants	19
5. Calculations rules	19
6. Stochastic processes	20
7. Some basic distributions	20
7.1. The multinomial distribution	20
7.2. The Gaussian distribution	20
7.3. The Poisson distribution	20
7.4. The Boltzmann distribution	22
8. Multivariate Gaussian distribution	22
9. Central limit theorem - Stable distributions	23
10. Entropy and probability	24
11. Correlation functions	26
12. Correlation and the Power Spectrum	27
13. Bayesian statistical Inference	28
Chapter 3. Brownian motion	31
1. Introduction	31
2. The Langevin equation ^{8;15}	32
3. Numerical integration of stochastic differential equations	34
4. Detailed balance and the Langevin equation	36
5. Diffusion equation and random walk: The Schmoluchowski equation	37
6. Return statistics : Transience and recurrence	39
7. An example of first passage probability: The gambler ruin problem	40
8. Path integral approaches to Brownien motion	41

9. The Caldeira-Leggett model	41
Chapter 4. The Fokker-Planck equation	45
1. Basic derivation	45
2. The Fokker-Planck equation and the Langevin equation	47
3. The Fokker-Planck equation and the diffusion equation	48
4. Boundary conditions for the Fokker-Planck equation	49
5. The Peclet number	53
6. Diffusion in a force field	55
7. A First-passage problem: The escape over a potential barrier	57
Chapter 5. The Master equation	61
1. Introduction	61
2. Coarse-graining the phase space and the problem of entropy	61
3. Stochastic approach to chemical kinetics: The master equation	62
4. The Master equation	65
5. Thermostat and detailed balance	67
6. Monte-Carlo method	68
7. Heat And work	68
8. Conclusion	69
Chapter 6. Stochastic thermodynamics : Crooks and Jarsynski equalities	71
1. Heat and work	71
1.1. Statement of the Jarzynski equality	72
2. Consequences	72
3. The Szilard's Machine	73
4. Proof of a Jarzynski equality in a trivial case	74
5. Proof of the Jarzynski equality	74
6. Experiments in the nano-world, see ¹⁶	75
Chapter 7. The damped harmonic oscillator	77
1. Dynamical susceptibility	77
2. A mathematical interlude: Principal value of an integral	78
3. Analytical properties	79
4. Dissipation	81
5. The fluctuation dissipation theorem: A preview	81
6. Hydrodynamic Description	82
Chapter 8. Linear response theory	85
1. The micro-canonical ensemble	85
2. Macroscopic Einstein fluctuation theory	86
3. The fluctuation-dissipation theorem	87
4. The dynamical susceptibility and the fluctuation dissipation theorem	88
5. The electrical conductivity	90
6. The Liouville equation	91
7. Divertimento : The Schmoluchowsky equation	92
8. Time-dependent perturbation	93
9. Kubo relationship	94
10. Time-inversion symmetry	95
11. Quantum linear response theory	95
Chapter 9. Non-equilibrium Thermodynamics	99
1. The Onsager regression principle	99
2. Entropy production and generalized current and force	100
3. Symmetries and Onsager Relations	102

4. Phenomenological equations	102
5. Microscopic reversibility	103
6. Onsager's relations follows from the principle microscopic reversibility	103
7. The principle of least production of energy	105
8. Experimental verification	105
9. The Boltzmann equation	105
Chapter 10. Path integrals and quantum dissipation	107
1. Introduction	107
2. The picture	109
3. Path integral and Brownian motion	109
4. Principe variationnel	110
Calculus	111
Équation de Schrödinger	112
États stationnaires	114
5. Density matrices	115
6. Effective equilibrium density matrix	116
7. Decay of a metastable state	117
Chapter 11. Problems	119
Problem 1	125
Problem 2 : Brownian motion in a gravitational field	125
Problem 3	126
1. Problem 1	127
Problem 2	128
Problem 3	129
Chapter 12. Appendix	143
1. Gaussian integrals	143

CHAPTER 1

INTRODUCTION: EQUILIBRIUM AND NON-EQUILIBRIUM STATISTICAL MECHANICS WITH SOME EXAMPLES, GENERAL OVERVIEW

This chapter is a sneak preview of what will happen next

1. Some questions and useful references

Why do we need non-equilibrium statistical mechanics ?

- (1) Nanotechnology, biophysics and chemistry are using or studying smaller and smaller objects: nanomachines, biomolecules.
- (2) Statistical fluctuations (thermal and others) and are relatively larger for these systems.
- (3) Fluctuations may behave wildly different from the mean.
- (4) Energy can sometimes flow from a cold source to a hot one. We may have more than one reservoir: 'ssystems can be out of equilibrium.
- (5) Small engines are not simple rescaled versions of their larger counterparts. They cannot work at our scale.

What are we going to do in these lectures (introductory level):

- (1) Non-equilibrium steady states: systems with heat currents and/or under external drive.
- (2) What corresponds to the Boltzmann factor $e^{-\beta H}$ in non-equilibrium systems ? In equilibrium, everything (in principle) can be computed from this distribution. For out equilibrium systems, there is such prescription and we don't know yet how to start to compute the conductivity from a microscopic model. We shall see that we can use the concepts of stochastic thermodynamics (developed from 1990) to determine de probability $P(\mathcal{C}, \mathcal{C}')$ to jump from one microstate \mathcal{C}' to \mathcal{C} . The equation which describes the dynamics of $P(\mathcal{C}, \mathcal{C}')$, i.e. $dP(\mathcal{C}, \mathcal{C}')/dt$ is called the Master equation.
- (3) Thermodynamic potentials are only defined in equilibrium and conjugated forces do not derive from potentials (depend on the way transformations are performed).
- (4) What about systems arbitrarily far from equilibrium?
- (5) For small systems, everything fluctuates. Therefore, work and heat can only be defined in a statistical sense. What are the definitions and the consequences ?

Useful references are:

- (1) Equilibrium Statistical Physics, M. Plischke and B. Bergersen.
- (2) Statistical Mechanics: Entropy, Order Parameters and Complexity, James Sethna.

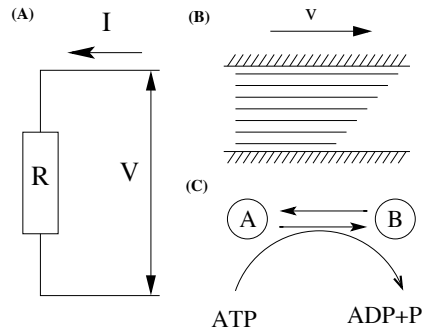


FIGURE 1. Examples of non-equilibrium systems: Discuss in each case why the system is out of equilibrium.

- (3) Noëlle Pottier. Physique statistique hors d'équilibre : équation de Boltzmann, réponse lineaire. DEA. 2006. <cel-00092930>
- (4) Bernard Derrida, cours du Collège de France 2015-2016, Fluctuations et grandes déviations autour du Second Principe, vidéos sur le site web du College de France, <https://www.college-de-france.fr/site/bernard-derrida/>.
- (5) Michel Le Bellac, Non equilibrium statistical mechanics. DEA. Cours aux Houches, août 2007, 2007. <cel-00176063>
- (6) Daniel Arovav Department of Physics University of California, San Diego, Lecture Notes on Nonequilibrium Statistical Physics.
- (7) L. Peliti, Doctoral Course on Fluctuation Relations and Nonequilibrium Thermodynamics, <http://www.peliti.org>.
- (8) P. Nozières, Variables d'état, fluctuations, irréversibilité: réflexions sur la thermodynamique près et loin de l'équilibre, Cours du Collège de France, 1993-1994.
- (9) Joel Keizer, Statistical thermodynamics of nonequilibrium Processes, Springer-Verlag, 1987.
- (10) Dilip Kondepudi and Ilya Prigogine, Modern Thermodynamics, From Heat Engines to dissipative structures, John Wiley & Sons, 1999.
- (11) A wonderful conference: <http://culturesciencesphysique.ens-lyon.fr/ressource/conference-ScienceEnergie2012-physique-statistique-Mallick.xml> by Kirone Mallick (in French).

Evaluation of the course:

- (1) Homework: 20 %;
- (2) Final exam: 80 %.

2. Equilibrium and non-equilibrium systems

An equilibrium system is a system where all observable quantities do not depend on time and where there is NO CURRENT (ENERGY, ENTROPY, PARTICLE). An isolated system is in equilibrium. A system in contact with only one thermostat is in equilibrium if observable quantities are averaged over a time period much larger than the characteristic time of the dynamics.

The simplest definition of non-equilibrium system is that it is not an equilibrium system (!). Non-equilibrium systems are systems with an energy-particle flux from the outside to the inside. As a prototypical example, glasses are aging systems and are in non-equilibrium. An interesting case of non-equilibrium system is a system with stationary currents. This is the case with a system in contact with two thermostats (particles, temperature) with a stationary current. Energy can be injected and dissipated. Mechanical systems (sand bag) and fluid systems (Couette flow) are systems where energy is injected at large scales and dissipated at small scales, so that there is an energy flow.

In summary, there are two general classes of non-equilibrium systems: (a) Systems which were at equilibrium and are slightly perturbed so that they relax to equilibrium; (b) Stationary states where the system stays in the same state as time elapses. Note that there are two ways to inject energy into the system. The Couette flow of Fig. 1 where the energy is injected through the boundaries and biological systems where energy (ATP) is consumed at the scale of its molecular components. The latter class is also coined "active gels" and they are considered as prototypical nonequilibrium systems.

3. Thermodynamics

Thermodynamics is a theory for macroscopic systems. One way to formulate the second principle is to postulate that for there exists for each equilibrium system a function S we call entropy. This function has the following property:

- (1) It is only defined for systems in equilibrium;
- (2) S depends only on macroscopic extensive parameters (state function);
- (3) S is an additive function;
- (4) S increases under changes of parameters and constraints. Transformations for which $\Delta S = 0$ are called reversible transformations. The ones for which $\Delta S > 0$ are called irreversible;
- (5) The entropy of a thermal bath depends on its energy:

$$(1) \quad \Delta S = -\frac{Q}{T}$$

where Q is the energy transferred to the system. Remember that this is the change of entropy of the reservoir, so that if we want de change of entropy of the system, we change the sign. When N particles are exchanged with a reservoir, the previous formula becomes

$$(2) \quad \Delta S = \frac{\mu N}{T}$$

where μ is the chemical potential.

As an example, consider a system cycling between different states $i = 1, 2, \dots$ where the state i is in contact with a thermostat at temperature T_i . Initially, the system is in contact with thermostat $i = 1$. At each contact, there is an energy Q_i transferred from the thermostat i to the system and the total change in entropy for the thermostat is ¹

$$(3) \quad \Delta S_{ther} = -\sum_i \frac{Q_i}{T_i}$$

Since the cycle ends with thermostat $i = 1$, $\Delta S_{system} = 0$.

According to the second principle

$$(4) \quad \Delta S_{total} \geq 0$$

so that we get the Clausius inequality

$$(5) \quad \sum_i \frac{Q_i}{T_i} \leq 0$$

The total energy is, however, conserved. If energy has been transferred to the system, work has been extracted and this work is

$$(6) \quad W_{extracted} = \sum_i Q_i$$

¹Note the trick: We use the entropy of the thermostat which is so large that it is always in equilibrium. We make no reference to the system that we consider as a black box and only count what goes in and out.

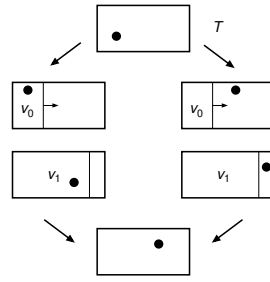


FIGURE 2. Depending on the initial condition, the wall is moved to the right or to the left. Averaging is done on the two possibilities for the initial condition.

As an example, consider the case of a system cycling between 2 thermostats. From

$$(7) \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0 \quad W_{extracted} = Q_1 + Q_2$$

we get the Carnot's inequality (after eliminating Q_2)

$$(8) \quad W_{extracted} \leq Q_1 \left(1 - \frac{T_2}{T_1}\right)$$

which sets an upper bound of the efficiency $W_{extracted}/Q_1$ (Carnot) for $T_1 > T_2$.

Another interesting case is the one with only one thermostat. Clausius inequality implies

$$(9) \quad W_{extracted} = Q \leq 0 \text{ since } \Delta S \geq 0$$

so that we cannot extract work if there is only one thermostat as in the case in equilibrium system (there exists no perpetual machine). As seen later, this statement of the second principle is only true for macroscopic systems where fluctuations are negligible. For very small systems, fluctuations which are neglected in macroscopic thermodynamics, change this picture. In these lectures, we will relate entropy to stochastic trajectories so that we will go beyond thermodynamics (which considers only average quantities and not fluctuations).

In particular, we shall explain that there exists an exact equality which replaces the maximum work theorem (remember, there is always dissipation)

$$(10) \quad W_{extracted} \leq F_{initial} - F_{final}$$

where the equality holds only for reversible processes. This equality known as the Jarzynski (1998) equality holds for reversible and irreversible processes and eq/ 10 is a consequence of it.

4. Can fluctuations beat the second principle ?

The Kelvin's statement follows from the second principle: There is no way to extract useful work from a single thermal reservoir. The following "Gedanken" experiment seems to violate this principle. The best is to do the following exercise.

EXERCICE 1.1. Consider the setup of Fig. 2. At the initial instant, we introduce a separation (a piston) that separates the volume v into two regions of volume v_0 and $v - v_0$ as in the figure. Then we move this piston very slowly so that in the final state the volume v_0 has become v_1 . Once in v_1 we remove the separation. During all this process, which is supposed to be very slow, the particle remains in equilibrium with the thermostat and therefore has its velocity distributed according to a Maxwellian at temperature T .

The perfect gas assumption is valid for one particle, so that $pv = kT$.

- (1) What is the work W done on the system in the two situations of the figure ?
- (2) What is the extracted work from the system in the two situations ?
- (3) Compute $\langle e^{-W} \rangle$ where $\langle \dots \rangle$ means averaging over the initial distribution. Can W have an arbitrary sign ? What are the consequences ?

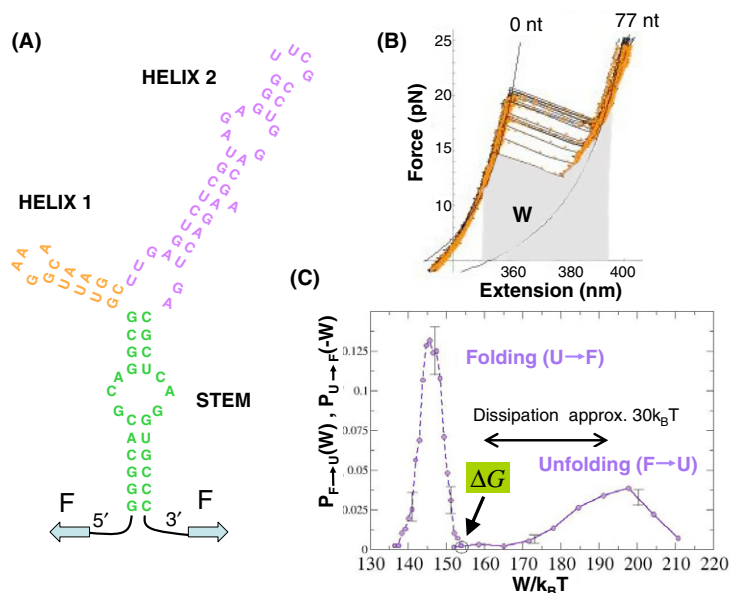


Figure 12. Recovery of folding free energies in a three-helix junction RNA molecule [193]. (A) Secondary structure of the junction containing one stem and two helices. (B) Typical force-extension curves during the unfolding process. The grey area corresponds to the work exerted on the molecule for one of the unfolding curves. (C) Work distributions for the unfolding or forward paths ($F \rightarrow U$) and the refolding or reverse ($U \rightarrow F$) paths obtained from 1200 pulls. According to the FT by Crooks (2) both distributions cross at $W = \Delta G$. After subtracting the free energy contribution coming from stretching the handles and the ssRNA these measurements provide a direct measure of the free energy of the native structure.

FIGURE 3. From Ritord¹⁶. Experiments on single molecules (here, RNA) are able to probe the "work distribution" during molecular folding and unfolding and to measure free energy changes. Since these experiments probe small systems with large statistical fluctuations, the field is termed "stochastic thermodynamics" to differentiate from standard thermodynamics (which concentrates on macroscopic averages).

Although such a discussion may appear quite abstract, we will see that fluctuation theorems have many applications in the lab. These experiments are based on the Crooks equality between the forward and reverse paths between two states with free energy difference ΔF

$$(11) \quad \frac{P_F(W)}{P_R(-W)} = \exp\left\{\left[\frac{W - \Delta F}{T}\right]\right\}$$

During the lectures, we will discuss the experiment schematized in Fig. 3 (with other experiments such as the ones testing the minimum dissipation necessary to erase a bit of information, see the Landauer principle).

5. The principle of detailed balance

How can we decide that a system is or is not in equilibrium? In equilibrium, there is no net flux (matter, energy etc.). This is entailed in the principle of detailed balance.

Consider the following reaction for a molecule with two internal states (i.e. two configurations). Let us call these two configurations C , C' :



Call p_C the probability to observe a molecule in state C and $p_{C'}$ for state C' . If the rate $k_{C \rightarrow C'}$ is interpreted as the conditional probability to jump from configuration C to configuration C' per unit times given that the molecule is in state C' , the flux (actually, a probability flux) from

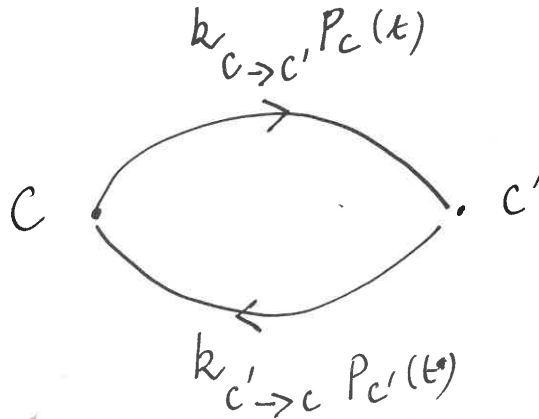


FIGURE 4. The local currents for the molecule with two configurations C and C' . To make this picture generic, the probabilities $p_{C,C'}$ depend on time t .

C to C' is

$$(13) \quad \text{Flux from } C \rightarrow C' = k_{C \rightarrow C'} p_C$$

since to go from C to C' , the molecule has to be in configuration C first. If we draw analogies with chemical kinetics, we have simply replaced the concentration of molecules in a given state by the probability to find the molecule in this state and the usual kinetic rate constant by the appropriate conditional probabilities.

The principle of detailed balance can be stated as follows: In the state of equilibrium, every elementary transformation is balanced by its exact opposite reverse. Detailed balance is connected to time-reversal symmetry which is fundamental microscopic property for Hamiltonian system. See Fig. 5. If there is no net flux between C and C' , then

$$(14) \quad k_{C \rightarrow C'} p_C = k_{C' \rightarrow C} p_{C'}$$

where $k_{C \rightarrow C'}$ is the rate per unit time for the transition from C to C' and $p_C k_{C \rightarrow C'}$ is the flux from C to C' . Using Boltzmann law gives the classical result

$$(15) \quad \frac{k_{C \rightarrow C'}}{k_{C' \rightarrow C}} = \frac{p_{C'}}{p_C} \propto \exp\left\{\frac{-(E_C - E_{C'})}{k_B T}\right\}$$

we will demonstrate later.

It is also valid for the exchange of matter and energy between two volume elements of a system in equilibrium. The amount of matter or energy between two regions of a system is balanced in detail: the amount of matter going from X to Y is balanced by exactly the reverse process. This principle does not hold for non-equilibrium processes (see ref.¹).

In conclusion: Violation of detailed balance is the source of macroscopic currents which maintain the system far from equilibrium. This violation can be due to different factors: (i) the existence of an external driving force that pushes the particles in a given direction; (ii) the presence of reservoirs of unequal chemical potential (or temperature) that generates a current. We will see that the principle of detailed balance is a consequence of the time-reversibility of the underlying Hamiltonian dynamics (the converse is also true).

EXERCICE 1.2. Consider the cycle of Fig. 5 with rate constants $k_{A \rightarrow B}$, $k_{B \rightarrow C}$, ... and probabilities p_A , p_B , p_C to be in state A , B or C . Show that equilibrium implies

$$(16) \quad \frac{k_{A \rightarrow B} k_{B \rightarrow C} k_{C \rightarrow A}}{k_{B \rightarrow A} k_{A \rightarrow C} k_{C \rightarrow B}} = 1$$

which means that the probability to run clockwise is equal to the probability to run counter-clockwise (Hints: Write a system of equations for dp_A/dt , dp_B/dt , dp_C/dt).

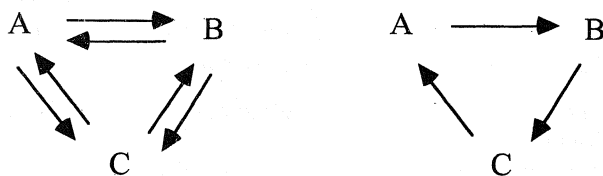


FIGURE 5. The equilibrium between three interconverting compounds A, B and C is the result of detailed balance between each pair compounds. The right picture shows a cycle. Although conversion from one compound to the other can produce concentration that remains constant in time, this state is not an equilibrium state. Why ?

6. Phase space

Non-equilibrium and equilibrium statistical mechanics share the same tools. The basic purpose of non-equilibrium statistical mechanics is to describe the dynamics of the system in the phase space (master and Fokker-Planck equation).

Let p, q be the momentum and the position vectors of N particules. The phase space is defined as the (q, p) phase with (huge) dimension $6N$. Assume we have a Hamiltonian

$$(17) \quad H(p, q) = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} U(q_i - q_j) + \sum_i V(q_i, t)$$

The first term is the kinetic energy, the second is the interaction between the particles and the third is the potential energy. It may depend on the time t . $V(q_i, t)$ takes into account the walls and it plays an analogous role to a piston in thermodynamics.

The dynamics of the system is given by the Hamilton's equations

$$(18) \quad \dot{q} = \frac{\partial H}{\partial p} \quad \dot{p} = -\frac{\partial H}{\partial q}$$

and the system evolves along a trajectory (which cannot intersect itself because there is only one trajectory for a given initial condition). For hamiltonian dynamics, trajectories are dense. This means that we can define a density $\rho(p, q, t)$ and that we can try to define an entropy via the formula

$$(19) \quad S(t) = -k \int dpdq \rho(p, q, t) \ln \rho(p, q, t)$$

Because of ergodicity (time average equals to ensemble average) ρ is constant. If $\rho = 1/\Omega$, where Ω is the volume of phase space. This gives the Boltzmann's formula

$$(20) \quad S = k \ln \Omega$$

This is nice but (19) cannot be correct. We will demonstrate that if S is defined this way, then S is constant and cannot increase. We will seek for an another definition (the whole problem of out of equilibrium thermodynamic is to define thermodynamic functions even if the system is a non-equilibrium system).

There are two well-known theorems in Hamiltonian dynamics. Before stating these two theorems, we have:

DEFINITION 6.1. The dynamic is a one-parameter family of transformation in phase space

$$(21) \quad g^t : (\mathbf{p}(0), \mathbf{q}(0)) \rightarrow (\mathbf{p}(t), \mathbf{q}(t))$$

THEOREM 1. LIOUVILLE: The volume is conserved. For all domains D :

$$(22) \quad \text{Vol}.g^t D = \text{Vol}.D$$

THEOREM 2. POINCARÉ: This theorem states that, for almost all "initial conditions", a conservative dynamic system whose phase space is of finite "volume" will repeatedly pass through time as close as one wants to its initial condition.

This theorem sheds new light on the notion of irreversibility. If a system returns arbitrarily close to its starting point, where does the fact that macroscopic systems appear irreversible come from? The answer is that Poincaré's return time increases very rapidly with the number of degrees of freedom. By coupling a particle with a thermal bath (i.e. by sending this number to infinity and replacing discrete sums by integrals), even if the coupling is weak, we will be able to simulate the irreversibility at the end of the course.

For a large system, the trajectory in phase space is chaotic. It means that two trajectories with almost equal initial conditions will be completely different after a short period of time. This is the way how randomness comes into play in statistical mechanics. Since it is hopeless to define the initial conditions with an infinite precision, we are forced to coarse grain the phase space into small boxes. The size of the boxes have nothing to do with the uncertainty principle of Heisenberg. There are here because we want to do statistics. If p_i is the probability to find the system in box i , then the correct definition of entropy is

$$(23) \quad S = -k \sum_i p_i \ln p_i$$

The problem is now to find how the p_i 's evolves with time. This is a central part in statistical mechanics and the equation of evolution is known as the master equation. Using this master equation, we will show that entropy increases.

EXERCICE 1.3. THE FUNDAMENTAL THEOREM OF NATURAL SELECTION (DERRIDA):

In the 1930s, the biologist and statistician Ronald Fisher showed that the fertility of a population increases on average as the variance of fertility increases. This theorem shows that the fertility of a population increases even in the absence of mutations. Fisher's result is obtained in a manner very similar to the calculation for the variance of energy or the number of particles that we shall see in the following. The starting point is to consider a model where the number of individuals n_i , whose fertility is σ_i , evolves according to

$$(24) \quad \frac{dn_i}{dt} = \sigma_i n_i$$

and to assume that the fertility σ_i is perfectly transmitted to the descendants without being modified. Show that the mean fertility

$$(25) \quad \langle \sigma \rangle = \frac{\sum_i n_i \sigma_i}{\sum_i n_i}$$

evolves according to

$$(26) \quad \frac{d\langle \sigma \rangle}{dt} = \langle \sigma^2 \rangle - \langle \sigma \rangle^2$$

Conclude (It is remarkable that the response of fecundity to a temporal change is given by the variance of that fecundity much as the derivative of energy with respect to temperature was given by the variance of that energy).

7. The Liouville equation

In statistical mechanics, average quantities are determined by the phase space distribution function $f(\mathbf{p}, \mathbf{q}, t)$ or more simply $f(\mathbf{X}, t)$. The probability of finding the system state in a region $d\mathbf{X}$ at time t is $f(\mathbf{X}, t)d\mathbf{X} = p_i$, where the index i labels the cell i . Probability is conserved; the total probability that the system is somewhere is unity at all times:

$$(27) \quad \int d\mathbf{X} f(\mathbf{X}, t) = 1$$

As in fluid or electrodynamics, whenever an integral of a quantity is conserved over an entire domain, there is a conservation law of the form:

$$(28) \quad \frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial \mathbf{X}} \cdot (\rho \mathbf{V})$$

where \mathbf{V} is a velocity and ρ a density. This equation tells us that the rate of change is simply equal to the divergence of a current. In phase space, the coordinates are the position \mathbf{q} and the momentum \mathbf{p} , so

$$(29) \quad \frac{\partial}{\partial \mathbf{X}} \rightarrow \left(\frac{\partial}{\partial \mathbf{q}}, \frac{\partial}{\partial \mathbf{p}} \right) \quad \mathbf{V} \rightarrow \left(\frac{\partial \mathbf{q}}{\partial t}, \frac{\partial \mathbf{p}}{\partial t} \right)$$

and

$$(30) \quad \frac{\partial f}{\partial t} = -\frac{\partial}{\partial \mathbf{q}} \cdot \left(\frac{d\mathbf{q}}{dt} f(\mathbf{q}, \mathbf{p}, t) \right) - \frac{\partial}{\partial \mathbf{p}} \cdot \left(\frac{d\mathbf{p}}{dt} f(\mathbf{q}, \mathbf{p}, t) \right)$$

Using Hamilton equation, we can define an operator (called the Liouville operator)

$$(31) \quad L = \frac{\partial H}{\partial \mathbf{p}} \cdot \frac{\partial}{\partial \mathbf{q}} - \frac{\partial H}{\partial \mathbf{q}} \cdot \frac{\partial}{\partial \mathbf{p}}$$

so that the Liouville equation is

$$(32) \quad \frac{\partial f}{\partial t} = -Lf$$

This equation has the formal operator solution:

$$(33) \quad f(\mathbf{X}, t) = e^{-tL} f(\mathbf{X}, 0)$$

The forme of this solution will be useful when we discuss the Fokker-Planck equation when one adds noise to the Liouville equation.

- REMARK. (1) For time reversal properties of a noisy signal (equilibrium versus non equilibrium), see¹⁸;
 (2) For interesting comments on detailed by balance, see¹;
 (3) Broken detailed balance and entropy production in the human brain, see[?].

CHAPTER 2

STOCHASTIC VARIABLES

1. Fundamental definitions

The natural mathematical setting of probability is set theory: Sets are collections of objects. In probability theory, each object is identified with an event. Let Ω be the set of all events and $A, B \subset \Omega$. For example, if we study the spreading of a disease in a population, the whole population is Ω , the group of people who have the disease is A and the set of individuals who tested positive for the disease is B . All that seems familiar ...

The set $A \setminus B$ contains all ω such that $\omega \in A$ and $\omega \notin B$.

We have the three basic axioms:

- (1) To each set A is associated a non-negative real number $P(A)$ called the probability of A .
- (2) $P(\Omega) = 1$.
- (3) If A_i is a collection of disjoint sets, i.e. $A_i \cap A_j = \emptyset, \forall i, j$

$$(34) \quad P(\cup_i A_i) = \sum_i P(A_i)$$

and the following property holds:

$$(35) \quad P(\Omega \setminus A) = 1 - P(A)$$

2. Bayesian Statistics

We introduce two additional probabilities:

- (1) The joint probability for sets A and B together $P(A \cap B)$.
- (2) The conditional probability of B given A .

We can compute the joint probability $P(A \cap B) = P(B \cap A)$ in two ways:

$$(36) \quad P(A \cap B) = P(A|B)P(B) = P(B|A)P(A).$$

Thus,

$$(37) \quad P(A|B) = \frac{P(B|A)P(A)}{P(B)}$$

a result known as Bayes' theorem.

If the event space Ω is partitioned as $\{A_i\}$, then

$$(38) \quad P(B) = \sum_i P(B|A_i)P(A_i)$$

so that,

$$(39) \quad P(A_i|B) = \frac{P(B|A_i)}{\sum_i P(B|A_i)P(A_i)}$$

EXAMPLE 2.1. As an example, consider the following problem in epidemiology. Suppose there is a rare but highly contagious disease A which occurs in 0.01% of the general population. Suppose further that there is a simple test for the disease which is accurate 99.99% of the time. That is, out of every 10,000 tests, the correct answer is returned 9,999 times, and the incorrect answer is returned only once.

Now let us administer the test to a large group of people from the general population. Those who test positive are quarantined. Question: what is the probability that someone chosen at random from the quarantined group actually has the disease?

We use Bayes' theorem with the binary partition $A, \Omega \setminus A$, meaning that we divide the population in two groups (the ones who have the disease and the other ones). Let B denote the event that an individual tests positive. Anyone from the quarantine group has tested positive. Given this datum, we want to know the probability that that person has the disease. That is, we want $P(A|B)$. But, what we know is $P(B|A) = 0.9999$!

Actually, we know more. Applying (39) with $A_1 = A$ and $A_2 = \Omega \setminus A$, we have

$$(40) \quad P(A) = 0.0001 \quad P(B|A) = 0.9999 \quad P(\Omega \setminus A) = 0.9999 \quad P(B|\Omega \setminus A) = 0.0001$$

and

$$(41) \quad P(A|B) = \frac{0.9999 \times 0.0001}{0.9999 \times 0.0001 + 0.0001 \times 0.9999} = \frac{1}{2}$$

despite the test being 99.99% accurate. The reason is that, given the rarity of the disease in the general population, the number of false positives is statistically equal to the number of true positives.

For continuous distributions, we speak of probability density. We then have

$$(42) \quad P(y) = \int P(y|x)P(x) dx$$

and

$$(43) \quad P(x|y) = \frac{P(y|x)P(x)}{\int dx' P(y|x')P(x')}$$

In probability theory, the quantities $P(A_i)$ are called the prior distribution.

3. Average, moments and cumulants

Averages are defined as:

$$(44) \quad \langle x^p \rangle = \int dx x^p P(x) \quad p \in \mathbb{R}$$

when it is possible (i.e. when the integral converges).

Cumulants tell us if the fluctuations are large. For example, for large fluctuations $\langle x^2 \rangle$ will significantly differ from $\langle x \rangle^2$. Thus we define

$$(45) \quad \langle x \rangle_c = \langle x \rangle$$

$$(46) \quad \langle x_i x_j \rangle_c = \langle x_i x_j \rangle - \langle x_i \rangle \langle x_j \rangle$$

$$(47) \quad \begin{aligned} \langle x_i x_j x_k \rangle_c &= \langle x_i x_j x_k \rangle - \langle x_i x_j \rangle \langle x_k \rangle - \langle x_j x_k \rangle \langle x_i \rangle \\ &\quad - \langle x_i x_k \rangle \langle x_j \rangle + 2 \langle x_j \rangle \langle x_i \rangle \langle x_k \rangle \end{aligned}$$

A very useful interpretation of cumulants is that they tell us about fluctuations. Are they large or small compared to the mean values ? Take, for example

$$(48) \quad \langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2$$

If the distribution of x is almost centered on a value x_0 (take $\delta(x - x_0)$), then $\langle x^2 \rangle \simeq 0$. However, if the distribution of x is broad enough

$$(49) \quad \langle x^2 \rangle - \langle x \rangle^2 \gg \langle x \rangle^2$$

4. Characteristic functions-Cumulants

The characteristic function of a stochastic variable x is

$$(50) \quad G(k) = \langle e^{ikx} \rangle = \int e^{ikx} P(x) dx$$

This function generates the moments μ_n by Taylor's expanding the exponential:

$$(51) \quad G(k) = \sum_{n \geq 0} \frac{(ik)^n}{n!} \mu_n$$

NOTE. The moments may not necessarily exist. As an example, consider the Lorentzian :

$$(52) \quad P(x) = \frac{1}{\pi} \frac{\gamma}{(x - a)^2 + \gamma^2}$$

The cumulants κ_m are of constant use in statistical physics. They are defined via the same generating function :

$$(53) \quad G(k) = e^{\sum_{n \geq 1} \frac{(ik)^n}{n!} \kappa_n}$$

Or,

$$(54) \quad \ln G(k) = \sum_{n \geq 1} \frac{(ik)^n}{n!} \kappa_n$$

We have $\kappa_1 = \mu_1$, $\kappa_2 = \sigma^2$, $\kappa_3 = \mu_3 - 3\mu_2\mu_1 + 2\mu_1^3$.

EXAMPLE 4.1. The Gaussian distribution:

$$(55) \quad P(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left\{-\frac{(x - \mu)^2}{2\sigma^2}\right\}$$

has the following generating function

$$(56) \quad G(k) = \exp\left\{ik\mu - \frac{1}{2}\sigma k^2\right\}$$

with $\ln G(k) = ik\mu - \frac{1}{2}\sigma k^2$, so that the cumulants of order ≥ 3 vanish.

5. Calculations rules

Consider the mapping $x \rightarrow y = f(x)$. We assume that x is distributed as $P_x(x)$. What is the distribution $P_y(y)$? We have

$$(57) \quad P_y(y)\Delta y = \int_{y < f(x) < y + \Delta y} dx P_x(x)$$

Thus,

$$(58) \quad P_y(y) = \int dx P_x(x) \delta(f(x) - y)$$

Remember the composition rule of the Dirac delta distribution

$$(59) \quad \delta(g(x)) = \sum_i \frac{\delta(x - x_i)}{|g'(x_i)|}$$

with x_i being the zeros of $g(x)$. We plug this formula into (58) and get the result.

EXERCICE 2.1. Show that

$$(60) \quad G_y(k) = \langle e^{ikf(x)} \rangle$$

6. Stochastic processes

A stochastic process $\mathbf{X} = \{X(t), t \in T\}$ is a collection of random variables. That is, for each t , $X(t)$ is a random variable. Depending on the situation, we have continuous or discrete stochastic processes depending on whether the time t is a continuous or a discrete variable. Any realization of \mathbf{X} is a sample path.

A prototypical example of a stochastic process is a random walk of a particle that moves along a discrete set of lattice sites. At each time step t_i , the particle moves to the right with probability $1/2$ and to the left with probability $1/2$ and the set of positions $X(t_i)$ is a stochastic process.

7. Some basic distributions

7.1. The multinomial distribution. Consider N molecules distributed in N_c compartments that are connected by diffusion. The steady-state distribution is spatially uniform, and it is known that it is multinomial with mean and variance ($i = \text{compartment } i$):¹

$$(63) \quad M_i = \frac{N}{N_c} \quad \sigma_i^2 = M_i \left(1 - \frac{1}{N_c}\right) = \frac{N}{N_c} \left(1 - \frac{N}{N_c}\right)$$

We can adopt the coefficient $c = \sigma_i/M_i$ as a measure of the noise. We have:

$$(64) \quad c = \sqrt{\frac{N_c - 1}{N}}$$

7.2. The Gaussian distribution. see Appendix

7.3. The Poisson distribution. Let us consider a counting process $N(t)$, $t \geq 0$ such that:

- (i) $N(0) = 0$.
- (ii) The process has independent increments.
- (iii) The number of events in any interval t is Poisson distributed with mean λ . That is, for all t and s

$$(65) \quad P[N(t+s) - N(s) = n] = e^{-\lambda t} \frac{(\lambda t)^n}{n!}$$

which means that $\langle N(t) \rangle = \lambda t$.

A key property of a Poisson process is that it is the only memoryless distribution and that the interarrival time distribution (i.e. the distribution of elapsed times between two consecutive events) is exponentially distributed. As a prototypical example, let us consider the chemical reaction



with rate k . The probability density for the time τ it takes a single-turnover trajectory is

$$(67) \quad p(\tau) = k \exp(-k\tau)$$

We deal with the subject through an exercise¹⁷.

¹The definition of the multinomial distribution is as follows:

$$(61) \quad \mathbb{P}(N_1 = n_1, N_2 = n_2, \dots, N_m = n_m) = \frac{n!}{n_1! \dots n_m!} p_1^{n_1} \dots p_m^{n_m}$$

with the constraints:

$$(62) \quad \sum_{i=1, m} N_i = m \quad \sum_{i=1, m} p_i = 1$$

What is p_i for the diffusion problem?

EXERCICE 2.2. The exponential distribution.

Let x be a random variable with exponential distribution:

$$(68) \quad f(x) = \begin{cases} \lambda e^{-\lambda x}, & x \geq 0 \\ 0, & x < 0 \end{cases}$$

- (1) Compute the moment generating function $\langle e^{tx} \rangle$, $t < \lambda$ and show $\langle x^2 \rangle = 2/\lambda^2$ and compute the variance. What is the probability $P(x)$ to observe the variable in the interval $[x, \infty[$?
- (2) A random variable x is said to be without memory if the c.d.f. (cumulative probability distribution) obeys

$$(69) \quad P(x > s + t | x > t) = P(x > s)$$

If we think of x as being the lifetime of some molecule, then Equation (69) states that the probability that the molecule lives for at least $s + t$ hours given that it has survived t hours is the same as the initial probability that it lives for at least s hours. In other words, if the molecule is alive at time t , then the distribution of the remaining amount of time that it survives is the same as the original lifetime distribution; that is, the molecule does not remember that it has already been in use for a time t . Show that this condition is equivalent to:

$$(70) \quad \frac{P(x > s + t, x > t)}{P(x > t)} = P(x > s)$$

or

$$(71) \quad P(x > s + t) = P(x > s)P(x > t)$$

- (3) Show that exponentially distributed random variables are memoryless.
- (4) Interpret X as being the lifetime of some item. Suppose that X has survived a time t and we want to compute the probability that it will *not* survive for an additional time dt . This probability is called the hazard (or failure) function. Show

$$(72) \quad P(X \in (t, t + dt) | X > t) = \frac{P(X \in (t, t + dt))}{P(X > t)}$$

Compute this probability for an exponential process. It follows that the distribution of remaining life for a t -year-old item is the same as for a new item (check).

- (5) Define the sequence $T_n, n, n = 1, 2, \dots$ as the sequence of interarrival times of a counting process. For example if $T_1 = 5$ and $T_2 = 15$, then the first event would have occurred at time 5 and the second at time 15. We define the waiting time until the n th event as

$$(73) \quad S_n = \sum_{i=1, n} X_i$$

where the X_i 's are the sequence of interarrival times

$$(74) \quad \begin{aligned} T_1 &= X_1 \\ T_2 &= X_1 + X_2 \\ &\dots \end{aligned}$$

S_n is, therefore, a random variable, each of which being distributed with density $\lambda \exp(-\lambda x)$. Recall that the density of the sum of two independent random variables can be found by convolving their densities. Show by recurrence that

$$(75) \quad f_{S_n}(t) = e^{-\lambda t} \frac{\lambda^n t^{n-1}}{(n-1)!}$$

7.4. The Boltzmann distribution. As an application of the Boltzmann distribution of a fluctuating quantity. The fluctuation amplitude is determined by the equipartition theorem which tells us that each distinct mode is just the thermal energy $k_B T$. We consider the case of an ideal solution of average solute concentration c consisting of n_c solute molecules in a volume V , $c = n_c/V$.

The minimum work at constant pressure and temperature to create a small fluctuation δn_c having equilibrium potential $\mu_c(T, P)$ is $\Delta W = \delta G - \mu_c \delta n_c$. Expanding around equilibrium, first order term disappears leaving

$$(76) \quad \Delta W = \frac{1}{2} \frac{\partial \mu_c}{\partial n_c} \Big|_{(P,T)} (\delta n_c)^2$$

The probability of this fluctuation is given by the Boltzmann distribution:

$$(77) \quad \propto e^{-W/k_B T}$$

The resulting Gaussian distribution of δn_c yields the mean square number fluctuation as

$$(78) \quad \langle (\delta n_c)^2 \rangle = \frac{k_B T}{\partial \mu_c / \partial n_c \Big|_{(P,T)}}$$

In an ideal or very dilute solution the chemical potential is

$$(79) \quad \mu_c = K_B T \ln n_c/V + \text{const.}$$

Therefore,

$$(80) \quad \langle (\delta n_c)^2 \rangle = n_c$$

Note that the temperature dependence cancels although we are dealing with thermal fluctuations.

8. Multivariate Gaussian distribution

Let $\mathbf{x} \in \mathbb{R}^n$. and A a symmetric positive definite $n \times n$ real matrix. The multivariate Gaussian distribution is

$$(81) \quad P(\mathbf{x}) = \frac{1}{Z} \exp \left\{ \left[-\frac{1}{2} \mathbf{x}^T A \mathbf{x} - \mathbf{b}^T \mathbf{x} \right] \right\}$$

Using Appendix A for Gaussian integrals, the characteristic function turns out to be:

$$(82) \quad G(\mathbf{k}) = \exp \left\{ \left[-\frac{1}{2} \mathbf{k}^T A^{-1} \mathbf{k} - i \mathbf{k}^T A^{-1} \mathbf{b} \right] \right\}$$

For an arbitrary joint probability distribution, we define the second order cumulant from the covariance matrix

$$(83) \quad \langle x_i x_j \rangle_c = \langle (x_i - \langle x_i \rangle_{x_i})(x_j - \langle x_j \rangle_{x_j}) \rangle$$

where

$$(84) \quad \langle x_i \rangle_{x_i} = \int d\mathbf{x} x_i P(\mathbf{x})$$

The variables x_i and x_j are said to be uncorrelated if and only if :

$$(85) \quad \langle x_i x_j \rangle_c = 0$$

If A is diagonal, then A^{-1} is also diagonal. The second order cross cumulant vanishes and the two variable are independent. The equivalence between the two properties is due to the fact that we have taken a Gaussian probability distribution. Otherwise, this equivalence is false (see next).

UNCORRELATED DOES NOT MEAN INDEPENDENT. We have seen that two variables are uncorrelated if and only if $\langle x_i x_j \rangle_c = 0$. Two variables are said to be independent if and only if $p(x, y) = p_x(x)p_y(y)$. Are these two notions equivalent? The answer is no! See next examples.

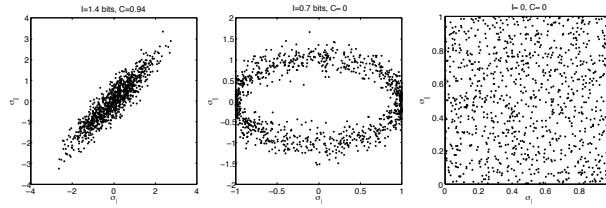


FIGURE 1. Examples of two variables x, y drawn from three joint distributions. Shown are the scatterplots of example draws. After ref. ¹⁹.

EXERCICE 2.3. Consider the three examples of Fig. 1. Tell in each case if the variables are correlated or not. What are the values of $\langle xy \rangle$ and $\langle xy \rangle_c$ in the second example.

EXERCICE 2.4. Let x be a Gaussian distributed random variable with $\langle x \rangle = 0$ and $\sigma^2 = 1$. Let w to take the value ± 1 with equal weight and define $y = wx$.

(1) Show that:

$$(86) \quad P(x, y) = \frac{1}{\sqrt{2\pi}} \exp\left\{-\frac{x^2}{2}\right\} \frac{1}{2} (\delta(x+y) + \delta(x-y))$$

(2) Show that:

$$(87) \quad P_x(x) = \int dy P(x, y) = \frac{1}{\sqrt{2\pi}} \exp\left\{-\frac{x^2}{2}\right\}$$

$$(88) \quad P_y(y) = \int dx P(x, y) = \frac{1}{\sqrt{2\pi}} \exp\left\{-\frac{y^2}{2}\right\}$$

so that $P(x, y) \neq P_x(x)P_y(y)$.

(3) Show that $\langle xy \rangle = \int dx dy xy P(x, y) = 0$.

EXERCICE 2.5. For a multivariate Gaussian distribution with zero mean, the following properties holds (due to Novikov)

$$(89) \quad \langle x_i f(\mathbf{x}) \rangle = \sum_m \langle x_i x_m \rangle \left\langle \frac{\partial f}{\partial x_m} \right\rangle$$

Use this property to recover Wick's formula

$$(90) \quad \langle x_i x_k x_l x_m \rangle = \langle x_i x_k \rangle \langle x_l x_m \rangle + \langle x_i x_l \rangle \langle x_k x_m \rangle + \langle x_i x_m \rangle \langle x_k x_l \rangle$$

9. Central limit theorem - Stable distributions

The importance of the Gaussian distribution is due to the fact that it is an 'attractor' in the space of distributions with finite variance. This theorem states the following:

If the distributions $P_{x_i}(x_i)$ have zero mean and variance σ^2 , the distribution of the scaled sum :

$$(91) \quad y = \frac{1}{\sqrt{n}} \sum_{1 \leq i \leq n} x_i$$

approaches

$$(92) \quad P_y(y) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-y^2/2\sigma^2}$$

The central limit theorem remains true if the variable are not identically distributed. What happens is the variance diverge ? This leads to a more general class known as stable distributions.

We give only an example. Levi distributions with maximum at $x = 0$ are such that their characteristic function is of the form:

$$(93) \quad G(k) = \exp\{-|k|^\mu\}, \quad \text{with } 0 < \mu \leq 2$$

The case $\mu = 1$ is the Cauchy distribution and $\mu = 2$ corresponds to a Gaussian distribution. We cannot have $\mu > 2$, since the probability density has to be positive. For $\mu \neq 2$, $P(x)$ behaves as $P(x) \simeq 1/|x|^{\mu+1}$, which yields to a divergent variance.

These distributions are called stable distributions because of the following definition:

Let x_1 and x_2 be independent stochastic variables with the same probability distribution $P(x)$. The distribution $P(x)$ is stable if for any constants a and b the stochastic variable $ax_1 + bx_2$ has the same distribution as $cx + d$ with appropriate c and d .

10. Entropy and probability

Since the work of C. Shannon, we say that entropy is a measure of information (or more precisely depending on the context, entropy measures how information is transmitted, or measure measure the amount of information necessary to describe a random variable). Suppose we observe that an event occurs with probability p . We associate with observation an amount of information $I(p)$. The information $I(p)$ should satisfy the following desiderata:

- (1) Information is non-negative, $I(p) > 0$.
- (2) If two events occurs independently, their joint probability is $p_1 \times p_2$. Information must be additive.
- (3) $I(p)$ is a continuous function of p .
- (4) There is no information to an event which is always observed, i.e. $I(1) = 0$.

From this properties it follows that the only possible function is (this is a theorem that we do not demonstrate because of time)

$$(94) \quad I(p) = -A \ln p$$

where A is constant which can be adsorbate in the definition of the logarithm by changing the base². Note that a rare event with $p \ll 1$ contains a lot information: It is like finding a useful message lost in noisy data.

Now if we have a set of events labeled by an integer n which occur with probability p_n , what is the expected amount of information in N observations ? Since each event occurs Np_n times, the average information per observation is

$$(95) \quad S = \frac{\langle I_N \rangle}{N} = - \sum_n p_n \ln p_n$$

which defines the entropy. Maximizing S is therefore equivalent of maximizing the information per observation.

EXERCICE 2.6. From Ref.⁶. We decide to measure the entropy using \ln_2

- (1) What is the entropy of a fair coin ?
- (2) Let $X = 1$ with probability p and $X = 0$ with probability $1 - p$. Draw a graph of the entropy associated with the random variable X and explain why it is maximal or minimal at some value of p .
- (3) Consider a random variable which has a uniform distribution over 32 outcomes. How many bits suffice the describe the outcome ? (5)
- (4) Compute the entropy of this random variable.
- (5) Compute the entropy associated with 8 outcomes with probabilities

$$(1/2, 1/4, 1/8, 1/16, 1/65, 1/64, 1/64, 1/64, 1/64, 1/64)$$

Conclude.

²If $I(p) = \ln_2 1/p$, I is measured in bits. The meaning has nothing to do with a variable whose value is 0 or 1.

The relative entropy, also known as the Kullback-Leibler divergence between two probability distribution on a random variable is a measure of the distance between them. Formally, given two probability distributions $p(x)$ and $q(x)$ over a discrete random variable, the relative entropy given by $D(p||q)$ is defined as follows:

$$(96) \quad D(p||q) = \sum_n p_n \ln \frac{p_n}{q_n}$$

In the definition above $0 \ln \frac{0}{0} = 0$.

We have $D(p||p) = 0$. We remark that the divergence is not symmetric. That is, $D(p||q) = D(q||p)$ is not necessarily true. Intuitively, the entropy of a random variable with a probability distribution $p(x)$ is related to how $p(x)$ diverges from the uniform distribution. Taking $q_n = 1$ to simulate the uniform probability distribution, we find:

$$(97) \quad S = -D(p||\text{Uniform})$$

D is also called the divergence in the literature.

EXERCICE 2.7. Mutual information¹⁹. We want to find some measure of the statistical interdependence of an input c and an output x . One can quantify this in terms of how much one's uncertainty in x is reduced by knowing c . Prior knowing c , the entropy is

$$(98) \quad S(P_x) = - \int dx P(x) \ln_2 P(x)$$

After c is specified, the entropy is

$$(99) \quad S(P_{x|c}) = - \int dx P(x|c) \ln_2(P(x|c))$$

So we define the mutual information by

$$(100) \quad I(c; x) = \int P(c) (S(P_x) - S(P_{x|c})) dc$$

- (1) Show that $I(c; x)$ is symmetric (use $P(x) = \int dc P(x, c)$ and Bayes' theorem).
- (2) What happens if the input and the output are independent ?
- (3) Show that the entropy of $P(c)$

$$(101) \quad P(c) = \frac{1}{\sqrt{2\pi\sigma_c^2}} e^{-\frac{(c-\bar{c})^2}{2\sigma_c^2}}$$

is $S(P) = \ln_2 \sqrt{2\pi\sigma_c^2}$

- (4) As an illustration, suppose that an input signal is corrupted by an additive Gaussian noise

$$(102) \quad x = c + \xi$$

where the process (i.e. transmission line) changes the input c into the output x , $c \rightarrow x$. We identify $P(\xi)$ with $P(x|c)$ so that

$$(103) \quad P(x|c) = P(\xi) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left\{-\frac{(x-c)^2}{2\sigma^2}\right\}$$

where σ^2 can be identified with the noise due the "transmission line".

- (a) We assume that the input itself c is a also a Gaussian distributed random variable (with $\bar{c} = 0$)

$$(104) \quad P(c) = \frac{1}{\sqrt{2\pi\sigma_c^2}} e^{-\frac{(c-\bar{c})^2}{2\sigma_c^2}}$$

Show that the probability distribution of x is a Gaussian (use $P(x) = \int dc P_c(c) P_\xi(x-c)$).

- (b) What is the mutual information ?

(c) Find $I(c; x)$ (answ.: $1/2 \ln_2(1 + \sigma_c^2/\sigma^2)$). What is the usual definition of the ratio σ_c^2/σ^2 ?

- (5) Let us now prove that the Gaussian distribution maximizes the entropy subject to a variance constraint. Consider the following functional

$$(105) \quad \mathcal{L}[p(c)] = - \int dc P(c) \ln P(c) - \lambda_0 \int dc P(c) - \lambda_1 \int dc c P(c) - \lambda_2 \int dc c^2 P(c)$$

with Lagrange multipliers. Solve the optimisation problem for a desired mean and variance. This shows that the Gaussian distribution has the largest entropy given the variance.

11. Correlation functions

Let us define for a random variable $x(t)$ (which can be a vector)³:

- (1) The probability $P(x, t)$ that the random variable $x(t)$ has a certain value x at time t .
- (2) The joint probability $P(x_2, t_2; x_1, t_1)$ that this random variable has a certain value x_2 at t_2 and, also, that it has an another value x_1 at time t_1 .
- (3) The conditional probability $P(x_2, t_2|x_1, t_1)$ that the random variable takes the value x_2 at time t_2 given that $x_1 = x(t_1)$ at time t_1 prior to t_2 .

Recall:

$$(106) \quad P(x_2, t_2; x_1, t_1) = P(x_2, t_2|x_1, t_1)P(x_1, t_1)$$

In a stationary process all probability distributions are invariant under time translation $t \rightarrow t + \tau$. Therefore:

$$(107) \quad P(x, t) = P(x) \text{ independent of } t$$

$$(108) \quad P(x_2, t_2; x_1, t_1) = P(x_2, t_2 - t_1; x_1, 0)$$

$$(109) \quad P(x_2, t_2|x_1, t_1) = P(x_2, t_2 - t_1|x_1, 0)$$

Consider a stationary process. Its probability distribution function is normalized as follows (x_0 is the initial condition):

$$(110) \quad 1 = \int dx P(x) = \int \int dx dx_0 P(x, \tau; x_0, 0)$$

which means

$$(111) \quad \int dx P(x, \tau|x_0, 0) = 1$$

Taking the limit $\tau \rightarrow 0$, we have

$$(112) \quad \lim_{\tau \rightarrow 0} P(x, \tau|x_0, 0) = \delta(x - x_0)$$

For any functions $f(x)$ and $g(x)$, we define the correlations:

$$(113) \quad \langle f(x_1)f(x_0) \rangle = \int \int dx_1 dx_0 f(x_1)g(x_0)P(x_1, t_1; x_0, t_0)$$

We can also the conditional average (conditional to the initial condition)

$$(114) \quad \langle f(x) \rangle_{\tau}^{x_0} = \int dx f(x)P(x, \tau|x_0, 0)$$

which depends on τ and on x_0 . A simple calculation leads to:

$$(115) \quad \langle f(x)g(x_0) \rangle = \langle \langle f(x) \rangle_{\tau}^{x_0} g(x_0) \rangle$$

where the outside bracket " $\langle \rangle$ " means that we average over all initial conditions x_0 . We see that here that there is a physical interpretation between a correlation function and a conditional

³We use the same notation to indicate both the random variable and the value that it can assume.

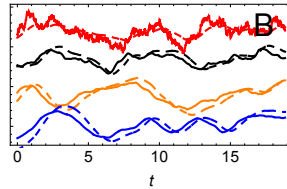


FIGURE 2. Examples of traces of signals obtained from (116) by increasing the damping coefficient. From ref.².

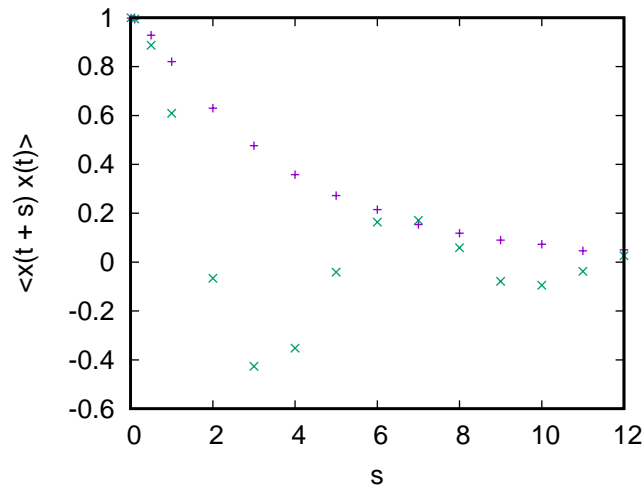


FIGURE 3. Correlation functions for the harmonic oscillator of Eq. (116). Top curve $\eta = 4$ (Markov), bottom curve, $\eta = 0.5$ (non Markov).

probability. This conditional probability is generally calculated as a propagator (other names are Green function or kernel).

The following situation illustrates this point. Consider the signal $x(t)$ generated by the harmonic oscillator

$$(116) \quad \begin{aligned} \partial_{\omega t} x &= p \\ \partial_{\omega t} p &= -x - \eta p + \sqrt{2\eta} \psi \end{aligned}$$

with unit white noise $\psi(t)$. This equation is a kind of stochastic equation we shall study later. The numerical solutions of this equations depend on the value of η are some of them are shown in Fig. 2. We define the correlation function as follows

$$(117) \quad \langle q(t')q(t'+t) \rangle = \sigma_q^2 r(t)$$

Tell if you expect $r(t)$ to be of the form

$$(118) \quad r(t) = \exp(-\lambda t)$$

If it is the case, the signals are said to be Markovian. Such signals have no memory.

12. Correlation and the Power Spectrum

Let us establish the Wiener-Kinchin theorem. We consider the power spectrum of a stochastic process $X(t)$, which is defined as the Fourier transform of the autocorrelation function of $X(t)$

$$(119) \quad S(\omega) = \int_{-\infty}^{+\infty} e^{i\omega\tau} C_X(\tau) d\tau C_X(\tau) = \langle X(t)X(t+\tau) \rangle$$

We define the Fourier transforme $\tilde{X}(\omega)$ as

$$(120) \quad \tilde{X}(\omega) = \int_{-\infty}^{+\infty} X(t)e^{i\omega t} dt$$

Since $X(t)$ is a real function, $\tilde{X}^*(\omega) = \tilde{X}(-\omega)$. Using the definition

$$(121) \quad \delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} dt$$

Show:

$$(122) \quad \langle \tilde{X}(\omega)\tilde{X}^*(\omega') \rangle = 2\pi S(\omega)\delta(\omega - \omega')$$

13. Bayesian statistical Inference

In this section, we introduce the basics of Bayesian data analysis. The key ingredients to a Bayesian analysis are the likelihood function, which reflects information about the parameters contained in the data, and the prior distribution, which quantifies what is known about the parameters before observing data. The prior distribution and likelihood can be easily combined to form the posterior distribution, which represents total knowledge about the parameters after the data have been observed. Simple summaries of this distribution can be used to isolate quantities of interest and ultimately to draw substantive conclusions.

To introduce this point, consider two events, A and B . From the identity

$$(123) \quad P(A)P(B|A) = P(A, B) = P(B)P(A|B)$$

we have

$$(124) \quad P(B|A) = \frac{P(B)P(A|B)}{P(A)}$$

This formula can be interpreted as follows:

- (1) We are interested in the event B , and begin with an initial, PRIOR probability $P(B)$ for its occurrence.
- (2) We then observe the occurrence of A .
- (3) The proper description of how likely B is when A is known to have occurred is the POSTERIOR probability $P(B|A)$.
- (4) Bayes' theorem can be understood as a formula for updating from prior to posterior probability, the updating consisting of multiplying by the ratio $P(A|B)/P(A)$.
- (5) It therefore describes how a probability changes as we learn new information.

EXERCICE 2.8. Let B^c the complement of B , i.e. $P(B^c) = 1 - P(B)$. Show:

$$(125) \quad P(A|B) - P(A) = (P(A|B) - P(A|B^c)) P(B^c)$$

As suspected, this means that using Bayesian inference increases the probability of B if $P(A|B) > P(A|B^c)$. The ratio $P(A|B)/P(A|B^c)$ is defined as the likelihood ratio.

EXERCICE 2.9. We prove Novikov's identity, see (89). Assume

$$(126) \quad P(\mathbf{x}) = \sqrt{\frac{\det A}{(2\pi)^n}} \exp\left\{\left[-\frac{1}{2}\mathbf{x}^t A \mathbf{x}\right]\right\}$$

with

$$(127) \quad E(\mathbf{x}) = \frac{1}{2} \sum x_i A_{i,j} x_j \quad \text{and} \quad A_{i,j} = A_{j,i}$$

- (1) Compute the derivative $\partial E/\partial x_m$ and show

$$(128) \quad x_i = \sum_m (A^{-1})_{i,m} \frac{\partial E}{\partial x_m}$$

(2) Show

$$(129) \quad \langle x_i f(\mathbf{x}) \rangle = \sum_m (A^{-1})_{i,m} \langle \frac{\partial f}{\partial x_m} \rangle$$

(3) Demonstrate

$$(130) \quad \langle x_i x_j \rangle = (A^{-1})_{i,j}$$

Conclude.

CHAPTER 3

BROWNIAN MOTION

1. Introduction

According to Caldeira and Legett¹, there are many systems whose dynamics does not conserve energy. A well-known example is the Brownian motion. The theoretical approach of this problem is through the Langevin equation which reads as

$$(131) \quad M\ddot{q} + \gamma\dot{q} + V'(q) = f(t)$$

where $f(t)$ is a fluctuating force such that $\langle f(t) \rangle = 0$ and $\langle f(t)f(t') \rangle = 2\eta k_B T \delta(t - t')$. The δ distribution means that the forces are correlated on a characteristic time $1/\lambda$

$$(132) \quad \langle f(t)f(t') \rangle = \langle f^2 \rangle e^{-\lambda|t-t'|}$$

with $1/\lambda$ much smaller than any macroscopic time (for example the time it takes for the particle to stop moving).

The exchange of energy between the particle and the bath appears through two terms:

- (1) The random force $f(t)$, where the particle takes energy from the bath;
- (2) The dissipative term, $\gamma\dot{q}$, where the particle gives energy back to the bath.

In summary, this equation is a good description if

- (1) The mass M of the particle is much larger than the mass m of the molecules composing the bath.
- (2) One is interested at times much larger than the average time between two collisions.

The Langevin equation is a stochastic equation where

- (1) $-V'(q)$ is a force due to a potential;
- (2) $f(t)$ is a random Gaussian variable (this force is due to the collisions with the "light" particles. The heavy particle experience many collisions and $f(t)$ is Gaussian because its is the sum of many random variables);
- (3) $-\gamma\dot{q} + f(t)$ describes the interaction with a thermostat.

There many systems with equivalent equations. For example, the dynamics of a charge stored in the capacitor of a RLC circuit obeys

$$(133) \quad L\ddot{Q} + R\dot{Q} + \frac{Q}{C} = V_f(t)$$

where $V_f(t)$ is a fluctuation voltage.

¹www.scholarpedia.org

2. The Langevin equation^{8;15}

The Caldeira-Leggett model answers to the following question: How the dissipation and the fluctuating forces arise when we couple a dissipative system with a thermal bath? As usual, there are two approaches to this problem: classical and quantum. For superconducting devices, the quantum approach is necessary. Here, we concentrate on the classical approach. We will see that dissipation arises because the movement of massive particle perturbs the distribution of the light particles which is no more Maxwellian.

Let us assume that the force $F(t)$ is a Gaussian white noise². This means that the values of $F(t)$ at two different times are independent stochastic variables. Their correlations takes the Dirac form:

$$(134) \quad \langle F(t)F(t') \rangle = \Gamma\delta(t - t')$$

The Langevin's equation

$$(135) \quad M\frac{dV}{dt} = -\gamma V + F(t)$$

is linear and can be easily integrated:

$$(136) \quad V(t) = V(0)e^{-\gamma t/M} + \frac{1}{M} \int_0^t dt' e^{-\gamma(t-t')/M} F(t')$$

In the permanent regime where the first term is negligibly small, this expression reduces to

$$(137) \quad V(t) = \frac{1}{M} \int_0^t dt' e^{-\gamma(t-t')/M} F(t')$$

Since $V(t)$ is a linear function of Gaussian variables, $V(t)$ is also a Gaussian variable. Its mean value (after averaging over $f(t)$):

$$(138) \quad \langle V(t) \rangle = V(0)e^{-\gamma t/M}$$

tends rapidly to zero and its variance is:

$$(139) \quad \langle V(t)^2 \rangle - \langle V(t) \rangle^2 = \frac{\Gamma}{2M\gamma} (1 - e^{-2\gamma t/M})$$

In the long time limit, the Gaussian distribution for the speed must tend to the equilibrium distribution at temperature T

$$(140) \quad \frac{1}{2}M \langle V(t)^2 \rangle \rightarrow \frac{1}{2}k_B T$$

Therefore, we have

$$(141) \quad \Gamma = 2\gamma k_B T$$

This relationship connecting the strength of the $F(t)$'s, see Eq.(134), to the dissipative part is general. To be at equilibrium, the heavy particle which gets some energy from the bath via the force $F(t)$ must give it back to the bath via the dissipative term. Otherwise, its energy will explode! An other view of the FD theorem is to state that it expresses the balance between the friction which drives the system to a "dead" state, and noise, which tends to keep the system "alive".

One can also obtain the correlation function:

$$(142) \quad \langle V(t)V(t') \rangle = \langle V(0)^2 \rangle \exp\{-\gamma|t - t'|/M\}$$

²All Fourier components have the same variance.

Integrating Eq. (136), we get for the displacement:

$$(143) \quad \begin{aligned} \langle (x(t) - x(0))^2 \rangle &= \left\langle \left[\int_0^t dt' V(t') \right]^2 \right\rangle \\ &= \frac{2k_B T}{\gamma} t - \frac{2Mk_B T}{\gamma^2} (1 - e^{-\gamma t/M}) \end{aligned}$$

In the large t limit (1s !), diffusion gives the leading term:

$$(144) \quad \langle (x(t) - x(0))^2 \rangle = \frac{2k_B T}{\gamma} t$$

where the diffusion constant is given by the Einstein relation³:

$$(145) \quad D = \frac{2k_B T}{\gamma}$$

The same calculation can be done for arbitrary force correlations which depend on the difference $t - t'$:

$$(146) \quad \langle F(t)F(t') \rangle = \langle F(0)F(t - t') \rangle$$

Repeating the same calculation, one finds:

$$(147) \quad D = \frac{1}{2\gamma^2} \int_{-\infty}^{\infty} \langle F(0)F(t') \rangle dt'$$

and

$$(148) \quad D = \int_0^{\infty} du \langle V(t)V(t+u) \rangle$$

One may ask about the validity of some hypothesis made in the Langevin's approach. The very simple form of the effective force is certainly an approximation. Hydrodynamic correlations do not decay exponentially as it is generally assumed but as a power law ($t^{-d/2}$). The viscous force can, however, be calculated in the small Reynolds number limit. For a sphere of size r , one gets the classical result $\gamma = 6\pi r\nu$. Using this relation, one finds

$$(149) \quad D = \frac{k_B T}{6\pi r\nu}$$

and this gives that a particle of size $1 \mu m$ explores a region of size $1 \mu m$ in $1 s^4$.

EXERCICE 3.1. Consider again the Langevin equation

$$(150) \quad m \frac{dv}{dt} = -\gamma v + \eta(t)$$

with $\langle \eta(t) \rangle = 0$ and $\eta(t)\eta(t') = \Gamma\delta(t - t')$, $\Gamma = 2\gamma k_B T$.

(1) Show that the stationary solution of the Langevin equation (for sufficiently large t)

$$(151) \quad v(t) = \frac{1}{m} \int_{-\infty}^t e^{-\frac{\gamma}{m}(t-t')} \eta(t') dt'$$

(2) Assume that $\eta(t)$ is a Gaussian variable. What is the distribution of $v(t)$? Compute the mean and the variance from the Langevin equation et give this probability distribution.

³In arbitrary dimension d , the factor 2 is $2d$.

⁴For water at room temperature, $\nu = 10^{-3} kg.m^{-1}.s^{-1}$ and $k_B = 1.410^{-23} JK^{-1}$ so that a particle of radius $r = 10^{-9} m$ has a diffusion constant $D \approx 100 \mu m^2/s$.

(3) From the Langevin equation, we know the correlations obey

$$(152) \quad \langle v(t)v(t') \rangle = \langle v^2 \rangle e^{-\frac{\gamma}{m}|t-t'|}$$

Show:

$$(153) \quad \langle (x(t) - x(t'))^2 \rangle = \left\langle \left[\int_{t'}^t v(t'') dt'' \right]^2 \right\rangle = \frac{2k_B T}{\gamma} \left(|t - t'| - \frac{m}{\gamma} e^{-\frac{\gamma}{m}|t-t'|} \right) + cst.$$

Deduce the characteristic property of the Brownian motion.

3. Numerical integration of stochastic differential equations

Let us consider the Brownian oscillator with the equation of motion (the usual convention is to take $\eta = \gamma/m$)

$$(154) \quad \begin{aligned} \dot{p} &= -kq - \frac{\gamma}{m}p + f(t) \\ \text{or } \dot{p} &= -kq - \eta p + f(t) \end{aligned}$$

To begin with we will consider a strongly overdamped oscillator, $\gamma \gg \sqrt{k/m}$. In this case one can drop the inertial term $\dot{p} = 0$. As before, we take $f(t)$ to be delta-correlated:

$$(155) \quad \langle f(t)f(t') \rangle = 2\eta\delta(t - t')$$

In this regime, we obtain the stochastic differential equation for the coordinate

$$(156) \quad \dot{q} = \Omega q + r(t)$$

where $\Omega = k/\eta$ and

$$(157) \quad \langle r(t)r(t') \rangle = \frac{2}{\eta}\delta(t - t')$$

In the literature of stochastic differential equations, this equation is written in incremental form

$$(158) \quad dq_t = -\Omega q_t dt + \sqrt{2D} dW_t$$

where $D = T/\eta$ and the notation q_t is used to denote the value of the stochastic process at time t . The term dW_t is an increment of a stochastic process that is most simply described as a succession of random increments, $W_{t_1}, W_{t_2}, W_{t_3}, \dots$. Each increment $dW_{t_i} = W_{t_{i+1}} - W_{t_i}$ is sampled from a normal distribution with zero mean and VARIANCE $t_{i+1} - t_i$. Such a process is generally called a Wiener process. The properties of a Wiener process can be summarized in the following relations:

$$(159) \quad W_0 = 0, \langle W_t \rangle = 0, \langle (W_t - W_s)^2 \rangle = |t - s|$$

EXERCICE 3.2. Consider a typical additive noise problem where

$$(160) \quad dW_t = \int_0^{t+dt} dt' \eta(t')$$

where $\langle \eta(t)\eta(t') \rangle = \delta(t - t')$. Show

$$(161) \quad \langle (dW_t)^2 \rangle = dt$$

meaning tyhat, as far as averages are concerned, $dW_t \propto \sqrt{dt}$.

Stochastic integrals with respect to W_t can be defined as limits of Riemann sums

$$(162) \quad \int_0^t q_t dW_t = \lim_{n \rightarrow \infty} \sum_{i=1, n} q_t (W_{t_i} - W_{t_{i-1}})$$

where we have ignored all mathematical considerations.

A simple approximate integration scheme follows immediately from (158)

$$(163) \quad q_{t+\Delta t} = q_t - \Omega q_t \Delta t + \sqrt{2D\Delta t} \phi_t$$

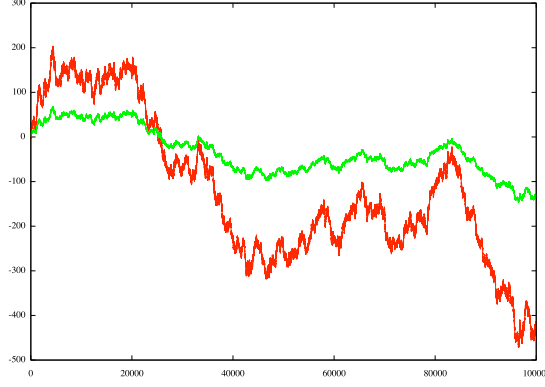


FIGURE 1. Numerical Langevin simulation of a Brownian particle in a 300K bath (water), see Eq. (163). Time is measured in ps and distances in Nm. The red curve is obtained for a 10nm particle and the green curve corresponds to a 100nm particle. Note how the fluctuations decrease with the size of the particle.

where Δt appears in the $\sqrt{2S\Delta t}$ and where ϕ_t is a Gaussian random variable with zero mean and unit variance. The reason for this is that $\sqrt{\Delta t}$ is the typical value of

$$(164) \quad \int_t^{t+\Delta t} dW_t \simeq \sqrt{\Delta W_t^2} = \sqrt{\Delta t}$$

The former property will be proved later on. Given an algorithm to generate random numbers with a Gaussian distribution (GSL library), we can write a simple program to find q_n at a sequence of time intervals $t_n = n\Delta t$, see Fig. 1.

Here is the Python code to generate the sequence for the positions and the momenta for the simple oscillator

$$(165) \quad \begin{aligned} \frac{dx}{dt} &= p \\ \frac{dp}{dt} &= -q - \eta p + \sqrt{2\eta}\xi(t) \end{aligned}$$

where $\xi(t)$ is a random variable with variance 1. Arrays $x[n]$ and $p[n]$ are defined as numpy arrays and n is the number of time intervals covered by the whole sequence. This program can be used to compute the correlation functions as in Fig. 3 of the previous chapter.

```
def verlet_1st_order(x,p, n, dt):
    x[0] = 0
    p[0] = 0
    eta = 0.5
    sigma = np.sqrt(2. * eta * dt)
    np.random.seed(2022) # use same sequence
    alea = np.random.randn(n)
    for i in range(n - 1):
        x[i+1] = x[i] + p[i]*dt
        p[i + 1] = p[i] + (F(x[i]) - eta * p[i]) * dt + sigma * alea[i]

    where F[q] = -q.
```

EXERCICE 3.3. A NEW VERSION OF THE FLUCTUATION-DISSIPATION THEOREM: The fluctuation-dissipation theorem is based on the assumption that the response of a system in thermodynamic equilibrium to a small applied force is the same as its response to a fluctuation.

Suppose that $x(t)$ is the response and that $f(t)$ is the force

$$(166) \quad x(t) = \int_{-\infty}^{+\infty} \chi(\tau) f(t - \tau) d\tau, \quad \chi(\tau) = 0 \text{ for } \tau < 0$$

Define

$$(167) \quad S_x(\omega) = \int_{-\infty}^{+\infty} e^{i\omega\tau} C_x(\tau) d\tau, \quad C_x(\tau) = \langle x(t)x(t + \tau) \rangle$$

The FD theorem states that

$$(168) \quad S_x(\omega) = \frac{2k_B T}{\omega} \text{Im} [\tilde{\chi}(\omega)]$$

- (1) Use the lecture notes to compute $S_x(\omega)$ for the process studied in the Brownian motion section (Ornstein-Uhlenbeck process).
- (2) An other proof of the FD theorem.
- (3) Show that:

$$(169) \quad \langle x(0)^2 \rangle = \int_{-\infty}^{+\infty} S_x(\omega) \frac{d\omega}{2\pi}$$

- (4) Recall that $\chi(\tau)$ is causal, meaning that $\chi(\tau) = 0$ for $\tau < 0$. It follows that $\tilde{\chi}(\omega)$ is analytic in the upper half-plane. This also means that $\tilde{\chi}^*(\omega) = \tilde{\chi}(-\omega)$ is analytic in the lower complex half-plane. Show:

$$(170) \quad \int_{-\infty}^{+\infty} \frac{\text{Im} [\chi(\omega)]}{\omega} \frac{d\omega}{2\pi} = \frac{1}{2i} \int_{\mathcal{C}_+} \frac{\chi(\omega)}{\omega} \frac{d\omega}{2\pi} - \frac{1}{2i} \int_{\mathcal{C}_-} \frac{\chi(\omega)}{\omega} \frac{d\omega}{2\pi}$$

and give \mathcal{C}_\pm .

- (5) Apply residue theorem to show:

$$(171) \quad \int_{-\infty}^{+\infty} \frac{\text{Im} [\chi(\omega)]}{\omega} \frac{d\omega}{2\pi} = \frac{1}{2} \tilde{\chi}(0)$$

- (6) Deduce

$$(172) \quad \langle x(0)^2 \rangle = k_B T \tilde{\chi}(0)$$

- (7) Show that for an Ornstein-Uhlenbeck process

$$(173) \quad \frac{1}{2} \kappa \langle x(0)^2 \rangle = \frac{1}{2} k_B T$$

4. Detailed balance and the Langevin equation

In the case of small particles (i.e. the low Reynolds number limit), one neglects the inertial term in the Langevin equation. This means that we assume fast relaxation for the speed. This leads to

$$(174) \quad \gamma \frac{dx}{dt} = F(x) + \eta(t)$$

where we assume that the force is the derivative of a potential. This limit corresponds to a so-called Ornstein-Uhlenbeck process and $F(x) = -dU/dx$ as usual. Here we show that the dynamics obeys detailed balance, meaning (the symbol $P(x' \leftarrow x)$ is the probability to jump to x' starting from x)

$$(175) \quad \frac{P(x' \leftarrow x)}{P(x \leftarrow x')} = \exp \left\{ \left[-\frac{(x - x')}{k_B T} \frac{dU}{dx} \right] \right\}$$

where the factor in the exponential is the work done by the force when the particle jumps from x to x' . If the ratio of probability obeys this equality, the dynamics is said to obey detailed balance. Detailed balance is a trademark of equilibrium systems and dynamics which does not obey detailed balance are characteristic of out-of-equilibrium systems.

For a small time interval Δt .

$$(176) \quad x' \equiv x(t + \Delta t) = x + \frac{F(x)}{\gamma} + B$$

where B is a Gaussian number

$$(177) \quad B = \frac{1}{\gamma} \int_t^{t+\delta t} \eta(t') dt' \quad \langle B \rangle = 0 \quad \langle B^2 \rangle = \frac{\Gamma}{\gamma^2} \Delta t$$

since

$$(178) \quad \langle B^2 \rangle = \frac{1}{\gamma^2} \iint_t^{t+\Delta t} dt dt' \langle \eta(t) \eta(t') \rangle = \frac{\Gamma}{\gamma^2} \Delta t$$

Note that (176) gives an Euler integration scheme to integrate a stochastic differential equation and that B is proportional to $\sqrt{\Delta t}$ and not to Δt as one might have thought.

From (176), we deduce B as a function of $x' - x$ and, since we know that B is Gaussian, we deduce that the probability to go from x to x' has the form

$$(179) \quad P(x' \leftarrow x) = C \exp \left\{ \left[-\frac{((x' - x)\gamma - F(x)\Delta t)^2}{2\Gamma\Delta t} \right] \right\}$$

We have also

$$(180) \quad P(x \leftarrow x') = C \exp \left\{ \left[-\frac{((x - x')\gamma - F(x)\Delta t)^2}{2\Gamma\Delta t} \right] \right\}$$

which means

$$(181) \quad \frac{P(x' \leftarrow x)}{P(x \leftarrow x')} = \exp \left\{ \left[-\frac{2(x' - x)F(x)\gamma}{\Gamma} \right] \right\}$$

If $\Gamma = 2k_B T \gamma$ and if the force is the derivative of a potential

$$(182) \quad (x' - x)F(x) \approx \int_x^{x'} F(x) dx = U(x) - U(x')$$

then the Langevin equation describes an equilibrium system, since the detailed balanced principle is verified.

5. Diffusion equation and random walk: The Schmoluchowski equation

What is a random walk ? Random walks are paths that take successive steps in random direction. They arise in physics as partial sums of fluctuating quantities, as trajectories of particles undergoing repeated collisions, or as shape for long and linked polymers.

We start by deriving the diffusion equation by taking the continuum limit of an ensemble of random walks. Consider a random walk where at each time step Δt the particle position changes by a step l (1d)

$$(183) \quad x(t + \Delta t) = x(t) + l(t)$$

Let the probability distribution of each step be $\rho(l)$. We will assume that the first few moments of $\rho(l)$ are:

$$(184) \quad \int dl \rho(l) = 1$$

$$(184) \quad \int dl l \rho(l) = 0$$

$$(185) \quad \int dl l^2 \rho(l) = a^2$$

What is the probability $P(x, t + \Delta t)$ given the probability distribution $P(x', t)$? To go from x to x' the step has to be $x' - x$. The probability to be at x' at t is $P(x', t)$ and the probability to have a given step is $\rho(x - x')$. We have:

$$(186) \quad \begin{aligned} P(x, t + \Delta t) &= \int dx' \rho(x - x') P(x', t) \\ &= \int dz P(x - z, t) \rho(z) \end{aligned}$$

If $P(x, t)$ does not vary too much on the length scale of a typical step, we may Taylor expand

$$P(x - z, t) = P(x, t) - z dP/dx + z^2/2 d^2P/dx^2$$

in the integral. We have:

$$(187) \quad P(x, t + \Delta t) = P(x, t) + \frac{1}{2} \frac{a^2}{\Delta t} \frac{\partial^2 P}{\partial x^2}$$

So that we recover the diffusion equation:

$$(188) \quad \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} \quad D = \frac{1}{2} \frac{a^2}{\Delta t} \quad \text{with } d = 1$$

An interesting question is to know what happens when the particle is subjected to a drift. This drift is due to an external force F which biases the random walk as

$$(189) \quad x(t + \Delta t) = x(t) + \frac{1}{\gamma} F \Delta t + l(t)$$

where γ is a mobility.

Repeating the previous steps, we get:

$$(190) \quad \frac{\partial P}{\partial t} = D \frac{\partial^2 P}{\partial x^2} - \frac{1}{\gamma} F \frac{\partial P}{\partial x}$$

The second term proportional to the first derivative is the drift. We can rewrite this equation in the most general form (this our first example of the Schmoluchowsky equation):

$$(191) \quad \frac{\partial P}{\partial t} = - \frac{\partial J}{\partial x}$$

Where the total current is the sum of the diffusion and of the drift terms.

$$(192) \quad J = \frac{1}{\gamma} F(x, t) P(x, t) - D \frac{\partial P}{\partial x}$$

An interesting consequence of this definition is that the distribution $P(x, t)$ can be derived under very general conditions.

At equilibrium, the net current is zero. Assuming that the force is the derivative of a potential $U(x)$, the stationary condition $J = 0$ leads to

$$(193) \quad \frac{1}{\gamma} \frac{dU}{dx} P(x) + D \frac{\partial P}{\partial x} = 0$$

with solution

$$(194) \quad P(x) = \exp \left\{ \left[- \frac{D}{\gamma} U(x) \right] \right\}$$

where the temperature T is defined through an equivalent relation of (145)

$$(195) \quad k_B T = \frac{\gamma}{D}$$

EXERCICE 3.4. Sometimes it is more interesting to work with a discretized space, i.e. a square lattice, with unit vector \hat{e}_μ , $\mu = 1, \dots, d$. For a square lattice, each site has $2d$ nearest neighbors.

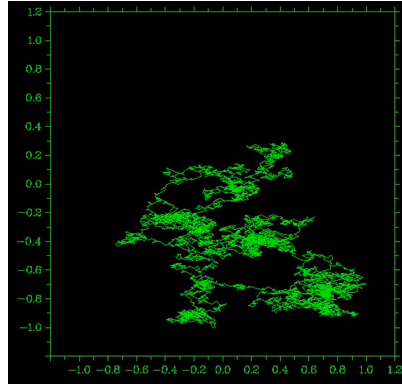


FIGURE 2. One realization of a random walk in $d = 2$. Note that the trajectory does not appear to cover the plane uniformly for a finite number of steps. The walker seems to make long excursions followed by short inspections in localized neighborhoods around certain points.

- (1) A r.w. can jump from one lattice site to a neighboring one with a rate γ per unit time. What are the events which can take place during a time interval dt and what are the associated probabilities ?
- (2) Show that the discretized version of diffusion equation is

$$(196) \quad \frac{\partial P(\mathbf{x}, t)}{\partial t} = \gamma \sum_{\mu=1, d} [P(\mathbf{x} + a\hat{e}_\mu, t) + P(\mathbf{x} - a\hat{e}_\mu, t) - 2P(\mathbf{x}, t)]$$

as it can be seen by Taylor expanding to second order in the lattice spacing a Eq. (196). This equation being an equation for a probability is called a Master equation.

6. Return statistics : Transience and recurrence

In arbitrary dimensions, the solution of the diffusion equation is

$$(197) \quad P(\mathbf{x}, t) = (4\pi Dt)^{-d/2} e^{-\mathbf{x}^2/4Dt}$$

with initial conditions:

$$(198) \quad P(\mathbf{x}, 0) = \delta(\mathbf{x} = 0) = \delta(x_1 = 0)\delta(x_2 = 0) \dots \delta(x_d = 0)$$

The variance of \mathbf{x} at time t is

$$(199) \quad Var[\mathbf{x}(t)] = \int d^d x x^2 P(\mathbf{x}, t) = -\nabla_{\mathbf{k}} \tilde{P}(\mathbf{k}, t)|_{\mathbf{k}=0} = 2dDt$$

where d is the space dimension. Thus the root mean square distance covered by the particle from the initial position is $\sqrt{2dDt}$.

Suppose that a random walk begins at the origin of an infinite lattice at $t = 0$. Does the random walker eventually return to its starting point? Remarkably, the answer depends only on the spatial dimension d .

If the random walker jumps every second, the number of sites visited over a time interval t is simply t although a given site may be visited more than once. The density of visited sites is then $t/(2dDt)^{d/2} \propto t^{1-d/2}$ and thus decreases with t when $d > 2$. Some sites may never be visited (transience). For $d = 1$, this density increases, which means that the walker returns to any site with probability 1. The case $d = 2$ is marginal. The exact result is a logarithm and the density is still infinite when $t \rightarrow \infty$. In $d = 2$, the probability to visit any given site is still 1 (after an infinite number of steps). This can be summarized as follows: In $d = 2$, the random walk is said to be recurrent. For $d = 3$ and above, the random walk is transient.

EXERCICE 3.5. Knowing that the r.w. started at the origin at time $t = 0$, let $P(\mathbf{r}, t)$ be the probability for the r.w. to be at point \mathbf{r} at time t . Let $F(\mathbf{r}, t)$ be the probability to visit the

site \mathbf{r} for the first time at time t . Clearly, $F(\mathbf{r}, t)$ and $P(\mathbf{r}, t)$ are different, since the r.w. can make loops and return to any point which has been visited in the past. Both probabilities are related:

$$(200) \quad P(\mathbf{r}, t) = \int_0^t F(\mathbf{r}, t') P(\mathbf{0}, t - t') dt' + \delta_{\mathbf{r}, \mathbf{0}} \delta(0)$$

where $\delta_{\mathbf{r}, \mathbf{0}} = 1$ if $\mathbf{r} = \mathbf{0}$.

- (1) Discuss this equation;
- (2) Recall that the Laplace transform of any function $g(t)$ is defined by

$$(201) \quad \tilde{g}(s) = \int_0^\infty g(t) e^{-st} dt$$

Determine $\tilde{F}(\mathbf{r}, s)$ as a function of $\tilde{P}(\mathbf{r}, s)$ (recall that the Laplace transform of a convolution is the product of the Laplace transforms);

- (3) What is the probability of an eventual return to the origin (meaning the probability to return at some time) as a function of $\tilde{F}(s = 0, t)$?
- (4) Recall this rule for the Laplace transform:

$$(202) \quad t^{-\mu} \quad \text{with} \quad \mu < 1 \leftrightarrow \Gamma(1 - \mu) s^{\mu-1}$$

and $\Gamma(1/2) = \sqrt{\pi}$. Compute $\tilde{F}(s = 0, t)$ for $d = 1$ and conclude.

- (5) We are interested in the mean return time to the origin. What is the Laplace transform of $tF(\mathbf{r} = \mathbf{0}, t)$? Conclude.

7. An example of first passage probability: The gambler ruin problem

EXERCICE 3.6. Consider a r.w. on a finite interval of length N . The two boundary sites are absorbing, i.e. the random walker immediately disappears upon reaching these sites. Suppose that the starting position of the r.w. is n , with $0 \leq n \leq N$. What is F_n , the probability that the r.w. first reaches the boundary at site N , i.e. without touching site number 0, first? We will write a simple recursion relation for F_n .

- (1) What is F_0 and F_N ?
- (2) With probability $1/2$, the walk steps to site $n - 1$ at which the probability to escape at site $n - 1$ is F_{n-1} . Similarly, the walk steps at site $n + 1$ with probability $1/2$. Explicit the recurrence relation :

$$(203) \quad F_n = F(F_{n-1}, F_{n+1})$$

- (3) Show $F_n = n/N$.

This exit probability also represents the solution of the gambler ruin problem. In a casino, you continue to bet as long as you have money. Let n represent your wealth which that changes by a small amount ± 1 with equal probability by a single beat with the casino. You lose if your wealth hits zero and you break the casino is your wealth hits N (the total sum of your wealth and the one of the casino). This calculation shows that the probability to break the casino is n/N . Conclusion: Owning the casino is a good idea, gambling in the casino is a bad idea.

EXERCICE 3.7. We derive a simple relation between the diffusion constant and the integral of the equilibrium time-correlation function of the velocity of a Brownian particle. This is a particular (and very illustrative) example of the Green-Kubo formulae relating transport coefficients and equilibrium time-correlation functions, a main result of nonequilibrium statistical mechanics.

Let us consider the net displacement of a Brownien particle position during the time interval 0 and t

$$(204) \quad \mathbf{x}(t) = \int_0^t \mathbf{v}(s) ds$$

(1) What does it mean to do an ensemble average ?

(2) Show

$$(205) \quad \frac{d}{dt} \langle \mathbf{x}^2(t) \rangle = 2 \int_0^t ds \langle \mathbf{v}(t) \cdot \mathbf{v}(s) \rangle$$

(3) The velocity correlation function generally decays to zero in a short time. What is the order of magnitude of the characteristic time scale of the decay ?

(4) Let us consider the number of $n(\mathbf{x}, t)$ of particules at distance \mathbf{x} of the origin. This density obeys the diffusion equation

$$(206) \quad \frac{\partial n(\mathbf{x}, t)}{\partial t} = D \nabla^2 n(\mathbf{x}, t)$$

Solve this equation using the Fourier transform of the particle density

$$(207) \quad \tilde{n}(\mathbf{k}, t) = \int_{\mathbb{R}^d} e^{i\mathbf{k} \cdot \mathbf{x}} n(\mathbf{x}, t) d\mathbf{x}$$

together with the initial condition

$$(208) \quad n(\mathbf{x}, 0) = N \delta(\mathbf{x})$$

(5) To derived the simplest example of the Green-Kubo relation of a transport coefficient to a time correlation function, show ($d = 3$)

$$(209) \quad D = \frac{1}{3} \int_0^\infty du \langle \mathbf{v}(u) \cdot \mathbf{v}(0) \rangle$$

8. Path integral approaches to Brownien motion

Let us rewrite the Langevin equation in the overdamped limit as

$$(210) \quad \xi(t) = \gamma \frac{dx}{dt} + \frac{dV}{dx}$$

where $V(x)$ is the (non-random) potential. We know that the random forces $\xi(t)$ come from a Gaussian distribution

$$(211) \quad P[\xi(t)] \propto \exp \left\{ -\frac{1}{4\gamma k_B T} \int_{t_0}^{t_1} dt \xi^2(t) \right\}$$

so that it is tempting to say that the probability of observing the trajectory $x(t)$ is given by

$$(212) \quad P[x(t)] \simeq \exp \left\{ -\frac{1}{4\gamma k_B T} \int_{t_0}^{t_1} dt \left[\gamma \frac{dx}{dt} + \frac{dV}{dx} \right]^2 \right\}$$

As said by W. Bialek⁴, this is almost right, but we miss the Jacobian for the transformation $\xi(t) \rightarrow x(t)$. This Jacobian is temperature independent so that Eq. (688) has the form $\exp\{-E/T\}$ and the exponential temperature dependent term will dominate in the low T regime.

9. The Caldeira-Leggett model

Consider a brownian particle of mass M interacting with particles of mass m . We will assume that $M \gg m$. Because the heavy particle has a much larger mass than the light particles, there are two very different time scales in the problem.

(1) The first effect is viscosity. The heaviest particle will be submitted to a friction because of collisions. If the heaviest particle has a velocity \mathbf{v} , the transfer of momentum with the particles of the bath will not be the same if the light particle are located at the front or at the back of M . It results a force. To first order the force is proportional to \mathbf{v} with a minus sign :

$$(213) \quad \mathbf{F} = -\alpha \mathbf{v}$$

with α being a friction coefficient. The ratio $\gamma = \alpha/M = 1/\tau$ defines the first time scale. This time scale is the time that the particle takes to stop when initially animated with a velocity \mathbf{v} . This time scale is, therefore, macroscopic (1s for a typical bacteria).

- (2) There is also a microscopic time scale entering into the problem. Due to the random character of the collisions between the bath particles, there are strong fluctuations in the force experienced by the M particle. These forces fluctuate on a typical time scale of the order of $\tau_c = 10^{-12}s$.

Because $\tau_c \ll \tau$, the slow modes correspond to the heaviest particle motion. The fast modes are the dynamical variables of the bath m particles. This very difference in time scales leads to the phenomenon of decoherence. We will study the $1d$ case.

A way to represent a thermostat is to imagine that it consists of a very large number of N degrees of freedom and to assume that the total system (thermostat + system) possesses a Hamiltonian dynamics. If N is finite, the Poincaré theorem tells us that the system must return arbitrarily close to its initial state if we wait long enough. To obtain an irreversible behaviour at long times, it is therefore necessary to take first the limit of an infinite system and then the limit of long times (and these two limits do not necessarily commute):

$$(214) \quad \lim_{t \rightarrow \infty} \left[\lim_{N \rightarrow \infty} (\dots) \right]$$

Taking into account both types of particles, the total Hamiltonian reads as:

$$(215) \quad H = \frac{P^2}{2M} + \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_i m_i \omega_i^2 (X - x_i)^2$$

where the first two terms are the kinetic energies (bath particles are indexed by $1 \leq i \leq N$). The last term couples the heavy particle of position X to all particles in the bath via an effective spring constant. For clarity, let us define

$$(216) \quad \kappa = \sum_i m \omega_i^2$$

We can rewrite the Hamiltonian as a sum of three terms:

$$(217) \quad H = \left[\frac{P^2}{2M} + \frac{1}{2} \kappa X^2 \right] + \left[\sum_i \frac{p_i^2}{2m} + \frac{1}{2} m_i \omega_i^2 x_i^2 \right] - \left[X \left(\sum_i m_i \omega_i^2 x_i \right) \right]$$

$$(218) \quad = H_1 + H_R + V$$

The last term describes the interaction between the M particle and the bath. It will be useful to define anew symbol:

$$(219) \quad F_0(t) = \sum_i m_i \omega_i^2 x_i(t)$$

with the dimension of a force.

With these notations, the equation of motion for the heaviest particle takes the simple form:

$$(220) \quad \dot{P} = -\kappa X + F_0(t)$$

where $F_0(t)$ describe the influence of the bath on the particle.

We can also write the equation of motion of the bath particles. There are N such equations. If we neglect the influence of the heaviest particle, the Hamiltonian for the bath is a sum of harmonic oscillators. We can compute $F(t)$ as a function of the initial conditions $x_i(0)$, $p_i(0)$:

$$(221) \quad F_0(t) = \sum_i [m_i \omega_i^2 x_i(0) \cos \omega_i t + \omega_i p_i(0) \sin \omega_i t]$$

The next step is to take into account the back action of the heaviest particle and to calculate how $F_0(t)$ is modified as $F(t) = F_0(t) + \delta F(t)$. Since $F(t)$ is a dynamical quantity, we can apply the Kubo theory of the preceding chapter (cf. 540)

$$(222) \quad \chi_{AB}(t) = -\beta \frac{d}{dt} \langle B(0) \delta A(t) \rangle$$

to get:

$$(223) \quad \delta F(t) = \int_0^t \chi(t-t') X(t') dt' = -\beta \int_0^t \dot{C}(t-t') X(t') dt'$$

where:

$$(224) \quad C(t) = \langle F_0(0) F_0(t) \rangle$$

with $F_0(t)$ being the unperturbed force field of eq. (219)⁵.

Changing variable $t' \rightarrow t' - t$ and integrating by part, we finally obtain:

$$(226) \quad \dot{P} = -\kappa X(t) + \beta C(0) X(t) - \beta C(t) X(0) + F(t) - \beta \int_0^t C(t') \dot{X}(t-t') dt'$$

Although (226) looks intimidating, it can be simplified further since the first three terms vanish ! Instead of (226), we get:

$$(227) \quad \dot{P} = +F(t) - \beta \int_0^t C(t') \dot{X}(t-t') dt'$$

where $F(t)$ being a sum of random variables is distributed according to a normal distribution (here, we assume that that we have an infinite set of small particles, so that we use the central limite theorem).

It is easy to compute $C(t)$. From Kubo formula (616), $C(t)$ is given by the equilibrium average (see Eq. (221)) :

$$(228) \quad C(t) = \langle \sum_{i,i'} (m_i \omega_i^2 x_i(0) \cos \omega_i t + \omega_i p_i(0) \sin \omega_i t) m_{i'} \omega_{i'}^2 x_{i'}(0) \rangle$$

But $x_i(0)$ and $p_i(0)$ are distributed according to the Maxwell distribution, since the i 's are uncoupled particles (remember that averages in the Kubo formula correspond to the unperturbed hamiltonian) :

$$(229) \quad \rho(x_i(0)) \propto \exp\{-m_i \omega_i^2 x_i^2(0)/2k_B T\} \quad \rho(p_i(0)) \propto \exp\{-p_i^2(0)/2m_i k_B T\}$$

We get:

$$(230) \quad m_i \omega_i^2 \langle x_i(0) x_{i'}(0) \rangle = k_B T \delta_{i,i'} \quad \langle x_i(0) p_{i'}(0) \rangle = 0$$

so that

$$(231) \quad \beta C(0) = \kappa$$

and the first two terms in (226) cancel out ! Note that by passing from discrete sums to integrals we assume an infinite set of degrees of freedom, $N \rightarrow \infty$.

When $t \gg 2\pi/\omega_i$, i.e. for time much larger than the characteristic times of the fast modes, the cos and sin in eq. (228) average to zero. Here we approximate discrete sums by integrals and this where we assume $N \rightarrow \infty$. As foreseen, this means that the memory of the initial conditions in eq. (226) is lost. For this reason, we call $C(t)$ a memory kernel.

⁵For each particle i , $m_i \omega_i^2 X(t)$ plays the role of $A(t)$. We look for

$$(225) \quad \delta F(t) = \sum_i m \omega_i^2 \delta x_i(t)$$

The short term memory of $C(t)$ allows us to simplify further (226).

$$(232) \quad -\beta \int_0^t C(t') \dot{X}(t-t') dt' = -\beta \dot{X}(t) \int_0^\infty dt' C(t') dt'$$

$$(233) \quad = -\beta \dot{X}(t) \int_0^{+\infty} dt' \langle F(t)F(0) \rangle$$

Finally, we get a viscous force

$$(234) \quad F_{visc} = -M\gamma \dot{X}(t) \quad \gamma = \frac{\beta}{M} \int_0^{+\infty} dt' \langle F(t)F(0) \rangle$$

with the Langevin equation of motion

$$(235) \quad M \frac{dV}{dt} = -\gamma V + F(t)$$

It is interesting to note that the viscous coefficient γ in eq. (234) is proportional to the fluctuation of the random force. This is the fluctuation-dissipation theorem where the back action of the heavy particle on the bath particles gives the dissipative, or viscous, term.

Eq.(234) is a single first order ordinary stochastic equation. Such a process is defined in the literature as an Ornstein-Uhlenbeck process²⁰ and is valid in the low Reynolds limit where inertial terms can be neglected.

CHAPTER 4

THE FOKKER-PLANCK EQUATION

1. Basic derivation

Suppose $x(t)$ a random variable distributed according to $P(x, t)$. This means that at each time t , the value of x is a random variable. By definition, $x(t)$ is a stochastic process and averaging $\langle \rangle$ means averaging over all realizations of the stochastic process $x(t)$. What is the probability of the whole sequence $P(x_n, t_n; x_{n-1}, t_{n-1}; \dots; x_0, t_0)$?

We define the quantity

$$(236) \quad \delta x(t) = x(t + \delta t) - x(t)$$

and we assume that the jumps $\delta x(t)$ are distributed with a probability distribution such that:

$$(237) \quad \langle \delta x(t) \rangle = F_1(x(t))\delta t \quad \langle [\delta x(t)]^2 \rangle = F_2(x(t))\delta t$$

with $\langle [\delta x]^n \rangle = o(\delta t)$ for $n > 2$ ¹. Not all processes obey this scaling property, but a large class does: this class is that of diffusive processes. When $n = 1$, the term is the drift. When $n = 2$, we will refer as the diffusion term (For pure diffusion, $F_1(x) = 0$, $F_2(x) = 2D$ in 1d).

EXERCICE 4.1. Use :

$$(238) \quad \int_{-\infty}^{+\infty} dx x^n e^{-ax^2} = \frac{1}{a^{(n+1)/2}} \frac{(n-1)!}{2^{n/2}} \sqrt{\pi} \text{ if } n \text{ is even, and } 0 \text{ otherwise}$$

to show that Brownian motion is a diffusive process (hence the definition !).

Now consider the conditional probability density

$$(239) \quad P(x, t | x_0, t_0)$$

defined as the probability distribution for $x(t)$ given that $x(t_0) = x_0$. The question we ask in this chapter is how we can derive an equation for P .

The conditional probability distribution density satisfies the composition rule (see Fig. 1)

$$(240) \quad P(x_2, t_2 | x_0, t_0) = \int_{-\infty}^{+\infty} dx_1 P(x_2, t_2 | x_1, t_1) P(x_1, t_1 | x_0, t_0)$$

for ANY VALUE of t_1 . This also known as the Chapman-Kolmogorov equation and has a simple intuitive meaning. For the particle to be at $x = x_2$, it has to be somewhere else at intermediate time $t = t_1$. We sum over all possibilities for x_1 with $t_0 < t_1 < t_2$. What is not trivial is that the conditional probability from t_1 to t_2 is independent of t_0 (no memory).

¹ (δt^2) means much smaller than δt^2 . For example δt^3 .

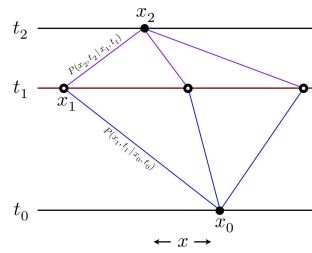


FIGURE 1. Figure illustrating the Chapman-Kolmogorov equation. We assume that $P(x_2, t_2 | x_1, t_1)$ does not depend on x_0 . This is so if the process is a Markov process (see later).

The Chapman-Kolmogorov equation is a non-linear functional equation governing ALL conditional probability densities of a Markov process. A Markov process is defined by the fact that ALL conditional probability densities enjoy the property

$$(241) \quad f(x_n, t_n | x_1, \dots, x_{n-1}; t_1, \dots, t_n) = f(x_n, t_n | x_{n-1}; t_{n-1})$$

That is, the conditional probability density at t_n , given the value at x_{n-1} at t_{n-1} , is not affected by the values at "earlier" times. In this sense, the process is without memory. No general solution of this equation is known. To make progress, we will start from this equation and, under some "general" assumptions, we will derive the Fokker-Planck equation and the Master equation.

Proceeding, we write

$$(242) \quad P(x, t + \delta t | x_0, t_0) = \int_{-\infty}^{+\infty} dx' P(x, t + \delta t | x', t) P(x', t | x_0, t_0)$$

But given a step size $\delta x(t)$, the probability for x is simply a delta function. Formally, we can expand the delta function as

$$(243) \quad P(x, t + \delta t | x', t) = \langle \delta(x - \delta x(t) - x') \rangle$$

$$(244) \quad = \left[1 + \langle \delta x(t) \rangle \frac{d}{dx'} + \frac{1}{2} \langle [\delta x]^2 \rangle \frac{d^2}{dx'^2} + \dots \right] \delta(x - x')$$

since the probability to get at x at time $t + \delta t$ starting from x' at t is the probability to have made a jump $\delta x = x - x'$ during δt . Averages are taken over the jump distribution. To check this expansion, we can use any well-behaved function $f(x)$. After integrating by parts, we get

$$(245) \quad \int dx P(x, t + \delta t | x', t) f(x) = f(x') - \langle \delta x(t) \rangle f'(x') + \frac{1}{2} \langle \delta x(t)^2 \rangle f''(x') + \dots$$

Such an expansion is known as a moment expansion or the Kramer-Moyal expansion.

Now we take equation (243), plug it into (242), integrate by parts and divide by δt . Finally, we take the limit $\delta t \rightarrow 0$ and the result is the Fokker-Planck equation:

$$(246) \quad \frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} [F_1 P(x, t)] + \frac{1}{2} \frac{\partial^2}{\partial x^2} [F_2(x) P(x, t)]$$

where higher moments than 2 do not contribute because we have assumed $\delta x(t)^n = o(\delta t)$ for $n > 2$.

EXERCICE 4.2. For random diffusion

$$(247) \quad F_1 = \frac{\langle \Delta x \rangle}{\Delta t} = 0 \quad F_2 = \frac{\langle (\Delta x)^2 \rangle}{\Delta t} = \text{constant}$$

Check that the Fokker-Planck equation is nothing that the diffusion equation.

EXERCICE 4.3. We consider a particle in a force field $F(x)$

$$(248) \quad \frac{d}{dt}v(t) = \frac{1}{m}F(t) - \gamma v(t)$$

We assume that friction is so strong that we can neglect inertial terms. We also add a white noise $f(t)$, so the Langevin equation becomes

$$(249) \quad \frac{dx}{dt} = \frac{F(x(t))}{m\gamma} + f(t)$$

Compute the first moment

$$(250) \quad \langle \delta x(t) \rangle = F_1(x(t))\delta t$$

and show that one recovers the Schmoluchovski equation

2. The Fokker-Planck equation and the Langevin equation

Since the Langevin equation describes a stochastic process, it is better to think in terms of probability. As usual, we neglect the inertial term

$$(251) \quad \gamma \frac{dq}{dt} = F(q) + \eta(t)$$

We use a discrete time interval Δt and write

$$(252) \quad q(t + \Delta t) = q + \frac{F(q)}{\gamma}\Delta t + B + o(\Delta t)$$

where

$$(253) \quad \langle B \rangle = 0 \quad \text{and} \quad \langle B^2 \rangle = \Gamma \Delta t / \gamma^2$$

Then for any function $H(q)$ (be careful, $B = \langle B^2 \rangle = O(\Delta t)$, so we go to second order)

$$(254) \quad \begin{aligned} \langle H \rangle_{t+\Delta t} &= \langle H(q(t + \Delta t)) \rangle \\ &= \langle H(q + \frac{F(q)}{\gamma}\Delta t + B) + o(\Delta t) \rangle_t \\ &= \langle H(q) \rangle_t + \frac{\Delta t}{\gamma} \langle F(q)H'(q) \rangle_t + \langle BH'(q) \rangle_t + \frac{1}{2} \langle B^2 H''(q) \rangle_t + o(\delta t) \\ &= \langle H(q) \rangle_t + \frac{\Delta t}{\gamma} \langle F(q)H'(q) \rangle_t + \frac{\Gamma \Delta t}{2\gamma^2} \langle H''(q) \rangle_t + o(\delta t) \end{aligned}$$

It suffices now to integrate by parts

$$(255) \quad \langle F(q)H'(q) \rangle_t = \int dq P_t(q) F(q) H'(q) = - \int dq (P_t(q) F(q))' H(q)$$

to get the Fokker-Planck equation

$$(256) \quad \frac{\partial P_t(q)}{\partial t} = -\frac{1}{\gamma} \frac{\partial}{\partial q} [F(q)P_t(q)] + \frac{\Gamma}{2\gamma^2} \frac{\partial^2}{\partial q^2} P_t(q)$$

Here, We should derive the Fokker-Planck equation for the probability $P(x, v)$ in phase space (x, v) with a potential $U(x)$ which reads as follows

$$(257) \quad \frac{\partial P}{\partial t} = -\frac{\partial}{\partial x} [vP] + \frac{\partial}{\partial v} \left[\frac{\gamma v + \nabla U}{m} P \right] + \frac{\Gamma}{m^2} \frac{\partial^2 P}{\partial v^2}$$

which can be found in^{21?}. In the limit of large friction, this equation reduces to the simpler one.

EXERCICE 4.4. We have considered so far a free Brownian particle. What happens if the particle is subjected to an external force F ? If this force derives from a potential $\phi(x)$, the current is the sum of the usual drift term and a mobility term

$$(258) \quad J = -\mu P(x)\nabla\phi - D\nabla P$$

where the mobility μ is yet undetermined.

(1) Conservation of probability requires

$$(259) \quad \frac{\partial P}{\partial t} = -\nabla \cdot J$$

What is the equation for P ?

(2) Assume stationarity. What is the solution ?

(3) What happens if Einstein's relation holds ?

3. The Fokker-Planck equation and the diffusion equation

Let us apply the Fokker-Planck equation to the diffusion problem. For the earlier results, we have:

$$(260) \quad F_1(x) = F/\gamma M \quad F_2(x) = 2D$$

where F is the external force (which derives from a potential). Then, the Fokker Planck equation is

$$(261) \quad \frac{\partial P}{\partial t} = -u\frac{\partial P}{\partial x} + D\frac{\partial^2 P}{\partial x^2}$$

where u is the velocity. We can solve this equation by Galilean transformation (do it ! $y = x - ut$) or by Fourier transforming :

$$(262) \quad P(x, t) = \int d\tilde{q} e^{iqx} \tilde{P}(q, t) \quad \tilde{P}(q, t) = \int dx e^{-iqx} P(x, t) \quad \tilde{q} = q/(2\pi)$$

We get:

$$(263) \quad \frac{\partial}{\partial t} \tilde{P}(q, t) = -(Dq^2 + iqu)\tilde{P}(q, t)$$

with solution

$$(264) \quad \tilde{P}(q, t) = e^{-Dq^2 t} e^{-iqut} \tilde{P}(q, 0)$$

Going back to the real space

$$(265) \quad P(x, t) = \int d\tilde{q} e^{-Dq^2 t} e^{-iqut} \int dx' e^{-iqx'} P(x', 0) = \int dx' K(x - x', t) P(x', 0)$$

where

$$(266) \quad K(x, t) = \frac{1}{[4\pi Dt]^{d/2}} e^{-(x-x')^2/4Dt}$$

is the diffusion kernel ($d = 1$). The diffusion kernel solves the equation of motion for a delta initial condition. Eq. (265) gives the solution for arbitrary initial conditions with the following properties:

- The center of the distribution moves with velocity u due to the force. This is the drift.
- The distribution broadens with time due to diffusion.

4. Boundary conditions for the Fokker-Planck equation

We consider the diffusion problem. The Fokker-Planck equation is an equation for the full probability $P(\mathbf{x}, t)$. It is sometimes useful to interpret $P(\mathbf{x}, t)$ as the concentration $c(\mathbf{x}, t)$ itself (since P is a normalized histogram, i.e. the number of molecules at position \mathbf{x} divided by the total number of molecules). So, we can often make the change of variable

$$(267) \quad P(\mathbf{x}, t) \leftrightarrow c(\mathbf{x}, t)$$

to get more physical insights, since $c(\mathbf{x}, t)$ has the meaning of a probability.

Eq. (261) is, however, a partial differential equation. For this kind of problem, it makes no sense to find a solution without specifying the boundary conditions. Assume that we are interested in solving (261) on a domain $\Omega = [0, L]^d$. Popular boundary conditions are as follows:

- (1) One must specify the initial conditions at $t = 0$ over the domain of interest.
- (2) One must specify "something" (the value of P or the current) at the boundary of this domain.

Changing one of these conditions completely alters the solution and the physical consequences ! Here are some of the most popular boundary conditions for stationary solutions:

- (1) We fix the values of $P(\mathbf{x})$ on the boundaries of Ω (i.e. $P(0) = P(L)$ are given). If $P(\mathbf{x} \in \delta\Omega) = 0$, the boundaries are absorbing. All the walkers crossing the boundaries disappear (think of a random walk on a roof: if you hit the border, you get out of the system !).
- (2) We fix the outward current $dP/d\hat{\mathbf{n}}^2$. If $dP/d\hat{\mathbf{n}} = 0$, there is no current. The boundaries are perfectly reflecting walls.
- (3) We can also use a mixed boundary condition where the current is proportional to the probability (or the concentration):

$$(268) \quad k_{on}P(\mathbf{x}) = -DdP/d\hat{\mathbf{n}} \text{ , } \mathbf{x} \in \delta\Omega$$

where k_{on} is a constant. This type of boundary condition is called a radiative boundary condition and is useful to define the rates of chemical reactions (an example is given below for the trap problem and this boundary condition will be used later for diffusion controlled chemical reactions).

REMARK. It is common to work in different coordinate systems. In polar coordinates, we have:

$$(269) \quad \begin{aligned} \Delta f &= \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial f}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} & 2\text{D} \\ \Delta f &= \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial f}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial f}{\partial \theta} \right) \\ &\quad + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} & 3\text{D} \end{aligned}$$

EXAMPLE 4.1. The physical process of a trapping reaction is simple. Whenever a diffusing particle hits a trap, it is permanently trapped with some probability k_{on} . We assume that there is an infinite domain containing an initially uniform distribution of noninteracting diffusing particles which may react with a fixed trap of size a . The evolution of the concentration $c(\mathbf{x}, t)$ is given by the diffusion equation

$$(270) \quad \frac{\partial c}{\partial t} = D\Delta c$$

² $\hat{\mathbf{n}}$ is the outward normal at the boundary of Ω and $dP/d\hat{\mathbf{n}} = \hat{\mathbf{n}} \cdot \nabla P$.

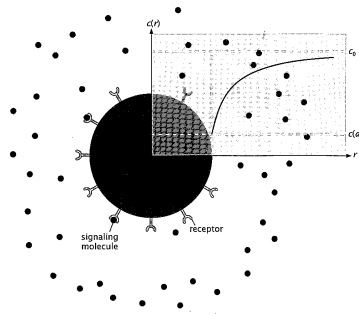


FIGURE 2. An absorbing sphere for a solute diffusing in the bulk. The concentration of solute decreases in the vicinity of the sphere. This depletion zone is characteristic of problem controlled by diffusion.

subject to the initial condition $c(\mathbf{x}, 0) = c_0$. The boundary conditions are $c(\infty, t) = c_0$ and, at the trap surface

$$(271) \quad D \left. \frac{\partial c}{\partial r} \right|_{r=a} = k_{on} c(r = a, t)$$

The latter condition is a radiative boundary condition. It says that the outgoing flux of particles leaving the system (i.e. particles which are trapped and thus leave the system) is proportional to the concentration of particles at the boundary of the trap. The chemical constant k_{on} is therefore the analog of a chemical rate. If $k_{on} = \infty$ the trap is perfect, otherwise the trap is imperfect.

Let us concentrate on 2D. A steady-state solution of this problem in cylindrical coordinate (r, θ) must have the form,

$$(272) \quad c_{ss}(r, \theta) = (A + B \ln r) f(\theta)$$

Since the boundary condition at infinity demands that $B = 0$, it is impossible to obtain a steady-state solution for any infinite trap (with $k_{on} > 0$). As a consequence, all particles are progressively trapped and $\lim_{t \rightarrow \infty} c(\mathbf{x}, t) = 0$. In 3D a steady-state solution is possible. The absence of steady-state solutions in 2 dimensions is due to the fact that random walks are recurrent in 2D but transient in 3D.

EXERCICE 4.5. Consider a perfect adsorbing sphere of radius a^3 . A molecule is initially located at a distance r_0 of the center of the sphere. In this problem, we will ask this simple question: What is the probability $p(a, r_0)$ for the molecule to be adsorbed? It turns out that the answer is quite simple. It is

$$(273) \quad p(a, r_0) = \frac{a}{r_0}$$

and not as a^2/r^2 as if the movement were ballistic (in that case, the result would be proportional to the cross-section). To answer to this problem, consider a sphere of radius $r_0 > a$ where the concentration is maintained at $c = c_m$. Assume that there is a second sphere of radius $b > r_0$ where the concentration is maintained at $c = 0$ (adsorbing conditions).

- (1) Solve the stationary diffusion equation in the two regions with the appropriate boundary conditions. To solve this equation, pose $u(r, t) = rc(r, t)$ in the diffusion equation where r is the radial coordinate. What is the equation for $u(r, t)$?
- (2) Compute the current at $r = a$ and $r = b$.
- (3) Compute the total flux of particles through the spheres a and b .
- (4) What is the probability that a random walk starting at r_0 bumps into a ? Same question for b .
- (5) Let $b \rightarrow \infty$ and recover (273).

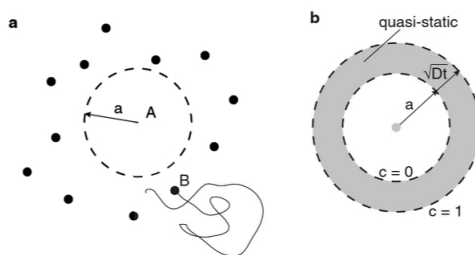


FIGURE 3. diffusion-limited reaction rate. (a) Diffusing molecules B in a neighborhood of a fixed target molecule A with reaction radius a . In (b) Quasi-static approximation for calculating time-dependent reaction rate.

EXERCICE 4.6. Consider the situation schematized in Fig. 1. Assume that the concentration at $r \rightarrow \infty$ is maintained at c_0 ³. The sphere of radius a is covered by sensors with surface density σ . The rate of uptake of solute molecules per unit surface is given by

$$(274) \quad \frac{dn}{dt} = \sigma k_{on} c(a)$$

This equation defines k_{on} as the usual kinetic rate in chemical reaction.

- (1) If M is the total number of receptors, give M as a function of σ .
- (2) Show that solution of the 3- d diffusion equation with symmetry of revolution is given by $c(r) = \beta + \alpha/r$.
- (3) Using mass conservation, show

$$(275) \quad -4\pi r^2 J(r) = M k_{on} c(a)$$

- (4) Use the last equation to compute the concentration as

$$(276) \quad c(r) - c(a) = \frac{M k_{on} c(a)}{4\pi D} \left(\frac{1}{a} - \frac{1}{r} \right)$$

- (5) Show

$$(277) \quad c(a) = \frac{c_0}{1 + M k_{on} / (4\pi D a)}$$

- (6) Plot $c(r)$.
- (7) Deduce that the net adsorption rate is

$$(278) \quad k = \frac{4\pi D a M k_{on}}{4\pi D a + M k_{on}}$$

- (8) Investigate the two limits of a perfect adsorber, $k_{on} \rightarrow \text{infy}$, and of a bad adsorber, $k_{on} \rightarrow 0$. Conclude that the net adsorption rate can be written as

$$(279) \quad \frac{1}{k} = \frac{1}{k_{on}} + \frac{1}{k_D}$$

where $1/k_D$ is a diffusion time which depends on the diffusion constant. Thus, our boundary condition together with the diffusion equations set two characteristic time scales. This is in contrast with the usual condition of perfect adsorption with only one time scale.

EXERCICE 4.7. We consider the bimolecular reaction



³The concentration is often expressed in Molars M with 1 Molar = 1000 moles / m^3

for which the concentrations usually evolve according to the law of mass action

$$(281) \quad \frac{d[AB]}{dt} = k[A][B]$$

Usually, the on rate k is independent of t . This will not be the case here. We assume that an A molecule and a B molecule react immediately to form a complex AB when they encounter each other within a reaction radius, so that the speed of reaction is limited by their encounter rate via diffusion. We consider the case of a spherical target A of radius a ($d = 3$). One way to formulate the problem is an idealized first passage process, in which the A molecule is fixed while the B molecule diffuse around. Let $c(r, t)$ be the concentration of B molecules.

The initial conditions and the boundary conditions are as follows

- (i) $c(r, t = 0) = c_0$ for $r > a$.
 - (ii) $c(r = a, t) = 0$, since there is an uptake of B molecules at $r = a$.
 - (iii) $c(r \rightarrow \infty) = c_0$ for a continuous supply of B molecules at infinity to counterbalance the rate of uptake of B at $r = a$.
- (1) Define $u(r, t) = ru(r, t)$. What is the equivalent-diffusion equation for $u(r, t)$?
 - (2) To solve this equation with the appropriate boundary conditions for $u(r, t)$, introduce the Laplace transform of $u(r, t)$

$$(282) \quad \tilde{u}(r, s) = \int_0^\infty dt u(r, t) \exp\{-st\}$$

Show

$$(283) \quad s\tilde{u}(r, s) - rc_0 = D\tilde{u}''(r, s)$$

(3) Show

$$(284) \quad \tilde{u}(r, s) = \frac{c_0}{s} \left[r - a \exp\left\{ \left[-(r-a)\sqrt{s/D} \right] \right\} \right]$$

(4) We assume that the inverse Laplace transform of

$$s^{-1} \left[1 - \exp\left\{ \left[-r\sqrt{s/D} \right] \right\} \right]$$

is

$$\operatorname{erf}(r\sqrt{4Dt})$$

where

$$(285) \quad \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-r^2} dr$$

where erf is the error function, see Fig. 4. Show:

$$(286) \quad c(r, t) = c_0 \left(1 - \frac{a}{r} \right) + \frac{ac_0}{r} \operatorname{erf} \left[\frac{r-a}{\sqrt{Dt}} \right]$$

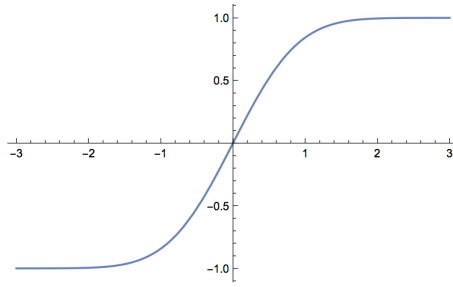
(5) Show that the time-dependent flux is

$$(287) \quad \phi = 4\pi a^2 D c_0 \left(1 + \frac{a}{\sqrt{\pi Dt}} \right)$$

(6) Make the $t \rightarrow \infty$ limit. Show $k = 4\pi a^2 D$. Remark that the rate k depends on the diffusion constant D . Conclude that the diffusion-limited rate is an upper bound of the true rate.

EXERCICE 4.8. The time-dependent reaction rate can be calculated using the quasi-static approximation. Because of its simplicity and general applicability, we detail the calculation in arbitrary dimension d .

We divide the region exterior to the adsorbing sphere into two zones. The "near" and the complementary "far" zone.

FIGURE 4. Plot of the function $\text{erf}(z)$.

- (1) In the near zone, $a < r \leq a + \sqrt{Dt}$, it is assumed that diffusing particles have sufficient time to explore the domain before being adsorbed by the target. The concentration is almost quasi static. What changes with time is the locus of the boundary which increases as \sqrt{Dt} .
- (2) In the complementary far zone, it is assumed that the probability of being adsorbed is negligible, since the particles are unlikely to diffuse more than \sqrt{Dt} in a time t . Thus, $c(r) \approx c_0$ in the far zone.

(1) Show that the static solution in $2d$ is $c(r) = A + B \ln r$.

(2) Match the solution to the boundary condition $c(a) = 0$ and $c(a + \sqrt{Dt}) = c_0$ and show

$$(288) \quad c(r, t) \approx \frac{c_0 \ln(r/a)}{\ln(\sqrt{Dt}/a)} \quad t \gg 1$$

(3) Compute the time-dependent flux

$$(289) \quad J(t) = 4\pi a^2 D \left. \frac{\partial c}{\partial r} \right|_{r=a}$$

(4) How J depends on the size of the adsorbing sphere? Conclude.

5. The Peclet number

The Peclet number is a dimensionless ratio. It is the ratio of two rates. The first rate is the rate at which a particle moves some distance λ due to being carried along by the flow of the liquid. The second rate is the rate at which it diffuses the same distance λ . Here λ is whatever distance we are interested in. So, the Peclet number is defined to be

$$(290) \quad \text{Pe} = \frac{R_1}{R_2}$$

where

- (1) R_1 = Rate at which flow carries molecules a distance λ .
- (2) Rate at which diffusion carries molecules a distance λ .

If the flow speed is u , the time taken to transport a molecule over a distance λ is λ/u . The rate is therefore u/λ . In contrast, the time to diffuse a distance λ is λ^2/D . As a result, the rate is D/λ^2 . Thus,

$$(291) \quad \text{Pe} = \frac{u\lambda}{D}$$

which depends on the length scale λ . On small scales, diffusion is faster than flow. On macroscopic scale, flow is faster. For E. Coli looking for nutrients, $D \approx 10^{-5} \text{cm}^2/\text{s}$ (for phosphate molecules), $u = 30 \mu\text{m}/\text{s}$ (speed of E. coli), $\lambda = 2 \mu\text{m}$ (size), $\text{Pe} = 0.02$.

EXERCICE 4.9. We consider the bimolecular reaction



for which the concentrations usually evolve according to the law of mass action

$$(293) \quad \frac{d[AB]}{dt} = k[A][B]$$

Usually, the on rate k is independent of t . This will not be case here. We assume that an A molecule and a B molecule react immediately to form a complex AB when they encounter each other within a reaction radius, so that the speed of reaction is limited by their encounter rate via diffusion. We consider the case of spherical target A of radius a ($d = 3$). One way to formulate the problem is an idealized first passage process, in which the A molecule is fixed while the B molecule diffuse around. Let $c(r, t)$ be the concentration of B molecules.

The initial conditions and the boundary conditions are as follows

- (i) $c(r, t = 0) = c_0$ for $r > a$.
 - (ii) $c(r = a, t) = 0$, since there is an uptake of B molecules at $r = a$.
 - (iii) $c(r \rightarrow \infty) = c_0$ for a continuous supply of B molecules at infinity to counterbalance the rate of uptake of B at $r = a$.
- (1) Define $u(r, t) = ru(r, t)$. What is the equivalent-diffusion equation for $u(r, t)$?
 - (2) To solve this equation with the appropriate boundary conditions for $u(r, t)$, introduce the Laplace transform of $u(r, t)$

$$(294) \quad \tilde{u}(r, s) = \int_0^\infty dt u(r, t) \exp\{-st\}$$

Show

$$(295) \quad s\tilde{u}(r, s) - rc_0 = D\tilde{u}''(r, s)$$

(3) Show

$$(296) \quad \tilde{u}(r, s) = \frac{c_0}{s} \left[r - a \exp\left\{-\left[(r-a)\sqrt{s/D}\right]\right\} \right]$$

(4) We assume that the inverse Laplace transform of

$$s^{-1} \left[1 - \exp\left\{-r\sqrt{s/D}\right\} \right]$$

is

$$\operatorname{erf}(r\sqrt{4Dt})$$

where

$$(297) \quad \operatorname{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-r^2} dr$$

where erf is the error function, see Fig. 4. Show:

$$(298) \quad c(r, t) = c_0 \left(1 - \frac{a}{r} \right) + \frac{ac_0}{r} \operatorname{erf} \left[\frac{r-a}{\sqrt{Dt}} \right]$$

(5) Show that the time-dependent flux is

$$(299) \quad \phi = 4\pi a^2 D c_0 \left(1 + \frac{a}{\sqrt{\pi Dt}} \right)$$

(6) Make the $t \rightarrow \infty$ limit. Show $k = 4\pi a^2 D$. Remark that the rate k depends on the diffusion constant D .

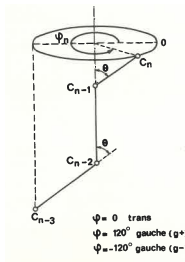


FIGURE 5. Three successive monomers of a flexible polymer chain. The angle θ is fixed, but the upper monomer can rotate by an angle ϕ . The three segments are coplanar when $\phi = 0$ (trans-configuration) and this configuration corresponds to the true minimum energy configuration (see Fig. 6). The two gauche configurations are obtained when $\phi = \pm 120^\circ$.

6. Diffusion in a force field

We have considered so far a free brownian particle. What happens if the particle is subjected to an external force F ? If this force derives from a potential $\phi(x)$, the current is the sum of the usual drift term and a mobility term

$$(300) \quad J = -\mu P(x)\nabla\phi - D\nabla P$$

where the mobility μ is yet undetermined.

Conservation of probability requires

$$(301) \quad \frac{\partial P}{\partial t} = \nabla \cdot J$$

and translates into

$$(302) \quad \frac{\partial P}{\partial t} = \frac{\partial}{\partial x} [-\mu P(x)\nabla\phi - D\nabla P]$$

Assuming stationarity

$$(303) \quad \begin{aligned} -\mu P(x)\nabla\phi - D\nabla P &= 0 \\ \text{or } \frac{dP}{dx} &= -\frac{\mu}{D} \frac{d\phi}{dx} P(x) \end{aligned}$$

whose solution is given by

$$(304) \quad P(x) = \frac{1}{Z} e^{-\frac{\mu}{D}\phi(x)}$$

where Z is some normalization constant. Remark that we have made no statement concerning equilibrium and we have only hypothesized that the process is stationary. If the process at equilibrium, we recover the Boltzmann's distribution if the Einstein relation holds

$$(305) \quad \frac{\mu}{D} = \frac{1}{kT}$$

Although this derivation is general, it is interesting to state clearly the hypotheses tacitly made to get (576). Since the probability $P(x, t)$ does depend only on the position and not on the speed, we have tacitly assumed that the speed relaxes very fast to some local equilibrium. Actually, (576) is only valid in the strong friction limit.

REMARK. In classical mechanics particles at rest occupy minimum energy states. Here, due to thermal fluctuations, the particle has a finite probability $p(U_i)$ to be in a state of energy U_i above the minimum energy state. Assuming thermal equilibrium, the probability $p(U_i)$ is

$$(306) \quad p(U_i) = \frac{1}{Z} e^{[-U_i/kT]}$$

where $Z = \sum_i \exp\{-U_i/kT\}$ so that $\sum_i p_i = 1$.

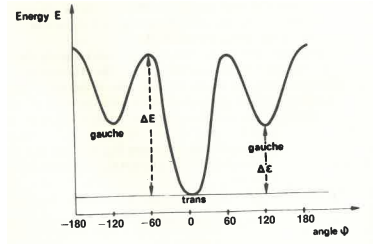


FIGURE 6. Potential profile as a function of the angle ϕ defined in Figure 5. The potential barriers are small with respect to the thermal energy kT , so that the polymer adopts the three configuration with almost equal probability

Consider a molecule with two conformational states with reaction coordinate x . The probability to be in state 1 is $p_1 = 1/Z \exp\{-U_1/kT\}$ ($1 \rightleftharpoons 2$). We have

$$(307) \quad \frac{p_1}{p_2} = \exp\{[-(U_1 - U_2)/kT]\}$$

At very low temperature, $p_1/p_2 \gg 1$ so that the only observable state is actually the minimum energy state. At finite temperature, however, state 2 is observable with a finite probability. This property is crucial for flexible polymer chains. The energy between successive groups is a function of one angle ϕ . The potential barrier $\Delta\epsilon$ between the two cis and the trans configuration is small, so that the chain is a flexible coil.

EXERCICE 4.10. Application : The Debye-Hückel theory. Interactions that occur between electrical charges fixed at surface and those which are free in solution play an important role in colloidal systems.

We consider negatively charged wall that is infinite in the x and y direction. The distance from the charged surface is z . The charge density on the wall is σ . Let $\Phi(z)$ be the electrical potential. Because of Gauss's law

$$(308) \quad \frac{d\Phi}{dz} = -\frac{\sigma}{\epsilon_0\epsilon_r}$$

The adjacent solution contains positively charged and negatively charged ions in equal quantity with homogeneous density c_0 when $\phi(z) = 0$. We assume that the ions bare a charge $\pm Ze$.

- (1) Calculate $c_{\pm}(z)$ as a function of $\Phi(z)$.
- (2) Write Gauss's theorem in the solution

$$(309) \quad \Delta\Phi(z) = -\frac{\rho(x)}{\epsilon_0\epsilon_r}$$

and show

$$(310) \quad \Delta\Psi(z) = -\frac{2eZc_0}{\epsilon_0\epsilon_r} \sinh\left[\frac{Ze\Psi(z)}{kT}\right]$$

- (3) Without solving this equation, show that there exists a characteristic length scale l_p which enters into the problem.
- (4) Assume

$$(311) \quad \sinh\left[\frac{Ze\Psi(z)}{kT}\right] \approx \frac{Ze\Psi(z)}{kT}$$

and solve the differential equation. What is the physical interpretation of l_p ?

- (5) Assume that the ions come from the dissociation of NaCl (0.1 M). What is the order of magnitude of l_p ?

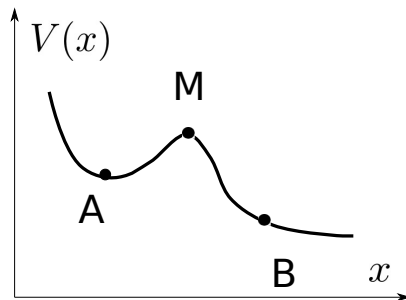


FIGURE 7. Potential profile for a brownian particle. The effect of a force applied to the equivalent chemical bond is to lower the potential barrier.

7. A First-passage problem: The escape over a potential barrier

What is a first passage probability ? This is the probability that a diffusing particle first reaches a specified site at a specified set of time. This problem has very large applicability.

We consider a brownian particle in a field of force. The force is the derivative of a potential $V(x)$ and to want the calculate the probability to escape from a metastable state. We will assume that the barrier is sufficiently large with respect to kT so that the particule will neither come back after having passed over the barrier. This problem is a first passage problem.

The x coordinate is a reaction coordinate. For a chemical reaction, x corresponds to the relative distance between two molecules A and B. When the relative distance between the two molecules is small, the two molecules form a chemical complex. The translocation of the particle over the barrier is, therefore, equivalent to the dissociation of the complex A–B.

If we assume first order kinetics, we describe the reaction as

$$(312) \quad \frac{d[A-B]}{dt} = -k_{\text{off}} [A-B]$$

where k_{off} has the dimension of 1/time. This is the characteristic time one has to wait before the chemical bond break spontaneously because of thermal fluctuations. In the Kramers problem, this time is the first passage time over the barrier.

This problem arises in countless number of systems modeling escape from a metastable equilibrium state driven by thermal fluctuations. The common theme underlying the description of escape processes is based on Brownian motion. In adopting this scheme, the motion of the principal degrees of freedom is treated explicitly while the interaction with other degrees of freedom, including those of the heat bath(s) coupled to the system of interest, are represented by frictional forces and noise; i.e., the deterministic equations governing the dynamics of the escape process must be complemented by random forces. These random forces present the key input allowing the system to get away from preferred states of local stability.

To describe this process, we will take the strongly overdamped limit where inertial terms can be neglected. We write the Smoluchowski equation as

$$(313) \quad \frac{\partial P}{\partial t} + \frac{\partial J}{\partial x} = 0$$

where (

$$(314) \quad J = -\frac{1}{\mu} P(x) \frac{dV}{dx} - D \frac{dP}{dx}$$

In what follows, we assume that the barrier is large with respect to kT

$$(315) \quad V_M - V_A \gg kT$$

and we compute the off-rate from the current of particle escaping from A as

$$(316) \quad k_{off} = \frac{J}{n_A}$$

where n_A is the number of particles in A . The current is small, so n_A does not vary. k_{off} has the right dimension, since $k_{off} = 1/\text{time}$.

In a stationary regime, the current is constant

$$(317) \quad J = \text{constant}$$

independent of the reaction coordinate x , since all particles which can escape will neither come back. Using (314) we obtain:

$$(318) \quad \frac{\partial V}{\partial x} P(x) + kT \frac{\partial P}{\partial x} = -\mu J$$

The general solution of this equation is

$$(319) \quad \begin{aligned} P(x) &= a(x) e^{-V(x)/kT} \\ a(x) &= \frac{J\mu}{kT} \int_x^{x_0} dx' e^{+V(x')/kT} \end{aligned}$$

where x_0 is a constant of integration to be determined by the boundary conditions.

These are as follows:

- (1) n_A is known because the number of particles near A is given by the Boltzmann's distribution (there is only a small number of particles which can escape). Note N_A is a neighborhood of A

$$(320) \quad \begin{aligned} n_A &= \int_{N_A} dx P(x) = \int_{N_A} dx a(x) e^{-V(x)/kT} \\ &\simeq a(x_A) e^{-V_A/kT} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}m\omega_A^2 y^2} dy \quad \text{with } \omega_A^2 = V''(x_A)/kT > 0 \end{aligned}$$

where $V(x) = V_A + \dots$ near the metastable minimum A (see Comment 7).

- (2) We define an arbitrary point B at the right of the barrier. The exact locus of B will not matter. We take $P(x = x_B) = 0$ at B as the equivalent condition for the particle neither to come back: B is a sink and the probability to find the particle at B is zero. We have, therefore, $x_0 = x_B$, so that $P(x_B) = 0$.

From (319) we get the current

$$(321) \quad J = \frac{kT}{\mu} \frac{a(x)}{\int_x^{x_B} e^{V(y)/kT} dy}$$

in particular for $x = x_A$

$$(322) \quad J = \frac{kT}{\mu} \frac{a(x_A)}{\int_{x_A}^{x_B} e^{V(y)/kT} dy}$$

But

$$(323) \quad \int_{x_A}^{x_B} e^{V(y)/kT} dy = e^{V_M/kT} \int_{-\infty}^{+\infty} e^{-\frac{1}{2}\omega_M^2 y^2} dy \quad \omega_M^2 = |V''(x_M)|/kT > 0$$

since $V_M \gg V_A$ and $V_M \gg V_B$. Taking the ratio, we get the well-known Arrhenius factor (Kramers, 1940)

$$(324) \quad k_{off} = \frac{J}{n_A} \simeq \frac{kT}{\mu} \frac{\omega_A \omega_M}{2\pi} e^{-(V_M - V_A)/kT}$$

In this regime, the rate of escape is limited by collisions when the particle is near the top of the barrier. The frictional forces imply that a typical reaction path does not go directly from

one side of the well to the neighboring well but rather may cross the barrier region many times, tottering back and forth before escaping.

REMARK. We want to evaluate the integral

$$(325) \quad I = \int_{-\infty}^{+\infty} dx g(x) e^{\lambda f(x)}$$

where $\lambda \gg 1$ and where the function $f(x)$ has a maximum. A useful approximation is the saddle-point method. Since $f(x)$ possesses a maximum at some point x_0 , the dominant contribution to the integral comes from a domain centered around x_0 . We Taylor expand $f(x)$ to second order

$$(326) \quad f(x) = f(x_0) + \frac{1}{2}(x - x_0)^2 f''(x_0) + \dots$$

and

$$(327) \quad \begin{aligned} I &= g(x_0) e^{\lambda f(x_0)} \int_{-\infty}^{+\infty} dx e^{\frac{1}{2}(x-x_0)^2 f''(x_0)} \\ &= \sqrt{\frac{2\pi}{|f''(x_0)|}} g(x_0) e^{\lambda f(x_0)} \quad \lambda \gg 1 \end{aligned}$$

If $f(x)$ possesses a minimum, take $\lambda < 0$

$$(328) \quad I \approx \sqrt{\frac{2\pi}{|f''(x_0)|}} g(x_0) e^{\lambda f(x_0)} \quad |\lambda| \gg 1$$

EXERCICE 4.11. Use this approximation for the integral representation of $n!$

$$(329) \quad (n+1)! = \int_0^{\infty} dt t^{n-1} e^{-t}$$

EXERCICE 4.12. Path integral method. The Langevin equation can be written as

$$(330) \quad f(t) = \mu \frac{dx}{dt} + \frac{dV}{dx}$$

We know that the random force $f(t)$ is drawn from a Gaussian distribution

$$(331) \quad P[f(t)] \propto \exp\left\{ \left[-\frac{1}{4\mu kT} \int dt f(t)^2 \right] \right\}$$

- (1) Why Eq. (330) is valid ?
- (2) Explain formula (331).
- (3) Show that the probability to observe a trajectory is

$$(332) \quad P[x(t)] = \mathcal{J} \exp\left\{ \left[-\frac{1}{4\mu kT} \int dt \left(\mu \frac{dx}{dt} + \frac{dV}{dx} \right)^2 \right] \right\}$$

where \mathcal{J} is independent of T (don't try to calculate \mathcal{J}). At low temperature, the exponential will dominate and we will drily ignore thereafter \mathcal{J}

CHAPTER 5

THE MASTER EQUATION

1. Introduction

To obtain from a microscopic description an entropy that increases with time, one must adopt a "coarse grained" definition of the phase space: the phase space is assumed to be partitioned into small cells $i = (p, q)$ and we adopt a "myopic" point of view where the only information we have is the probability $P_i(t)$ of finding the system in cell i at time t . The Master equation gives how $P_i(t)$ evolves with time.

2. Coarse-graining the phase space and the problem of entropy

Let us consider system with an Hamiltonian $H(\mathbf{p}, \mathbf{q})$. We will study its dynamics in the phase space (\mathbf{p}, \mathbf{q}) . Under Hamiltonian dynamics, the system will inspect different configurations. In the microcanonical ensemble, the probability density to observe the system at a particular point (\mathbf{p}, \mathbf{q}) in phase is given by the density $\rho(\mathbf{p}, \mathbf{q}, t)$ which can depend on t , since the Hamiltonian can depend on t .

As a first guess, let us define the entropy as

$$(333) \quad S = - \int_{\Omega(E)} d\Omega \rho \ln \rho$$

where $\Omega(E)$ is the number of configurations compatible with an energy E .

This definition seems to be correct, since for $\rho = 1/\Omega(E)$ (all microstates with equal energy E have equal probability), we get the Boltzmann's result (within the multiplicative constant k_B):

$$(334) \quad S = \ln \Omega(E)$$

However, our guess (334) cannot be correct. Liouville's theorem states that the volume in phase space is conserved. This means that the number of configurations in a small volume will stay constant with time (although the shape of the volume can be widely deformed under the dynamics). If ρ is constant, then the entropy will stay constant. This contradicts what we know from thermodynamics and we have to do something else¹.

To get out, we will coarse-grain the phase space to do probability. Each elementary cell i has some volume. When the system is in cell i , we don't know exactly what are the momentum \mathbf{p} and the position \mathbf{q} . Two systems initially in the same cell i can therefore jump into two different cells k and l at latter time, since their initial conditions differ. This is the case for a chaotic systems, since a slight change in initial condition leads to very different trajectories.

¹The increase of entropy is known as the Boltzmann's H-theorem.

We shall, therefore, assume that during a time interval dt the system jumps at random from one cell to another according to some kind of rate equation:

$$(335) \quad \text{Proba}(dt)_{j \rightarrow i} = dt \times W_{j \rightarrow i} \times \text{Proba}(\text{to be in cell } j)$$

where $W_{j \rightarrow i}$ is the conditional probability to jump for j to i (since to jump from cell j to cell i , one has to be first in cell j). We note that we always assume that the processes are of Markov type

$$(336) \quad W_{j \rightarrow i} \text{ is the equivalent of a kinetic rate coefficient in chemical physics. If we note}$$

$$W_{j \rightarrow i} = W_{i,j}$$

the $W_{i,j}$'s define a matrix and are conditional probabilities.

We will see shortly that our basic assumption is to state that the system evolves according to the Master equation

$$(337) \quad \frac{dP_i}{dt} = \sum_j (W_{ij}P_j - W_{ji}P_i)$$

where the entropy is defined as

$$(338) \quad S = - \sum_i P_i \ln P_i$$

This definition entails that the entropy can only increase $dS/dt > 0$.

REMARK. In general, Boltzmann approach to phase space is based on three properties:

- (1) Ergodicity: A system is ergodic when for almost all initial conditions, the trajectory is dense in phase space and the time average over a trajectory is equal to an average over phase space;
- (2) Chaos: the dynamics is in general chaotic, i.e., very close initial conditions tend to grow exponentially fast;
- (3) A very high-dimensional space and almost everywhere constant functions (geometry in high-dimensional space is weird).

3. Stochastic approach to chemical kinetics: The master equation

When dealing with macroscopic systems we can neglect fluctuations and work directly with average quantities. For small systems fluctuations are important and it is crucial to determine the time evolution of the whole probability distribution. This time evolution is given by an equation known as the master equation. We will study the master equation in the following chapter, but it is useful to give first an example of a master equation for a simple system. We consider a simple chemical reaction.

Let us consider the unimolecular reaction which occurs particularly in radioactive decay processes



where k is usually defined as a rate constant. To proceed with the master equation, we reinterpret the coefficient k as the probability per unit time that a A molecule decays into a B molecule. This means that the probability for a A molecule to decay into a B molecule during the time interval Δt is $k\Delta t$.

The random variable is the number $n_A(t)$ in the system at time t . The stochastic model is then completely defined by the following assumptions:

- (1) The probability of a transition $n_A \rightarrow n_A - 1$ in the time interval $[t, t + \Delta t]$ is $kn_A\Delta t = O(\Delta t)$.
- (2) The probability of a transition $n_A \rightarrow n_A - j$ with $j > 1$ is at least $O(\Delta t^2)$, since the time interval is considered to be small enough that one molecule undergoes a transition.
- (3) The reverse reaction occurs with probability 0.

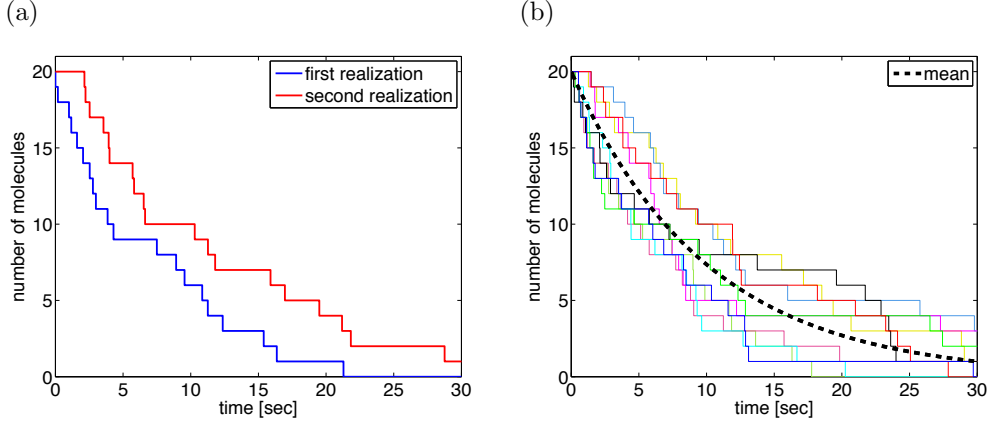


FIGURE 1. Stochastic simulation of the chemical reaction $A \rightarrow B$ with rate constant $k_a = 0.1 \text{ sec}^{-1}$. The left-hand figure shows 2 realizations. The right-hand figure shows different realizations with the mean $n_A(t=0)e^{-k_a t}$.

We calculate the probability to observe n_A molecules at time t by comparing $P(n_A, t + dt)$ with $P_A(n_A, t)$. A detailed balance gives :

$$(340) \quad P(n_A, t + \Delta t) = k(n_A + 1)\Delta t P(n_A + 1, t) + (1 - kn_A\Delta t)P(n_A, t)$$

since between t and $t + \Delta t$ only two events can happen :

- (1) One of the A molecules decays (first term).
- (2) Nothing happens (second term).

The probability that nothing happens is therefore $1 - kn_A\Delta t$ since the total must sum up to one. By the standard procedure of transposing from the right-hand side, dividing by Δt , and then taking the limit $\Delta t \rightarrow 0$, one gets the differential-difference equation:

$$(341) \quad \frac{\partial P(n_A, t)}{\partial t} = k(n_A + 1)P(n_A + 1, t) - kn_AP(n_A, t)$$

Eq. (341) being an equation for the probability, it is a master equation.

We solve this equation by means of the generating function that we define as:

$$(342) \quad G(s, t) = \sum_{n_A \geq 0} s^{n_A} P(n_A, t)$$

This is simply a kind of Laplace transform but for discrete variables, since replacing the discrete sum by an integral in (342) is the definition of a Laplace transform.

From (341) we get using $n_A = n$:

$$(343) \quad \frac{\partial G}{\partial t} = \sum_{n \geq 0} s^n \frac{dP(n, t)}{dt} = \sum_{n \geq 0} s^n k(n + 1)P(n + 1, t) - k \sum_{n \geq 0} ns^n P(n, t)$$

But

$$(344) \quad \begin{aligned} \sum_{n \geq 0} (n + 1)s^n P(n + 1, t) &= \frac{\partial}{\partial s} g(s, t) \\ \sum_{n \geq 0} ns^n P(n, t) &= s \sum_{n \geq 0} ns^{n-1} P(n, t) = s \frac{\partial}{\partial s} g(s, t) \end{aligned}$$

Therefore,

$$(345) \quad \frac{\partial G}{\partial t} = k(1 - s) \frac{\partial G}{\partial s}$$

which is a partial linear differential equation. The solution of this equation can be found using the general method of Characteristics. For any initial condition $n = n_0$ at $t = 0$ the sum in (342) is finite. The solution of this, subject to the initial condition $G(s, 0) = s^{n_0}$, is

$$(346) \quad G(s, t) = [1 + (s - 1)e^{-kt}]^{n_0}$$

REMARK. The method of characteristics is a general method for solving linear partial differential equations. Consider

$$(347) \quad a(x, t) \frac{\partial u}{\partial t} + b(x, t) \frac{\partial u}{\partial x} + f[u(x, t), x, t] = 0$$

with the initial condition $u(x, t = 0) = u_0(x)$. In the method of characteristics, one tries to find a relationship between x and t so that along the curve $x(t)$ the equation for u simplifies.

To go about this, we try to find general trajectories of both $x(s)$ and $y(s)$ as functions of a new coordinate s

$$(348) \quad \frac{du(x(s), t(s))}{ds} = \frac{dx}{ds} \frac{\partial u}{\partial x} + \frac{dt}{ds} \frac{\partial u}{\partial t}$$

Therefore, along s , the rate of change du/ds is identical with (347) provided

$$(349) \quad \frac{dt}{ds} = a(x(s), t(s)) \quad \text{and} \quad \frac{dx}{ds} = b(x(s), t(s))$$

often, $a(x, t) = 1$, and we can simply take $t = s$. The equation we want to solve becomes

$$(350) \quad \frac{dx}{dt} = b(x(t), t)$$

Therefore, along $x(t)$,

$$(351) \quad \frac{du(x(t), t)}{dt} + f[u(x(t), t), x(t), t] = 0$$

If this equation is integrable, then we have some hope for an analytical function.

To give a specific example, we consider (345) with the change of variable $x \rightarrow s$ and $u \rightarrow G$. Along the characteristic

$$(352) \quad \frac{ds}{dt} = -k(1 - s)$$

and $dG/dt = 0$, since $f = 0$. Therefore, $G(s(t), t)$ is a constant equal to $G(s(t = 0), 0) = s(t = 0)^{n_0}$

From $ds/dt = -k(1 - s)$, we find

$$(353) \quad 1 - s(t) = e^{kt}(1 - s(t = 0))$$

or

$$(354) \quad s(t = 0) = 1 - (1 - s(t))e^{-kt}$$

which means

$$(355) \quad G(s, t) = (1 + (s - 1)e^{-kt})^{n_0}$$

is solution.

By definition of the mean and the variance, we get :

$$(356) \quad \langle n_A \rangle (t) = \left. \frac{\partial G}{\partial s} \right|_{s=1} = n_0 e^{-kt}$$

$$(357) \quad \langle (n_A - \langle n_A \rangle)^2 \rangle (t) = \left. \frac{\partial^2 G}{\partial s^2} \right|_{s=1} + \left. \frac{\partial G}{\partial s} \right|_{s=1} - \left(\left. \frac{\partial G}{\partial s} \right|_{s=1} \right)^2 = n_0 e^{-kt} (1 - e^{-kt})$$

The mean value of the stochastic approach is therefore consistent with the mean value for the deterministic equation. The stochastic approach gives however higher moments as statistical

physics gives to thermodynamics. No only the moments, but the full probability distribution can be calculated. From (342) and expanding (342), we get:

$$(358) \quad P(n_A, t) = C_{n_A}^{n_0} e^{-n_A k t} (1 - e^{-k t})^{n_0 - n_A}$$

4. The Master equation

Let $P_i(t)$ be the probability that the system is a state $i = (p, q)$ at time t (quantum or classical). Consider a time interval dt . What is dP_i/dt ?

During dt , three types of events can take place:

- (1) one jump from some cell j to cell i (dt is so small that at most one such event can take place)
- (2) one jump from the cell i to an other cell j .
- (3) Nothing happens. Since $j \neq i$, the probability to stay in cell i is

$$1 - \sum_{j \neq i} W_{ji} dt$$

We have three events, since in the last case where the system was in cell i , we had to options (leave or not leave).

Summing over all cells j we have for events of type 1 which increase the number of points in cell i :

$$(359) \quad dt \sum_j W_{i,j} P_j$$

Summing over all cells j we have for events of type 2 which leave the probability to be in cell i unchanged during the time interval dt :

$$(360) \quad dt(1 - \sum_{j \neq i} W_{j,i}) P_i$$

since, knowing that the system was in cell i , the probability that nothing happens is : $1 -$ the probability that something happens. We have:

$$(361) \quad P_i(t + dt) = P_i(t) + dt \sum_{j \neq i} W_{i,j} P_j(t) - dt \sum_{j \neq i} W_{j,i} P_i(t)$$

which says that $P_i(t)$ evolves as

$$(362) \quad \frac{dP_i}{dt} = \sum_j (W_{ij} P_j - W_{ji} P_i)$$

This is known as the Master equation. An other form of the master equation is

$$(363) \quad \frac{dP_i}{dt} = -P_i(t) + \sum_{j \neq i} W_{i,j} P_j(t)$$

The fact that $W_{ij} \geq 0$ ² means that if each $P_i(t = 0) \geq 0$ then $P_i(t) \geq 0$ for $t > 0$. To see this, assume that at some time t one of the probability $P_i(t)$ is crossing zero and is about to become negative. Then by (365)

$$(365) \quad \frac{dP_i}{dt} = \sum_j (W_{ij} P_j - W_{ji} P_i) = \sum_j W_{ij} P_j > 0$$

and P_i will increase again at latter time. So $P_i(t)$ can never become negative.

²For example, Fermi's Golden rule says that

$$(364) \quad W_{ij} = \frac{2\pi}{\hbar} |\langle i | V | j \rangle|^2 \rho(E_j)$$

How do we choose the Markov matrix W_{ij} ? This is far from trivial and there is no microscopic theory (at the present time). For an isolated system, what we want is :

- a) $P_i = 1/\Omega(E)$ is a stationary solution
- b) Some kind of reversibility.

Let us start with point b) and assume that the W_{ij} obey to the micro-canonical detailed balance principle:

$$(366) \quad W_{ij} = W_{ji}$$

In other words, we assume that the Markov matrix is symmetric. If we define the entropy as

$$(367) \quad S = - \sum_i P_i \ln P_i$$

To have a correct entropy definition, S must increase

$$(368) \quad \begin{aligned} \frac{dS}{dt} &= - \sum_i (1 + \ln P_i) \frac{dP_i}{dt} \\ &= - \sum_i (1 + \ln P_i) \left[\sum_j (W_{ij}P_j - W_{ji}P_i) \right] \end{aligned}$$

Or,

$$(369) \quad \sum_i \frac{dP_i}{dt} = 0$$

since the sum over all probabilities is conserved.

$$(370) \quad \sum_i \sum_j \ln P_i W_{ji} P_i = \sum_j \sum_i \ln P_j W_{ij} P_j$$

which gives

$$(371) \quad \begin{aligned} \frac{dS}{dt} &= - \sum_{i,j} W_{ij} P_j (\ln P_i - \ln P_j) \\ &= - \sum_{i,j} W_{ij} P_j \ln \frac{P_i}{P_j} \end{aligned}$$

We now use $W_{ij} = W_{ji}$ and we make the above equation symmetric:

$$(372) \quad \frac{dS}{dt} = - \frac{1}{2} \sum_{i,j} W_{ij} (P_j \ln \frac{P_i}{P_j} + P_i \ln \frac{P_j}{P_i})$$

$$(373) \quad = - \frac{1}{2} \sum_{i,j} W_{ij} (P_j - P_i) \ln \frac{P_i}{P_j}$$

and we are done ! $dS/dt > 0$! Why ?

Consider $f(x, y) = (x - y) \ln(x/y)$. If $x > y$ then $\ln(x/y) > 0$ and $f(x, y) > 0$. If $x < y$, we find also that $f(x, y) > 0$. So that, for all $x, y > 0$

$$(374) \quad f(x, y) = (x - y) \ln \frac{x}{y} > 0$$

The increase of entropy is also known as the "H-theorem".

REMARK. The master equation says that the probability to jump from state i to state j during a time interval dt does depend only on states i, j but does not depend on the configurations prior to t . One says that the system evolves according to a Markov process. The master equation does not include the correlation between the thermostat and the system and thus assume that the dynamics of the thermostat is sufficiently chaotic so that one can neglect the

temporal correlations. The diffusion equation or the Langevin equation are typical examples of Markov processes.

5. Thermostat and detailed balance

Everything above applies to an isolated system (micro-canonical ensemble). Here we want to describe how a system can exchange heat with a thermostat (macro-canonical ensemble). To make things simple, we change notations and instead of writing $W_{i,j}$, we write $W(\mathcal{C}', \mathcal{C})$ where \mathcal{C}' , \mathcal{C} are two configurations. The simplest way is to assume that the probability to jump from configuration \mathcal{C} to \mathcal{C}' depends on the energy difference $E(\mathcal{C}) - E(\mathcal{C}')$ between the two configurations

$$(375) \quad \frac{W(\mathcal{C}', \mathcal{C})}{W(\mathcal{C}, \mathcal{C}')} = e^{[E(\mathcal{C}') - E(\mathcal{C})]/k_B T}$$

The energy given to the system by the thermostat is the heat (this is how we define the heat in statistical physics)

$$(376) \quad Q = E(\mathcal{C}') - E(\mathcal{C})$$

when the system jumps from \mathcal{C} to \mathcal{C}' . By definition, the change in entropy is the change of the entropy of the thermostat

$$(377) \quad \Delta S_{thermostat} = -\frac{Q}{T}$$

Condition (375) can be written in another way:

$$(378) \quad W(\mathcal{C}', \mathcal{C})P_{eq}(\mathcal{C}) = W(\mathcal{C}, \mathcal{C}')P_{eq}(\mathcal{C}')$$

where $P_{eq}(\mathcal{C})$ is the Boltzmann's distribution. Thus condition (375) secures that the Boltzmann's distribution is solution of the master equation. This condition is called the detailed balance condition. This condition is a principle, since this is a condition that the W 's must obey *a priori*. There is no general recipe to calculate the $W(\mathcal{C}, \mathcal{C}')$'s and a lot of Markovian processes will converge to the same Boltzmann's equilibrium distribution.³

As a final remark, we show that detailed balance implies reversibility. A trajectory in phase space is a series of configurations (from right to left):

$$(379) \quad \mathcal{C}_N \leftarrow \mathcal{C}_{N-1} \dots \mathcal{C}_1 \leftarrow \mathcal{C}_0$$

where we have decided to write from right to left with time t_0, t_1, \dots, t_N . The probability to observe this trajectory is the join probability and this can be written as

$$(380) \quad W(\mathcal{C}_N, \mathcal{C}_{N-1}) \dots W(\mathcal{C}_2, \mathcal{C}_1)W(\mathcal{C}_1, \mathcal{C}_0)P(\mathcal{C}_0)$$

$$(381) \quad W(\mathcal{C}_N, \mathcal{C}_{N-1}) \dots W(\mathcal{C}_2, \mathcal{C}_1)P(\mathcal{C}_1)W(\mathcal{C}_0, \mathcal{C}_1)$$

$$(382) \quad W(\mathcal{C}_N, \mathcal{C}_{N-1}) \dots P(\mathcal{C}_2)W(\mathcal{C}_1, \mathcal{C}_2)W(\mathcal{C}_0, \mathcal{C}_1)$$

$$(383) \quad \dots$$

In the third line, we write $W(\mathcal{C}_1, \mathcal{C}_2)W(\mathcal{C}_0, \mathcal{C}_1) = W(\mathcal{C}_0, \mathcal{C}_1)W(\mathcal{C}_1, \mathcal{C}_2)$ and so on. At the end, we see that the probability to observe the time ordered trajectory:

$$(384) \quad \mathcal{C}_N \leftarrow \mathcal{C}_{N-1} \dots \mathcal{C}_1 \leftarrow \mathcal{C}_0$$

is the same as the one for observing:

$$(385) \quad \mathcal{C}_0 \leftarrow \mathcal{C}_1 \dots \mathcal{C}_{N-1} \leftarrow \mathcal{C}_N$$

with a reverse sequence of times.

³There are $\Omega(E)^2$ matrix elements W 's and the detailed balance gives $\Omega(E)(\Omega(E) - 1)/2$ equations. Therefore, the detailed balance condition cannot give the W 's. Calculating the W 's is actually the whole problem of statistical physics ! The actual convergence towards the Boltzmann's distribution is given by a theorem under general condition (Perron-Frobenius theorem)

6. Monte-Carlo method

Dynamics satisfying the detailed balance are very often used in Monte Carlo simulations to sample systems at equilibrium. Let's take the example of an Ising system in its gas-on-lattice version. One considers a regular (say a square) lattice. To each site i , we associate a binary variable n_i which can take the value 0 or 1 depending on whether the site is occupied or not by a particle. A configuration of the system is then specified by the data of the variables n_i for each site i .

$$(386) \quad \mathcal{C} = n_1, n_2, \dots$$

To simulate an Ising model, we consider the following energy

$$(387) \quad E(\mathcal{C}) = \sum_{i,j} U_{i,j} n_i n_j + \sum_i V_i n_i$$

where the potential $U_{i,j}$ depends on the distance between sites i and site j and where V_i is an external potential.

The dynamics of Monte Carlo in its Metropolis version consists in building a suite of configurations $\mathcal{C}_1, \mathcal{C}_2, \dots, \mathcal{C}_t, \dots$ using the following algorithm: if the system is in a configuration \mathcal{C}_t , a pair of neighbouring sites is chosen at random and the occupancy numbers of the two sites are exchanged.

$$(388) \quad n_i, n_j \rightarrow n_j, n_i$$

A new configuration is \mathcal{C}^* is thus created. Obviously, the two are identical, i.e. $\mathcal{C}^* = \mathcal{C}_t$, if both sites are empty or occupied. If only one is occupied, this amounts to exchanging the particle between the two sites. A number z is then drawn at random according to a uniform probability distribution between 0 and 1 and one iterates according to the rule:

$$(389) \quad \mathcal{C}_{t+1} = \begin{cases} \mathcal{C}^* & \text{if } z \leq \exp\{(E(\mathcal{C}_t) - E(\mathcal{C}^*)) / k_B T\} \\ \mathcal{C}_t & \text{if } z > \exp\{(E(\mathcal{C}_t) - E(\mathcal{C}^*)) / k_B T\} \end{cases}$$

The series $\mathcal{C}_1, \mathcal{C}_2, \dots$ allows to sample an ensemble of configurations distributed to Boltzmann's law. For example, for any observable $F(\mathcal{C})$

$$(390) \quad \langle F \rangle = \frac{\sum_{\mathcal{C}} F(\mathcal{C}) e^{-E(\mathcal{C})/k_B T}}{\sum_{\mathcal{C}} e^{-E(\mathcal{C})/k_B T}}$$

we have for a series of N configurations

$$(391) \quad \langle F \rangle = \frac{1}{N} \sum_{\mathcal{C}_t} F(\mathcal{C}_t)$$

7. Heat And work

How do we define heat and work to recover thermodynamics ? Once given the matrix W_t , the time evolution for the probability is given by the master equation

$$(392) \quad \frac{dP(\mathcal{C})}{dt} = \sum_{\mathcal{C}'} W_t(\mathcal{C}, \mathcal{C}') P_t(\mathcal{C}') - W_t(\mathcal{C}', \mathcal{C}) P_t(\mathcal{C})$$

The interaction with the thermostat is at the origin of each jump from one configuration to another. The quantity of heat ΔQ supplied by the thermostat during an interval dt of time is given by averaging all possible jumps

$$(393) \quad \langle \delta Q \rangle = \sum_{\mathcal{C}, \mathcal{C}'} [E_t(\mathcal{C}') - E_t(\mathcal{C})] W_t(\mathcal{C}', \mathcal{C}) dt P_t(\mathcal{C})$$

which makes explicit the fact that the thermostat supplies an energy $E_t(\mathcal{C}') - E_t(\mathcal{C})$ during the jump $\mathcal{C} \rightarrow \mathcal{C}'$ (note that the energy of the configurations is time dependent). This last equation can be rewritten as

$$(394) \quad \begin{aligned} \langle \delta Q \rangle &= \sum_{\mathcal{C}, \mathcal{C}'} E_t(\mathcal{C}) [W_t(\mathcal{C}, \mathcal{C}')P(\mathcal{C}') - W_t(\mathcal{C}', \mathcal{C})P(\mathcal{C})] dt \\ &= \sum_{\mathcal{C}'} E_t(\mathcal{C}) \frac{dP_t(\mathcal{C})}{dt} dt \end{aligned}$$

In addition, one knows that the average energy of the system is

$$(395) \quad \langle E_t \rangle = \sum_{\mathcal{C}} E_t(\mathcal{C})P_t(\mathcal{C})$$

We deduce that the average amount of work provided to the system is

$$(396) \quad \langle \delta W_{supplied} \rangle = \langle \delta E_t \rangle - \langle \delta Q \rangle = \sum_{\mathcal{C}} \frac{dE_t(\mathcal{C})}{dt} P_t(\mathcal{C}) dt$$

We conclude: In Markov dynamics, the time dependence of $E_t(\mathcal{C})$ energies over time contributes to work while energy changes during jumps contribute to heat.

8. Conclusion

It is now useful to summarize all Markov processes studied in this chapter.

The starting point is the Chapman-Kolmogorov equation

$$(397) \quad f(x_3, t_3|x_1, t_1) = \int_{-\infty}^{+\infty} f(x_3, t_3|x_2, t_2)f(x_2, t_2|x_1, t_1) dx_2 \quad \forall t_2 \in [t_1, t_3]$$

If we assume a stationary process, we use a special notation

$$(398) \quad f(x_2, t_2|x_1, t_1) = p(x_2|x_1, \tau) \quad \tau = t_2 - t_1$$

and the Chapman-Kolmogorov equation reads as

$$(399) \quad p(x_3|x_1, \tau + \tau') = \int_{-\infty}^{+\infty} p(x_3|x_2, \tau')p(x_2|x_1, \tau) dx_2$$

This equation is useful in the following sense: From the knowledge of the transition probability at small times we can build up the transition probability at all times iteratively.

For a large class of processes, the transition probability has the following asymptotic form

$$(400) \quad p(x|z, \tau') = (1 - a_0\tau')\delta(x - z) + \tau'w(x|z) + o(\tau')$$

The meaning of this equation is rather simple: The time interval τ' is so small that we have only two options:

- (1) One "jump" event took place during τ' : second term.
- (2) Nothing happened during τ' : first term which is nothing but $1 -$ something where

$$(401) \quad a_0(x) = \int_{-\infty}^{+\infty} w(x|z) dz$$

We substitute (400) and get the Master equation:

$$(402) \quad \frac{\partial}{\partial \tau} p(x_3|x_1, \tau) = \int_{-\infty}^{+\infty} [w(x_3|x_2)p(x_2|x_1, \tau) - w(x_2|x_3)p(x_3|x_1, \tau)] dx_2$$

To derive the master equation, we have made one key assumption: The limit $\Delta t \rightarrow 0$ has NOT to be understood in a mathematical sense. At every time steps Δt , we have tacitly assumed that the microscopic variables - we need them to have an equilibrium - relaxes so fast that we are in equilibrium at time t and at time $t + \Delta t$. Thus they relax rapidly. This hypothesis

is called the "Stoßzahlansatz" (repeated randomness). Be careful, this evolution equation is conditioned by the initial conditions x_1 at time 0. If we make two assumptions, namely:

- (1) Small jumps $x_2 - x_1 \rightarrow 0$,
- (2) Small variations of $p(x_3 - x_1, \tau)$ with $x_3 - x_1$,

we get from the Master equation the Fokker-Planck equation:

$$(403) \quad \frac{\partial}{\partial \tau} p(y, \tau) = \frac{\partial}{\partial y} [a_1(y)p(y, \tau)] + \frac{1}{2} \frac{\partial^2}{\partial y^2} [a_1(y)p(y, \tau)]$$

with the a_n 's being the moments

$$(404) \quad a_n = \int_{-\infty}^{+\infty} \Delta y^n w(y, \Delta y) d\Delta y$$

This expansion is known as the Kramers-Moyal expansion.

The proof goes as follows: We note that $w(x_3|x_2)$ and $w(x_2|x_1)$ in eq. (402) are jump probabilities. They depend on the starting point and on the jump size, the latter being $x_3 - x_2$ for the first term and $x_2 - x_3$ for the second one. For the first term, the size is $x_3 - x_2$ and the starting point is $x_3 - r$. We write

$$(405) \quad w(x_3|x_2) = \omega(x_3 - r, r)$$

where $\omega(x, y)$ is a function of two independent variables, x being the starting point and y the jump size. Since x_1 and τ do not play any role, we drop them for clarity and rewrite (402) as

$$(406) \quad \int dr \omega(x_3 - r, r)p(x_3 - r) - p(x_3) \int dr \omega(x_3, -r)$$

We can now Taylor expand the shift $x_3 - r$ as

$$(407) \quad \omega(x_3 - r, r)p(x_3 - r) = \omega(x_3, r)p(x_3) + \sum_{m \geq 1} \frac{(-1)^m}{m!} r^m \frac{\partial^m}{\partial x_3^m} [\omega(x_3, r)p(x_3)]$$

Using this expansion with (??), we see that the first order term cancels out with the third term in (??). We are left with

$$(408) \quad \sum_{m \geq 1} \frac{(-1)^m}{m!} \frac{\partial^m}{\partial x_3^m} \left[\int dr r^m \omega(x_3, r)p(x_3) \right]$$

which is the moment expansion we were looking for.

CHAPTER 6

STOCHASTIC THERMODYNAMICS : CROOKS AND JARZYNSKI EQUALITIES

1. Heat and work

The second law of thermodynamics states that the total entropy of an isolated system always increases over time, or remains constant in ideal cases where the system is in a steady-state or undergoes a reversible process. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past. We shall see that this can only be true in the macroscopic world. In the nano-world, fluctuations play a significant role and this principle is only valid in a statistical sense, i.e. after averaging over many experimental events.

Before doing this, we have to define again what we call heat and work. The mean energy of a system at time t is defined as an averaged quantity over all possible configurations \mathcal{C}

$$(409) \quad \langle E_t \rangle = \sum_{\mathcal{C}} E_t(\mathcal{C}) P_t(\mathcal{C})$$

where all quantities depend on t and where the interaction of the system with the outside world may also depend on t . For example, we can move a piston, and the effect of moving the piston will change the interaction of the molecules with the walls. In turn, this will change the energy configurations of the system.

Taking the time derivative, we have 2 terms

$$(410) \quad \left\langle \frac{dE_t}{dt} \right\rangle = \frac{\delta Q}{dt} + \frac{\delta W}{dt}$$

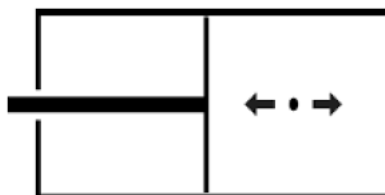


FIGURE 1.
A piston with one molecule inside the box.

with

$$(411) \quad \delta Q = \sum_{\mathcal{C}} E_t(\mathcal{C}) \dot{P}_t(\mathcal{C})$$

$$(412) \quad \delta W = \sum_{\mathcal{C}} \dot{E}_t(\mathcal{C}) P_t(\mathcal{C})$$

and this defines what we call heat and work in equilibrium and non-equilibrium systems. The energy transferred to the system corresponds to changing the energy of the configurations. This is what we do when we apply a force, since this force is the derivative of a potential. The heat is the change per unit time in the probability to be in a configuration \mathcal{C} . Since we must sum over all configurations, heat and work are only defined in a statistical sense.

NOTE. Recall from chapter 1 that the Hamiltonian can be formally written as

$$(413) \quad H(p, q) = \sum_i \frac{p_i^2}{2m} + \sum_{i < j} U(q_i - q_j) + \sum_i V(q_i, t)$$

The first term is the kinetic energy, the second is the interaction between the particles and the third is the potential energy. It may depend on the time t . $V(q_i, t)$ takes into account the walls and it plays an analogous role to a piston in thermodynamics.

1.1. Statement of the Jarzynski equality. Consider once again the piston of Fig. 1. We assume equilibrium at time $t = 0$. We now move the piston between time t and t' . This transformation can be fast or slow. We don't care.

Let W be the work given to the system. For a small system, W will fluctuate from one experiment to another one, since the position of the molecule inside the cylinder is a random variable. W is, therefore, a random variable. For a deterministic system, fluctuations are due to changes in initial conditions for the molecule inside the piston when we apply the transformation. The Jarzynski equality states that¹

$$(414) \quad \langle e^{-\beta W} \rangle_{\text{Experiments}} = e^{-\beta(F_{\text{final}} - F_{\text{initial}})}$$

where $\langle \rangle$ means that the mean is taken over many experiments. The symbols F 's appearing are free energies and this equation tells us that F_{final} is the free energy of the system in the final state AFTER WAITING ENOUGH FOR EQUILIBRATION. When we stop moving the piston, the system is not at equilibrium and takes some time to equilibrate. The final and the initial states have the same temperature, but they differ in a variable entering into the Hamiltonian (otherwise their free energy would be the same). In a fluid system like ours, this variable is the volume V . In short, the Jarzynski's relationship is a symmetry under time reversal of the distribution of work done on the system

This equality is true in thermodynamics: If the system is driven from an initial state to a final state by a REVERSIBLE process, the work done on the system is exactly $W = \Delta F$, so that equality (414) is true. If, in marked contrast, the process connecting the initial and the final state is IRREVERSIBLE, the work may be different. Taking the average over many processes, equality (414) shows that the inequality $\langle W \rangle > \Delta F$ holds. Usually, in standard thermodynamics, this inequality is written without taking the average. This can't be true, since the second law of thermodynamics is statistical per nature. Note that (414) is a rigorous equality and not an inequality.

2. Consequences

Eq. (414) gives the second law of thermodynamics. If we move the piston in such way that the initial and final states are the same, we have:

$$(415) \quad F_{\text{final}} - F_{\text{initial}} = 0 \text{ so that } \langle e^{-\beta W} \rangle_{\text{Experiments}} = 1$$

¹This equality has been obtained by C. Jarzynski in 1997. Other equalities similar to this one have been previously obtained 20 years before by Bochkov and Kuzovlev.

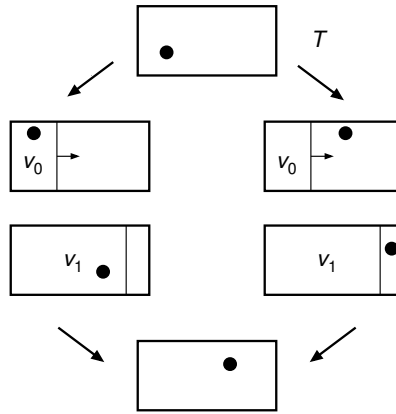


FIGURE 2. The Szilard's machine and the Jarzynski's equality. The two cases correspond to the configuration where the particle is initially in the compartment of volume v_0 or not. We don't know a priori in which compartment the particle is, so that one must average over the initial distribution to get mean values.

For any random variable, the Jensen inequality gives ²

$$(418) \quad \langle e^{-x} \rangle \geq e^{-\langle x \rangle}$$

so that

$$(419) \quad e^{-\beta \langle W \rangle_{\text{Experiments}}} \leq 1$$

or

$$(420) \quad \langle W \rangle_{\text{Experiments}} \geq 0$$

which is the statement we were looking for.

The statement

$$(421) \quad \langle e^{-\beta W} \rangle_{\text{Experiments}} = 1$$

goes however one step farther. For the mean value of the exponential to be exactly one, some experiments must give $W < 0$. Otherwise, the mean value of the exponential would be strictly larger than 1. We conclude that some experiments must violate the second law of thermodynamics.

3. The Szilard's Machine

The Szilard's machine is an example where the distribution of work can be exactly calculated. The system is a one particle system in a box. At $t = 0$, a wall (i.e. a piston) is introduced and divides the system into two compartments of respective volume v_0 and $v - v_0$. This piston is then smoothly moved in a such a way that the volume initially at v_0 becomes v_1 . When the volume is at v_1 , the wall is suppressed. We assume that the particle inside the box is always at equilibrium and thus possesses a Maxwellian distribution at temperature T whatever the position of the piston. This assumption is valid if the piston is gently displaced so that the molecule experiences many bumps against the walls during the experiment. In the case where

²The Jensen equality states that that for any convex function $f(x)$

$$(416) \quad \langle f(x) \rangle \geq f(\langle x \rangle)$$

Or: $\phi(x)$ is convex and $g(x)$ continuous

$$(417) \quad \phi \left(\frac{1}{b-a} \int_a^b g(x) dx \right) \leq \frac{1}{b-a} \int_a^b \phi(g(x)) dx$$

the particle is inside the compartment of initial volume v_0 , the work done on the system is

$$(422) \quad W = - \int_{v_{\text{initial}}}^{v_{\text{final}}} p \, dv = -kT \ln \frac{v_{\text{final}}}{v_{\text{initial}}}$$

since, for one molecule, $pv = kT$!

We then average over the initial position of the particle. The molecule has the probability v_0/v to be in the left compartment v_0 at $t = 0$ and the probability $(v - v_0)/v$ to be on the right-hand side. So we have

$$(423) \quad W = \begin{cases} -kT \ln \frac{v_1}{v} & \text{with probability } \frac{v_1}{v_0} \\ -kT \ln \frac{v-v_1}{v} & \text{with probability } \frac{v-v_1}{v-v_0} \end{cases}$$

and we can check

$$(424) \quad \langle e^{-W/kT} \rangle = 1$$

4. Proof of a Jarzynski equality in a trivial case

This demonstration is due to B. Derrida. Imagine that the energy change of all configurations is almost instantaneous. For example, we move the piston so fast that the positions and the speeds of all particles cannot change during the move.

A state \mathcal{C} with initial energy $E_i(\mathcal{C})$ has an energy $E_f(\mathcal{C})$ after the change in the position of the piston. If the initial state was \mathcal{C} , the work done on the system is

$$(425) \quad W = E_f(\mathcal{C}) - E_i(\mathcal{C})$$

We can now average over the initial states. One obtains:

$$(426) \quad \begin{aligned} \langle e^{-W} \rangle &= \sum_{\mathcal{C}} e^{-\beta(E_f(\mathcal{C}) - E_i(\mathcal{C}))} P_{eq}^{(i)}(\mathcal{C}) \\ &= \sum_{\mathcal{C}} e^{-\beta(E_f(\mathcal{C}) - E_i(\mathcal{C}))} \frac{e^{-\beta E_i(\mathcal{C})}}{Z_i} \\ &= \frac{Z_f}{Z_i} = e^{-\beta(E_f - E_i)} \end{aligned}$$

which is the Jarzynski's equality.

The way we have moved the piston is, however, very sudden. The system is not in equilibrium after the change in the position of the piston. Here, the probability to find the system in state \mathcal{C} is given by $P_{eq}^{(i)}(\mathcal{C})$ but this probability is going to relax to $P_{eq}^{(f)}(\mathcal{C})$

$$(427) \quad P_i^{(f)}(\mathcal{C}) \neq P_{eq}^{(f)}(\mathcal{C})$$

The system relaxes by interacting with its environment and releases heat (if you stretch a rubber band, its temperature increases and then cools down).

5. Proof of the Jarzynski equality

Consider a thermally isolated system at $t = 0$. We work in the microcanonical ensemble where the system can only exchange work and not heat.

The Hamiltonian depends on dynamical variables \mathbf{x} (shorthand notation for \mathbf{x}, \mathbf{p}) and on a control parameter $\lambda(t)$ which varies with time. The dynamical variables obey a deterministic law between their initial states \mathbf{x}_i and their final states \mathbf{x}_f :

$$(428) \quad \lambda(t) : \mathbf{x}_i \rightarrow \mathbf{x}_f$$

During evolution, the system receives work from the outside (remember there is no exchange of heat) and

$$(429) \quad H_f(\mathbf{x}_f) - H_i(\mathbf{x}_i) = W$$

The work W is a random variable: We sample over the initial states \mathbf{x}_i by taking average within an energy shell δE for the initial state. Among the \mathbf{x}_i 's we keep only those which obey (429), so the probability $P_E(W)$ of observing W is

$$(430) \quad P_e(W) = \frac{\int d\mathbf{x}_i \delta(H_i(x_i) - E) \delta(W - H_f(\mathbf{x}_f) + H_i(x_i))}{\Omega_i(E)}$$

where $\Omega_i(E)$ is the initial phase space volume

$$(431) \quad \Omega_i(E) = \int d\mathbf{x}_i \delta(H_i(x_i) - E)$$

so that $P(W)$ is properly normalized

$$(432) \quad \int dW P_e(W) = 1$$

Consider now the time reversed process. All velocities take a minus sign and we use the symbol $\bar{\mathbf{x}}$ for the dynamical variables. An initial point $\bar{\mathbf{x}}_f$ evolves into a final state $\bar{\mathbf{x}}_i$ and we take the average over the energy shell

$$(433) \quad H_f(\bar{\mathbf{x}}_f) = E + W$$

The probability distribution $P_{E+W}(-W)$ to observe $-W$ is

$$(434) \quad \bar{P}_e(-W) = \frac{\int d\bar{\mathbf{x}}_f \delta(H_f(\bar{\mathbf{x}}_f) - E - W) \delta(H_f(\bar{\mathbf{x}}_f) - H_i(\bar{\mathbf{x}}_i) - W)}{\Omega_f(E + W)}$$

Liouville theorem states that $d\bar{\mathbf{x}}_f = d\mathbf{x}_i$ so that

$$(435) \quad \frac{P_E(W)}{\bar{P}_{E+W}(-W)} = \frac{\Omega_f(E + W)}{\Omega_i(E)} = e^{(S_f(E+W) - S_i(E))/k_B}$$

In an appropriate thermodynamic limit, entailing $E \rightarrow \infty$, the work distributions converge to functions $P(W)$ and $\bar{P}(-W)$ independent of the energy of the system, while the temperature T , $\partial S/\partial E = T$, is a well defined constant (the same for the initial and final distributions). Since $\Delta F = \Delta E - T\Delta S$ and $\Delta E = W$ the internal energy difference, one recovers the Crooks relation

$$(436) \quad \frac{P(W)}{\bar{P}(-W)} = \exp\left\{\left[\frac{\Delta S}{k_B}\right]\right\} = e^{\beta(W - \Delta F)}$$

Or

$$(437) \quad \int dW P(W) e^{-\beta W} = e^{-\beta \Delta F} \int dW P(W) = e^{-\beta \Delta F}$$

by normalisation of the probability distribution. To obtain this result, we have assumed that ΔF is independent of W . This is true in the thermodynamic limit $E \rightarrow \infty$, $W/E \rightarrow 0$, $\Delta F = W - T(S_f(E + W) - S_i(E)) = -T(S_f(E) - S_i(E))$.

Note: For a new 2018 experimental proof of the Jarzynski equality, see⁹.

6. Experiments in the nano-world, see¹⁶

The Jarzynski equality can be used to recover the equilibrium free energy differences between molecular states of complex molecules: See Fig. 3 for a pulling experiment on RNA molecules. For example, let us consider the case of a molecule (e.g. a DNA or RNA hairpin or a protein) initially in thermal equilibrium in the folded (F) or native state. By applying mechanical force (e.g. using AFM) the molecule can be mechanically unfolded and the conformation of the molecule changed from the native to the unfolded (U) state. The unfolding event is observed

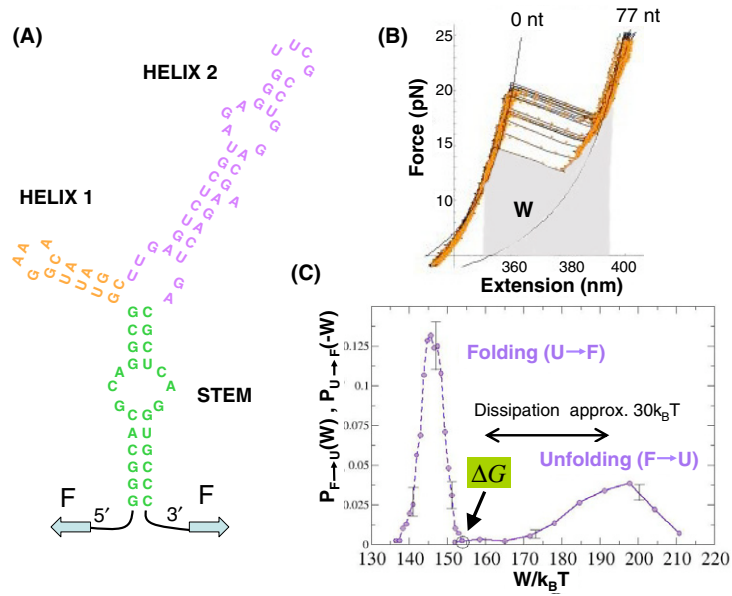


Figure 12. Recovery of folding free energies in a three-helix junction RNA molecule [193]. (A) Secondary structure of the junction containing one stem and two helices. (B) Typical force-extension curves during the unfolding process. The grey area corresponds to the work exerted on the molecule for one of the unfolding curves. (C) Work distributions for the unfolding or forward paths ($F \rightarrow U$) and the refolding or reverse ($U \rightarrow F$) paths obtained from 1200 pulls. According to the FT by Crooks (2) both distributions cross at $W = \Delta G$. After subtracting the free energy contribution coming from stretching the handles and the ssRNA these measurements provide a direct measure of the free energy of the native structure.

FIGURE 3.

by a rip in force-extension curve and the work done by the cantilever between the initial x_i and the final elongation state x_f .

$$(438) \quad W = \int_{x_i}^{x_f} F dx$$

The work done upon the molecule along a given path corresponds to the area below the force-extension curve that is limited by the initial and final extensions, x_i and x_f (grey shaded area in figure 3). Because the unfolding of the molecule is a stochastic (i.e. random) process, the value of the force at which the molecule unfolds changes from experiment to experiment and so does the value of the mechanical work required to unfold the molecule. Upon repetition of the experiment many times a distribution of unfolding work values for the molecule to go from the folded (F) to the unfolded (U) state is obtained, $P_{F \rightarrow U}(W)$. A related work distribution can be obtained if we reverse the pulling process by releasing the molecular extension at the same speed at which the molecule was previously pulled, to allow the molecule to go from the unfolded (U) to the folded (F) state. In that case the molecule refolds by performing mechanical work on the cantilever or the optical trap. Upon repetition of the folding process many times the work distribution, $P_{U \rightarrow F}(W)$ can be also measured.

From the Jarzynski equality, we observe that

$$(439) \quad P_{F \rightarrow U}(\Delta G) = P_{U \rightarrow F}(\Delta G)$$

where ΔG is the free energy difference between the two conformations, so the forward and reverse work probability distributions cross each other at $W = G$. By repeatedly measuring the irreversible mechanical work exerted upon the molecule during the unfolding process and the mechanical work delivered by the molecule to the instrument during the refolding process, it has been possible to reconstruct the unfolding and refolding work probability distributions and extract the value of the work $W = G$ at which both distributions cross each other.

CHAPTER 7

THE DAMPED HARMONIC OSCILLATOR

We introduce in this chapter two useful concepts: The response function (what is the response of a system driven out equilibrium by an exterior field) and what is a hydrodynamic description (it suffices to say that there are fast and slow variables and that their relaxations to equilibrium are different).

1. Dynamical susceptibility

A simple example of an irreversible process is the damped harmonic oscillator. If we assume that the oscillator is forced, the equation of motion is

$$(440) \quad \ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{F(t)}{m} = f(t)$$

In the absence of external force, $f(t) = 0$, the equation of motion reads as

$$(441) \quad \ddot{x} + \gamma\dot{x} + \omega_0^2 x = 0$$

and it is not invariant under time reversal because of the first derivative $\gamma\dot{x}$. If we define $\bar{x}(t) = x(-t)$ - and this is equivalent to run the movie backward, - the equation of motion for \bar{x} is

$$(442) \quad \ddot{\bar{x}} - \gamma\dot{\bar{x}} + \omega_0^2 \bar{x} = 0$$

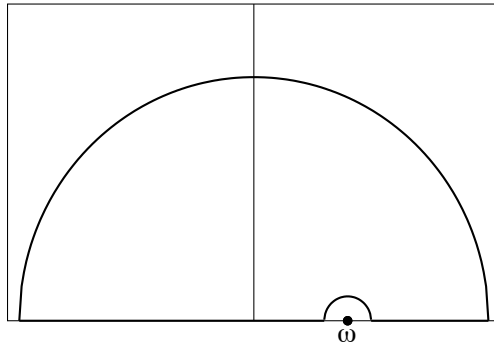
so that the viscosity accelerates the pendulum ! The reason for this is that the viscous force is a phenomenological term which takes into account the complicated interactions between the mass and the reservoir. If we were able to solve the total Hamiltonian mass + fluid, the equations of motion would have been invariant under time reversal. We get a non-invariant equation because we restrict our-selves to the pendulum. As we shall see in a next chapter, the full description for the compound system particle + Bath is time reversal invariant. This description is actually valid because of the presence of two widely differing time scales (see later), where the characteristic time scale for the pendulum is much larger than the characteristic time scale of the bath particles (time between collisions).

The solution of (440) is given by the dynamical susceptibility $\chi(t, t')$

$$(443) \quad x(t) = \int_{-\infty}^{+\infty} \chi(t, t') f(t') dt' = \int_{-\infty}^t \chi(t, t') f(t') dt'$$

This relationship is the most general one we can get assuming i) linearity and ii) causality. If we assume time translational symmetry (which is not true for aging phenomena), $\chi(t, t')$ is a function of $t - t'$. An other way of writing (443) is use the notation for functional derivative

$$(444) \quad \frac{\delta x(t)}{\delta f(t')} = \chi(t - t')$$

FIGURE 1. Integration path in the complex plane for $\alpha > 0$.

From now on, we assume time translational symmetry.

2. A mathematical interlude: Principal value of an integral

When $g(a) \neq 0$ the integral

$$(445) \quad \int_{x_1}^{x_2} \frac{g(x)}{x-a} dx$$

makes no sense. For some problems, it may be useful to study the limit

$$(446) \quad \lim_{\epsilon \rightarrow 0^+} \left(\int_{x_1}^{a-\epsilon} + \int_{a+\epsilon}^{x_2} \right) \frac{g(x)}{x-a} dx$$

When this limit exist, we call it the principal value (or the Cauchy value). Note that the criterion for the principal value to exist is "weaker" than the criterion for the integral to exist. For the integral to make sense, the following limit must exist:

$$(447) \quad \lim_{\epsilon_1 \rightarrow 0^+, \epsilon_2 \rightarrow 0^+} \left(\int_{x_1}^{a-\epsilon_1} + \int_{a+\epsilon_2}^{x_2} \right) \frac{g(x)}{x-a} dx$$

EXAMPLE 2.1. Show:

$$(448) \quad P. \int_{-\infty}^{+\infty} \frac{dx}{x^3} = 0$$

EXAMPLE 2.2. Show

$$(449) \quad P. \int_{-\infty}^{+\infty} \frac{e^{i\alpha x}}{x} dx = i\pi \text{sign}(\alpha)$$

with the contour given in Fig. 1.

THEOREM 3. Assume now that $f(x)$ is some function that tends to 0 when $|x|$ goes to infinity. We have

$$(450) \quad \lim_{\epsilon \rightarrow 0^+} \int_{-\infty}^{+\infty} \frac{f(x)}{x+i\epsilon} dx = P. \int_{-\infty}^{+\infty} \frac{f(x)}{x} dx - i\pi f(0)$$

Why? We have for all a

$$(451) \quad \left(\int_{-\infty}^{-a} + \int_{-a}^a + \int_a^{+\infty} \right) \frac{f(x)}{x+i\epsilon} dx$$

so that we can reorder

$$(452) \quad \left(\int_{-\infty}^{-a} + \int_a^{+\infty} + \int_{-a}^a \right) \frac{f(x)}{x+i\epsilon} dx$$

and take the limit $\epsilon \rightarrow 0$ first and then $a \rightarrow 0$. The first two integrals gives the principal value

$$(453) \quad \lim_{a \rightarrow 0} \lim_{\epsilon \rightarrow 0^+} \left(\int_{-\infty}^{-a} + \int_a^{+\infty} \right) \frac{f(x)}{x + i\epsilon} dx = P \int_{-\infty}^{+\infty} \frac{f(x)}{x} dx$$

The last one can be evaluated if we replace $f(x)$ by $f(0)$, since a goes to zero

$$(454) \quad \begin{aligned} \lim_{a \rightarrow 0} \lim_{\epsilon \rightarrow 0^+} \int_{-a}^{+a} \frac{f(x)}{x + i\epsilon} &= \lim_{a \rightarrow 0} \lim_{\epsilon \rightarrow 0^+} \int_{-a}^{+a} \frac{f(0)}{x + i\epsilon} \\ &= \lim_{a \rightarrow 0} f(0) \lim_{\epsilon \rightarrow 0} \ln \left[\frac{a + i\epsilon}{-a + i\epsilon} \right] \\ &= -i\pi f(0) \end{aligned}$$

with

$$(455) \quad \ln(z) = \ln|z| + i(\arg(z) + 2k\pi) \quad k \in \mathbb{Z}$$

so we take the value $-\pi$ for the logarithm, since the value inside the logarithm is $-1 - 2i\epsilon/a$, so that the branch cut of the log is approached from below.

3. Analytical properties

Causality is a fundamental property of the dynamic susceptibility. This means $\chi(t) = 0$, $t < 0$. As a consequence, we can define the Fourier-Laplace transform $\tilde{\chi}(z)$ as

$$(456) \quad \tilde{\chi}(z) = \int_0^{+\infty} dt e^{+izt} \chi(t) \quad \text{Im } z > 0$$

Note that the $+$ sign in the exponential is crucial. The usual Fourier transform is obtained by taking the limit where z approaches the real axis from above

$$(457) \quad \tilde{\chi}(\omega) = \lim_{\epsilon \rightarrow 0^+} \tilde{\chi}(\omega + i\epsilon)$$

Since $\chi(t)$ is a real function, the real part and the imaginary parts of $\tilde{\chi}(\omega)$ are even and odd functions, respectively. This is demonstrated from the definition

$$(458) \quad \chi'(\omega) = \text{Re } \tilde{\chi}(\omega) = \lim_{\epsilon \rightarrow 0^+} \int_0^{+\infty} dt \chi(t) e^{-\epsilon t} \cos(\omega t) \quad \tilde{\chi}'(\omega) = \tilde{\chi}'(-\omega)$$

$$(459) \quad \chi''(\omega) = \text{Im } \tilde{\chi}(\omega) = \lim_{\epsilon \rightarrow 0^+} \int_0^{+\infty} dt \chi(t) e^{-\epsilon t} \sin(\omega t) \quad \tilde{\chi}''(-\omega) = -\tilde{\chi}''(\omega)$$

because $\cos(-\omega t) = \cos(\omega t)$ and $\sin(-\omega t) = -\sin(\omega t)$.

We can now rewrite (456) using the step function

$$(460) \quad \theta(t) = \begin{cases} 1 & \text{if } t > 0 \\ 0 & \text{if } t < 0 \end{cases}$$

with the result

$$(461) \quad \tilde{\chi}(\omega) = \int_{-\infty}^{+\infty} dt \theta(t) \chi(t) e^{i\omega t}$$

In general, an arbitrary function $f(t)$ can be decomposed into an even and an odd function as

$$(462) \quad f(t) = f_e(t) + f_o(t) = \frac{1}{2}(f(t) + f(-t)) + \frac{1}{2}(f(t) - f(-t))$$

which means here

$$(463) \quad \chi_o(t) = \frac{1}{2}(\chi(t) - \chi(-t)) \quad \chi_e(t) = \frac{1}{2}(\chi(t) + \chi(-t))$$

so that

$$(464) \quad \chi(t) = 2\chi_o(t) \quad \text{for } t > 0$$

The Fourier transform of the odd part can easily be evaluated

$$(465) \quad \int_{-\infty}^{+\infty} \frac{1}{2} [\chi(t) - \chi(-t)] e^{i\omega t} dt = i \int_0^{+\infty} \chi(t) \sin(\omega t) dt \\ = i\tilde{\chi}''(\omega)$$

so that the odd part $\chi_o(t)$ can be obtained using the inverse Fourier transform of $i\tilde{\chi}''(\omega)$ as (we make use of (464))

$$(466) \quad \tilde{\chi}(z) = 2i \int_0^{+\infty} dt e^{izt} \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi} \tilde{\chi}''(\omega) e^{-i\omega t}$$

Performing the integration over the time t^1 we get the dispersion relation for $\tilde{\chi}(z)$

$$(467) \quad \tilde{\chi}(z) = \frac{1}{\pi} \int_{-\infty}^{+\infty} du \frac{\tilde{\chi}''(u)}{u - z}$$

where we made the change in notation $\omega \rightarrow u$. Posing $z = \omega + i\epsilon$ gives a relationship between the real and imaginary part

$$(468) \quad \tilde{\chi}'(\omega) = \frac{1}{\pi} \text{P} \int_{-\infty}^{\infty} du \frac{\tilde{\chi}''(u)}{(u - \omega)}$$

where we have made use of the integral identity (see theorem 3)

$$(469) \quad \int_{-\infty}^{+\infty} \frac{du}{\omega - u - i\epsilon} = i\pi \int_{-\infty}^{+\infty} du \delta(\omega - u) + \text{P} \int_{-\infty}^{+\infty} \frac{du}{\omega - u}$$

This dispersion relation is a consequence of causality. THE REAL AND THE IMAGINARY PARTS OF A CAUSAL FUNCTION ARE NOT INDEPENDENT. These relationships are the so-called Kramers-Kronig relationships. One remarks that, because of causality, the knowledge of $\tilde{\chi}''(\omega)$ suffices to know $\tilde{\chi}'(\omega)$ and vice et versa.

EXERCICE 7.1. Show:

$$(470) \quad \tilde{\chi}''(\omega) = -\frac{1}{\pi} \text{P} \int_{-\infty}^{\infty} du \frac{\tilde{\chi}'(u)}{(u - \omega)}$$

EXAMPLE 3.1. For the damped harmonic oscillator, one finds:

$$(471) \quad \tilde{\chi}(\omega) = \frac{-1}{\omega^2 + i\gamma\omega - \omega_0^2}$$

Taking the imaginary part

$$(472) \quad \tilde{\chi}''(\omega) = \frac{\omega\gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2\gamma^2} \geq 0 \quad \text{with} \quad \tilde{\chi}''(-\omega) = -\tilde{\chi}''(\omega)$$

As we shall see, $\tilde{\chi}''$ is related to dissipation. What tells us this equation is general: dissipation goes through maximum at resonance.

EXERCICE 7.2. Consider the contour integral Fig. 1. Since there is no pole in the upper half-plane, the contour integral gives 0.

$$(473) \quad \oint_c \frac{\chi(z)}{z - \omega} dz = 0$$

Show :

$$(474) \quad \chi(\omega) = \frac{1}{i\pi} \text{P} \int_{-\infty}^{-\infty} \frac{\chi(\omega')}{\omega' - \omega} d\omega'$$

¹Don't forget the ϵ to make sure that all integrals converge.

Show (separate into real and imaginary parts and use that $\chi'(\omega)$ is even)

$$(475) \quad \chi'(\omega) = \frac{1}{\pi} \text{P} \int_{-\infty}^{+\infty} d\omega' \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2}$$

$$(476) \quad \chi''(\omega) = -\frac{\omega}{\pi} \text{P} \int_{-\infty}^{+\infty} d\omega' \frac{\chi'(\omega')}{\omega'^2 - \omega^2}$$

4. Dissipation

If the damped harmonic oscillator is in a state of stationary motion, we must provide with energy. Otherwise, the motion would stop because of the viscosity which dissipates energy. Assume that the force is harmonic

$$(477) \quad f(t) = f_0 \cos \omega t = \text{Re} [f_0 e^{i\omega t}]$$

We find that $x(t)$ is given by

$$(478) \quad x(t) = \text{Re} \left[f_0 e^{i\omega t} \int_0^\infty \chi(t') e^{i\omega t'} \right]$$

$$(479) \quad = f_0 \text{Re} [f_0 e^{i\omega t} \tilde{\chi}(-\omega)]$$

$$(480) \quad = f_0 [\chi'(-\omega) \cos \omega t - \chi''(-\omega) \sin \omega t]$$

$$(481) \quad = f_0 [\chi'(\omega) \cos \omega t + \chi''(\omega) \sin \omega t]$$

EXERCICE 7.3. Show that that one obtains the same result if one chooses

$$(482) \quad f(t) = f_0 \cos \omega t = \text{Re} [f_0 e^{-i\omega t}]$$

As a consequence, the real part $\tilde{\chi}'(\omega)$ governs the response which is in phase with the excitation. On the other hand, the imaginary part $\tilde{\chi}''(\omega)$ controls the out of phase response.

The power dissipated per unit time is equal to the work done by the external force per unit time. We have:

$$(483) \quad \frac{dW}{dt} = f_0 \dot{x}(t) \cos \omega t$$

Using (540) and averaging over time gives

$$(484) \quad \left\langle \frac{dW}{dt} \right\rangle = \frac{1}{2} \omega f_0^2 \tilde{\chi}''(\omega)$$

Because $\langle dW/dt \rangle > 0$, we have $\omega \tilde{\chi}''(\omega) > 0$. for a passive system. For an active non-equilibrium system producing energy, $\tilde{\chi}''(\omega)$ can be negative. This proof is general and applies to a wide class of systems. Anyway, we have shown that the imaginary part $\tilde{\chi}''(\omega)$ is related to dissipation.

5. The fluctuation dissipation theorem: A preview

What we have said for the harmonic oscillator can be stated in a very general way. If we perturb a system out of equilibrium by applying an external or force, we can always define a response function with the same properties as above. It took Onsager to realize that the way a system responds to a perturbation - which creates a fluctuation - is connected to the way that the same fluctuation decays when the system is at equilibrium (spontaneous thermal fluctuation without force). Consider a system at equilibrium with Hamiltonian H_0 . We are going to perturb this system by applying a force $f(t)$ which depends on time. Thus the system is driven out of equilibrium by the force. The total Hamiltonian becomes therefore

$$(485) \quad H = H_0 - f(t)A$$

where A is the conjugate variable to the force. Let us give two examples. For a gaz, the force is nothing that a change in pressure and the conjugate variable (within a minus sign) is the change in volume. For a polymer, $f(t)$ is a real force, and A is the end-to-end distance. Note that the conjugate variable to the force is not necessarily the one which is measured (i.e. the variable

measured as the response to the applied force). Consider, for example, a particle immersed in a viscous fluid. The conjugate variable to the force is the position, since the work is the displacement times the force and one measures the speed of the particle which is proportional to the force.

Let us consider first the case where there is no force. We can calculate and measure $\langle A \rangle_0$ at equilibrium. Since A fluctuates in time, we take the average. Fluctuations in A are correlated and we can measure their correlations by considering the first cumulant:

$$(486) \quad C(t) = \langle A(t)A(0) \rangle_0 - \langle A(0)^2 \rangle_0$$

It should be noted that correlation are directly accessible in scattering experiments.

Let us now change the stage and add a force. The system is driven out of equilibrium and the most general linear relationship we can write is

$$(487) \quad \langle A(t) \rangle = \langle A(t) \rangle_0 + \int_{-\infty}^t dt' \chi(t, t') f(t')$$

This relationship respects causality, so that the upper limit in the integral cannot exceed t . Otherwise, the response of the system at time t would depend on the force at time later than t .

We know remark that because of time translational invariance:

$$(488) \quad \begin{aligned} C(t) &= C(-t) \\ \chi(t, t') &= \chi(t - t', 0) \end{aligned}$$

We claim the following. The results of the two different experiments (measuring the fluctuations and measuring the response function) are related

$$(489) \quad k_B T \chi(t) = -\frac{dC}{dt}$$

This will be proved in the next chapter. This is the so-called fluctuation dissipation theorem. The reason why it is called this way is that the Fourier transform

$$(490) \quad \tilde{\chi}(\omega) = \int_0^{+\infty} dt e^{i\omega t} \chi(t) \quad \tilde{C}(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} C(t)$$

are related to each other by

$$(491) \quad \tilde{C}(\omega) = \frac{k_B T}{\omega} \tilde{\chi}''(\omega)$$

where $\tilde{\chi}(\omega) = \tilde{\chi}'(\omega) + i\tilde{\chi}''(\omega)$. Since $\tilde{\chi}''(\omega)$ is related to the dissipation, the previous relationship connects the fluctuations to the dissipation.

6. Hydrodynamic Description

How a macroscopic variable (which is conserved) can relax ? Let us consider a magnetic system with spin variable $\sigma(\mathbf{x})$. The total magnetization is

$$(492) \quad \mathbf{M} = \sum_i \sigma(\mathbf{x} - \mathbf{x}_i(t))$$

where the spin on the particle i moves with the particle i . The question we want to address is know how a fluctuation relaxes. The spin variable is general and can thought as a density $\rho(\mathbf{x}, t)$. Typically, we have the equation of conservation (particle are not created nor destroyed)

$$(493) \quad \partial_t \mathbf{M}(\mathbf{x}, t) = -\nabla \cdot \mathbf{j}(\mathbf{x}, t)$$

where $\mathbf{j}(\mathbf{x}, t)$ is the magnetic current. \mathbf{j} is simply the magnetic moment times the velocity:

$$(494) \quad \mathbf{j} = \sum_i \sigma_i \mathbf{v}_i$$

The equation of conservation (493) is equivalent to the condition:

$$(495) \quad \frac{d}{dt} \int d\mathbf{x} \mathbf{M}(\mathbf{x}, t) = 0$$

Eq. (493) does not give a complete description. We must know the relations between the current and the magnetization. The traditional way to solve the problem is to postulate a constitutive equation

$$(496) \quad \mathbf{j} = -D\nabla\mathbf{M}(\mathbf{x}, t)$$

where, in general, D is a phenomenological transport coefficient. Here, it is a simple diffusion coefficient as for the classical diffusion problem for particles. Using the equation of conservation, we must solve:

$$(497) \quad \partial_t \mathbf{M} - D\nabla^2 \mathbf{M} = 0$$

To solve this equation, we assume some initial magnetization modulation and Fourier transform the initial condition:

$$(498) \quad \mathbf{M}(\mathbf{k}, 0) = \int d\mathbf{x} e^{-i\mathbf{k}\cdot\mathbf{x}} \mathbf{M}(\mathbf{x}, 0)$$

Without loss of generality, we take:

$$(499) \quad \mathbf{M}(\mathbf{k} = \mathbf{0}, 0) = 0$$

since, if $M(\mathbf{x}, t)$ solve (497), $M(\mathbf{x}, t) - Cste.$ is also a solution.

Fourier transform in space the last equation

$$(500) \quad \mathbf{M}(\mathbf{k}, t) = \int d\mathbf{x} e^{-i\mathbf{k}\cdot\mathbf{x}} \mathbf{M}(\mathbf{x}, t)$$

where we use the same symbol for the function and its spatial Fourier transform. We also Laplace transform the last equation in time.

$$(501) \quad \tilde{\mathbf{M}}(\mathbf{k}, z) = \int_0^\infty dt \mathbf{M}(\mathbf{k}, t) e^{izt}$$

where z is a \mathbb{C} number in the half plane $\text{Im } z \geq 0$.

Because

$$(502) \quad \int dz e^{izt} \partial_t \mathbf{M}(\mathbf{k}, t) = [e^{izt} \mathbf{M}(\mathbf{k}, t)]_{t=0}^{+\infty} - \int dt \partial_t [e^{izt}] \mathbf{M}(\mathbf{k}, t)$$

We get

$$(503) \quad \tilde{\mathbf{M}}(\mathbf{k}, z) = \frac{i}{z + iD\mathbf{k}^2} \mathbf{M}(\mathbf{k}, 0)$$

Since $\mathbf{M}(\mathbf{k}, 0)$ is given by the initial conditions, the last equation tell us how the initial condition spreads with time through the system.

From (503), the solution $\tilde{\mathbf{M}}(\mathbf{k}, z)$ is an analytic function in the \mathbb{C} -plane but at the the point $z = -iD\mathbf{k}^2$. The pole for $z = -iD\mathbf{k}^2$ is characteristic of a hydrodynamic mode. Taking the inverse Laplace transform, we get:

$$(504) \quad \mathbf{M}(\mathbf{k}, t) = e^{-D\mathbf{k}^2 t} \mathbf{M}(\mathbf{k}, 0)$$

This equation is characteristic of a hydrodynamic mode. It is exponentially damped with a time scale $1/D\mathbf{k}^2$ tending to infinity in the long wavelength limit $\mathbf{k} \rightarrow 0$.

This was foreseen. The system has a priori many channels to relax a perturbation. We have, however, a conservation law. This conservation law tells us that for a fluctuation to relax, matter or spin must be transported in space via diffusion and transport takes times to relax long wavelength fluctuations.

We are now in position to see how an initial perturbation relaxes. Assuming the initial condition $\mathbf{M}(\mathbf{x}, 0) = \mathbf{M}_0\delta(\mathbf{x})$, we get the classical result (in 3 dimensions)

$$(505) \quad \langle \mathbf{M}(\mathbf{x}, t) \rangle = \frac{\mathbf{M}_0}{(4\pi Dt)^{3/2}} \exp\{-\mathbf{x}^2/6Dt\}$$

REMARK. To conclude, \mathbf{M} is what one calls a slow variable. The relaxation time of $\mathbf{M}(\mathbf{k}, 0)$ diverges in the $k \rightarrow 0$ limit, i.e. when the size of the system goes to infinity. Slow variables are macroscopic variables where we can write a phenomenological equation. Fast variables relaxes on very short time scales and will give noise in the equation for the slow variables. Including noise, we will see that the most general equation takes the form

$$(506) \quad \partial_t \mathbf{M} = D\nabla^2 \mathbf{M} + AT\eta(x, t)$$

where T is the temperature, A some constant to be evaluated and $\eta(x, t)$ a white noise term.

There are 3 types of slow variables:

- (1) Quantities which are conserved (i. e. concentration);
- (2) Quantities with a soft mode due to a global symmetry (also called Nambu-Goldstone mode);
- (3) Critical variables in the vicinity of a critical point with the critical slowing down phenomenon.

CHAPTER 8

LINEAR RESPONSE THEORY

1. The micro-canonical ensemble

The microcanonical ensemble is an equilibrium description as an ensemble of all possible initial conditions with energy E . We calculate the properties of this ensemble by averaging over states with energies in a shell $(E, E + \delta E)$ taking the limit $\delta E \rightarrow 0$. δE is introduced by hand in order to do statistics. In the quantum case, δE is larger than the level spacing. It should be noted that δE has nothing to do with the uncertainty principle due to Heisenberg. It is introduced by hand, because we want to do statistics. We define the phase-space volume $\Omega(E)$ of the thin shell as:

$$(507) \quad \Omega(E)\delta E = \int_{E < H(\mathbf{x}, \mathbf{p}) < E + \delta E} d\mathbf{x} d\mathbf{p}$$

More formally, we can write the energy shell $E < H(\mathbf{x}, \mathbf{p}) < E + \delta E$ in terms of the Heaviside step function $\Theta(x) = 1$, if $x > 0$ and 0 otherwise. We see that

$$(508) \quad \Theta(E + \delta E - H) - \Theta(E - H)$$

takes the value 1 in the energy shell and 0 otherwise. In the limit $\delta E \rightarrow 0$, we can write Ω_E as a derivative:

$$(509) \quad \begin{aligned} \Omega(E)\delta E &= \int_{E < H(\mathbf{x}, \mathbf{p}) < E + \delta E} d\mathbf{x} d\mathbf{p} = \int [\Theta(E + \delta E - H) - \Theta(E - H)] d\mathbf{x} d\mathbf{p} \\ &= \delta E \frac{\partial}{\partial E} \int d\mathbf{p} d\mathbf{x} \theta(E - H) \end{aligned}$$

Since all the states with the shell have equal probability, the expectation of a general operator O is:

$$(510) \quad \begin{aligned} \langle O \rangle &= \frac{1}{\Omega(E)} \int d\mathbf{p} d\mathbf{x} [\Theta(E + \delta E - H) - \Theta(E - H)] O(\mathbf{x}, \mathbf{p}) d\mathbf{x} d\mathbf{p} \\ &= \frac{1}{\Omega(E)} \frac{\partial}{\partial E} \int d\mathbf{p} d\mathbf{x} \Theta(E - H) O(\mathbf{x}, \mathbf{p}) d\mathbf{x} d\mathbf{p} \end{aligned}$$

Since the derivative of the Heaviside function is the Dirac's function, we have:

$$(511) \quad \Omega(E) = \int \delta(E - H(\mathbf{x}, \mathbf{p})) d\mathbf{x} d\mathbf{p} \quad \langle O \rangle = \frac{1}{\Omega(E)} \int d\mathbf{p} d\mathbf{x} \delta(E - H(\mathbf{x}, \mathbf{p})) O(\mathbf{x}, \mathbf{p}) d\mathbf{x} d\mathbf{p}$$

which means that the probability, or the probability measure, is $\delta(E - H(\mathbf{x}, \mathbf{p}))$.

This equation can be written in another way. Recall that we consider an isolated system of energy E . Let B be an observable and $\Omega(E, B)$ be the number of configurations of energy

E for which the observable takes the value B . The probability $P(B)$ to get B is:

$$(512) \quad P(B) = \frac{\Omega(E, B)}{\sum_{B'} \Omega(E, B')}$$

The Boltzmann's entropy is defined as:

$$(513) \quad S(E, B) = k_B \ln \Omega(E, B)$$

and the microcanonical temperature as:

$$(514) \quad \frac{1}{T} = \left. \frac{\partial S}{\partial E} \right|_{B_i}$$

where all other extensive variables, i.e. densities B_i , are kept fixed.

2. Macroscopic Einstein fluctuation theory

Let B be an extensive quantity, i.e. proportional of the number of molecules or of the volume, different from the energy. We work in the micro-canonical ensemble. At equilibrium the probability of observing a value B different from the equilibrium value is given by the number of configurations $\Omega(E, B + \delta B)$. Using (513)

$$(515) \quad P(\delta B) \propto e^{S(E_{eq}, B_{eq} + \delta B)}$$

where S is the entropy and E_{eq} the energy of the equilibrium configuration. Using stationarity of the entropy with respect to variations of B (recall that the value of B we observe at equilibrium maximises the entropy, so that the first order term in the Taylor expansion cancels out)

$$(516) \quad S(E_{eq}, B) = S(E_{eq}, B_{eq}) + \left. \frac{(\delta B)^2}{2} \frac{\partial^2 S}{\partial B^2} \right|_{E_{eq}, A_{eq}} + \dots$$

since B_{eq} is a maximum. It follows that the second derivative is negative (otherwise, fluctuations will grow). From the definition of entropy, the first derivative of the entropy with respect to the extensive variable is the conjugate intensive variable. The second derivative is, therefore, inversely proportional to a susceptibility¹

$$(517) \quad \left. \frac{\partial^2 S}{\partial B^2} \right|_{E_{eq}} = -\frac{1}{T\chi_B} < 0$$

and the probability to observe a fluctuation is therefore given by:

$$(518) \quad P(\delta B) = \frac{1}{\sqrt{2\pi T\chi_B}} e^{-\frac{(\delta B)^2}{2T\chi_B}}$$

Because $P(\delta B)$ is Gaussian, we have:

$$(519) \quad T\chi_B = \langle B^2 \rangle - \langle B \rangle^2$$

We shall later on that χ_B is a susceptibility. From (517), χ_B is an extensive quantity. (519) shows that the fluctuations of B are sub-extensive, i.e. $\propto \sqrt{V}$. This result is not trivial. As we shall see, (519) is an example of the fluctuation-dissipation theorem.

A consequence of (517) is as follows. If the susceptibility χ_B is large, the fluctuations of the quantity B are also large. This is precisely what happens at a critical point (see lectures on critical phenomena and renormalization group). At a critical point, $T = T_c$ (critical temperature) where the system experiences a continuous transition, the susceptibility diverges. If B corresponds to the magnetization M , this means that the magnetic fluctuations are large.

¹We use

$$\frac{\partial x}{\partial y} = \left[\frac{\partial y}{\partial x} \right]^{-1}$$

This approach is initially due to Einstein who proposed formula (515) for the probability of a fluctuation. The point of view we have developed in this section is the THERMODYNAMICS point of view where entropy is defined as the fundamental quantity. For a fluctuation, the thermodynamic entropy change is:

$$(520) \quad \Delta S = -\frac{C_V(\delta T)^2}{2T^2} - \frac{1}{2T\kappa_T} \frac{(\delta V)^2}{V} - \frac{\partial}{\partial N} \left(\frac{\mu}{T} \right) \frac{(\delta N)^2}{2}$$

In what follows, we will start from the microscopic point of view and derive directly the fluctuation dissipation theorem.

3. The fluctuation-dissipation theorem

Assume first that the system is in equilibrium at temperature T . The time-independent distribution is

$$(521) \quad \rho(p, q) = \frac{1}{Z} e^{-\beta H(p, q)}$$

where p, q are N momenta and positions. An equilibrium average of a dynamical variable $A(p, q)$ is taken as

$$(522) \quad \langle A \rangle = \int dpdq A(p, q) \rho(p, q)$$

Let us perturb the system with a time-independent potential V .

$$(523) \quad H \rightarrow H + V \text{ with } V = -fA$$

where f is a numerical factor controlling the strength of the perturbation. Thus, we can take the limit $f \rightarrow 0$ and apply this way a small perturbation. We limit ourselves to linear order in f . To order f , the new partition function is (by Taylor expanding the Boltzmann's factor)

$$(524) \quad Z(H + V) = \frac{Z}{Z} \int dpdq e^{-\beta H} (1 - \beta V) = Z(1 - \beta \langle V \rangle)$$

where $\langle \dots \rangle$ means average with respect to the UNPERTURBED Hamiltonian ($f = 0$).

Let us introduce a second dynamical variable $B(p, q)$. B is arbitrary. The TRUE average \bar{B} to first order in f is

$$(525) \quad \bar{B} = \frac{1}{Z(1 - \beta \langle V \rangle)} \int dpdq e^{-\beta H} (1 - \beta V) B(p, q)$$

$$(526) \quad = (1 + \beta \langle V \rangle) (\langle B \rangle - \beta \langle VB \rangle)$$

$$(527) \quad = \langle B \rangle + \beta (\langle B \rangle \langle V \rangle - \langle VB \rangle) = \langle B \rangle - \beta \langle VB \rangle_c$$

where we have identified the connected part

$$(528) \quad \langle VB \rangle_c = \langle VB \rangle - \langle V \rangle \langle B \rangle$$

The variation of B is therefore

$$(529) \quad \bar{B} - \langle B \rangle = -\beta \langle VB \rangle_c = \beta f \langle BA \rangle_c$$

The static susceptibility χ_{BA} is the derivative of the response $\bar{B} - \langle B \rangle$ with respect to f . We find

$$(530) \quad \chi_{BA} = \frac{\partial \bar{B}}{\partial f} = \beta \langle BA \rangle_c$$

This is the fluctuation-dissipation theorem². The response of the system to a perturbation is given by the connected part of the correlation function $\beta \langle BA \rangle_c$ with respect to the UNPERTURBED Hamiltonian. Expression (530) is very useful. We do not need to calculate the full partition function with a magnetic field which is generally not possible. It suffices to calculate the cumulant at zero field which is generally much more simpler.

²Or the fluctuation-response theorem

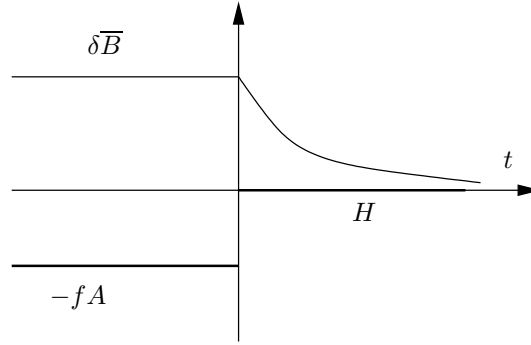


FIGURE 1. The magnetic field is switched off at $t = 0$ and the magnetization relaxes to zero.

EXERCICE 8.1. Suppose we wish to compute the electric susceptibility χ of an ideal gas of nonpolarizable dipolar molecules with dipole moment μ . Using an equivalent expression as (530), show that the polarization P_x along the field $\mathbf{E} = E_x \hat{\mathbf{u}}_x$ is (density = N/V)

$$(531) \quad P_x = \frac{N}{V} \frac{\mu^2}{3k_B T} E_x$$

4. The dynamical susceptibility and the fluctuation dissipation theorem

Let us now assume that the perturbation is applied at $t = -\infty$ but is switched off at $t = 0$, see Fig. 1. The question we are asking is as follows: How does the system relax back to equilibrium? The total Hamiltonian is therefore time-dependent

$$(532) \quad H_1(p, q) = \begin{cases} H_0(p, q) - fA(p, q) & \text{if } t < 0 \\ H_0(p, q) & \text{if } t > 0 \end{cases}$$

Again, the notation are standard. It may be useful to think of f as a magnetic field H and of $B = A$ as the magnetization M .

For convenience, we may assume that the average of B in the unperturbed system vanishes. To understand how $\langle B(t) \rangle$ relaxes to equilibrium on average, we must average over all initial conditions at $t = 0$ in phase space. An initial condition occur with probability $\propto \exp\{-\beta[-\beta(H_0 - fA(t=0))]\}$ and we average over all possible initial conditions at $t = 0$. If the system started at some point Γ in phase space at $t = 0$

$$(533) \quad \langle B(t) \rangle = \frac{\int d\Gamma \exp\{-\beta(H_0 - fA(t=0))\} B(t)}{\int d\Gamma \exp\{-\beta(H_0 - fA(t=0))\}}$$

where $B(t)$ depends on the initial conditions (the time evolution of $B(t)$ will be given by the Langevin equation in the next chapter). In the limit of a small perturbation, we can write

$$(534) \quad \langle B(t) \rangle = \beta f \frac{\int d\Gamma \exp\{-\beta H_0\} A(0) B(t)}{\int d\Gamma \exp\{-\beta H_0\}}$$

or (if $\langle B(t) \rangle_0$ in the unperturbed system does not vanish)

$$(535) \quad \langle B(t) \rangle - \langle B(t) \rangle_0 = \beta f \langle B(t) A(0) \rangle_c$$

The key point is that this correlation describes the decay of a spontaneous fluctuation in B at equilibrium, since the average is done with respect to the unperturbed Hamiltonian.

The function $\langle B(t) A(0) \rangle_c$ is known as a Kubo function. In the limit where t goes to infinity, $B(t)$ is not correlated with $A(0)$ and the correlation function must tend to 0:

$$(536) \quad C_{BA}(t) = \langle B(t) A(0) \rangle_c \rightarrow 0 \text{ as } t \rightarrow \infty$$

EXAMPLE 4.1. Consider one again the example of a dipolar molecule in an electrical field \mathbf{E} . The perturbation is $-E_x P_x$. When the field is switched off, this dipole moment decays as

$$(537) \quad \langle P_x(t) \rangle = \beta E_x \langle P_x(0) P_x(t) \rangle$$

In other words, the systems returns to equilibrium in a way that the derivative of the observable $\delta \bar{B}$ with respect to f is proportional to the unperturbed correlation function. This is the essence of the Onsager regression hypothesis. The system can be brought out of equilibrium either by adding a small magnetic field or because of a small random fluctuations. The system goes back to equilibrium in the same way for both processes.

To connect this correlation function with the dynamical susceptibility, we recall the general definition of the susceptibility

$$(538) \quad \langle \delta B \rangle = \langle B(t) \rangle - \langle B(t) \rangle_0 = \int_{-\infty}^t dt' \chi_{BA}(t-t') f(t')$$

In the a situation similar as before, where the field is switched off at $t = 0$, this expression becomes

$$(539) \quad \langle \delta B(t) \rangle = f \int_{-\infty}^0 dt' \chi_{BA}(t-t') = f \int_t^{\infty} dt' \chi_{BA}(t')$$

Taking the time-derivative, we get using (535)

$$(540) \quad \frac{d\delta \bar{B}}{dt} = \beta f \dot{C}_{BA}(t) = \begin{cases} -f \chi_{BA}(t) & \text{for } t > 0 \\ = 0 & \text{otherwise} \end{cases}$$

where the last equality comes from the fact that $\langle B \rangle$ is constant for $t < 0$.

This equation can be rewritten as

$$(541) \quad \chi_{BA}(t) = -\beta \theta(t) \dot{C}_{BA}(t) = -\beta \theta(t) \langle A(0) \dot{B}(t) \rangle_c$$

This is the most general form we can get. The dynamical response function is connected to the time derivative of a correlation function.

To make things simpler, let us take $B = A$. From time translational invariance : $\langle A(t)A(0) \rangle = \langle A(0)A(-t) \rangle = \langle A(-t)A(0) \rangle$. Therefore, $C(t) = \langle A(0)A(t) \rangle_c$ is an even function of t and its derivative is an odd function of t . This is precisely the definition of $\chi_o(t)$. Recall

$$(542) \quad \chi_o(t) = \frac{1}{2} (\chi(t) - \chi(-t))$$

which means

$$(543) \quad \chi(t) = 2\theta(t)\chi_o(t)$$

the Fourier transform of $\chi_o(t)$ is $i\tilde{\chi}''(\omega)$ After Fourier transforming (616), we arrive at

$$(544) \quad \tilde{\chi}''(\omega) = \frac{1}{2} \beta \omega \tilde{C}(\omega)$$

Since the odd part of $\chi(t)$ is related to energy dissipation, energy dissipation is also related to Kubo correlation function (i.e. a fluctuation). The usefulness of (616) is that we have a microscopic equation to calculate the susceptibility (it is enough to calculate the correlation function to get the imaginary part of the susceptibility. Then, we apply the Kramer-Kronig relationship to get the real part).

EXERCICE 8.2. To give a specific example, consider the mobility of a molecule in an external field F_x . The steady-state velocity is $v_x = \mu F_x$.

- (1) What is the perturbed Hamiltonian ?

(2) Using our the preceding discussion, show

$$(545) \quad \langle v_x(t) \rangle = F_x \int_0^\infty d\tau \chi_{v_x, x}(\tau)$$

Use stationarity for the correlation function to show

$$(546) \quad \frac{d}{dt} \langle A(t)B(t+t') \rangle = 0$$

and find

$$(547) \quad \mu = \beta \int_0^\infty dt \langle v_x(0)v_x(t) \rangle$$

EXERCICE 8.3. Consider an isolated system consisting of two parts. A left part and a right part (these parts communicate arbitrarily). Let $N_R(t)$ be the number of particles in the right part of the system and we consider the following total energy

$$(548) \quad E = E_0 - V(t)N_r(t)$$

if the potential $V(t)$ varies over time, this leads to a variation in the number of particles $N_R(t)$ in the right part of the system. Recall the fluctuation dissipation theorem

$$(549) \quad C_{AB}(t) = kT \int_t^{+\infty} \chi_{AB}(t') dt'$$

Assume that the system is in equilibrium for $t < 0$ with $V(t = 0)$ and that $V(t)$ is suddenly increased at $t = 0$ to a constant value V

$$(550) \quad V(t) = \begin{cases} 0 & \text{for } t < 0 \\ V & \text{for } t > 0 \end{cases}$$

- (1) Apply linear response theory and give a general expression for $\langle N_R(t) \rangle_V - \langle N_R(t) \rangle_0$.
- (2) By computing the difference

$$(551) \quad \int_0^\infty \chi(t') dt' - \int_t^\infty \chi(t') dt'$$

show

$$(552) \quad \langle N_R(t) \rangle_V - \langle N_R(0) \rangle_V = \frac{\beta V}{2} \langle (N_R(t) - N_R(0))^2 \rangle_0$$

5. The electrical conductivity

The question is how do we calculate the electrical conductivity. But there is a problem. If we switch on an electrical field, we put the system in a non-equilibrium stationary state and the preceding analysis does not apply (recall that if we switch on a magnetic field, we assume that the system reaches equilibrium so that we can calculate the magnetization using a partition function. If the system is out of equilibrium, this approach makes no sense, since there is no partition function for non equilibrium systems). The trick is to switch on/off a weak uniform vector potential \mathbf{A} . The Hamiltonian becomes

$$(553) \quad H = \sum_{i=1, N} \frac{1}{2m} \left(p_i - \frac{e}{c} A \right)^2$$

The system will be in equilibrium. If we abruptly switch off the vector potential \mathbf{A} , we generate an electrical field recall, that there is no electrical potential)

$$(554) \quad \mathbf{E} = -\frac{1}{c} \dot{\mathbf{A}}$$

so that \mathbf{E} will be an "infinitesimal" delta function in time.

To first order in A , the Hamiltonian reads as

$$(555) \quad \begin{aligned} H &= H_0 - \frac{\mathbf{A}}{c} \int d^d r \sum_{i=1, N} \frac{e}{m} \mathbf{p}_i \delta(r_i - r) \\ &= H_0 - \frac{\mathbf{A}}{c} \int d^d r \mathbf{j}(\mathbf{r}) \end{aligned}$$

This is the same kind of formula as before (see (532)), except that we have now an integral over the volume V

From this, it follows that the average current density at time t due to perturbation theory is given by

$$(556) \quad \langle \mathbf{j}(t) \rangle = \frac{\mathbf{A}}{cV k_B T} \iint d^d r d^d r' \langle \mathbf{j}(\mathbf{r}, 0) \mathbf{j}(\mathbf{r}', t) \rangle$$

where we have divided by the volume to get an extensive quantity. To calculate the electrical conductivity $\sigma(t - t')$, we notice that

$$(557) \quad \begin{aligned} \langle j(t) \rangle &= \int_{-\infty}^t \sigma(t - t') \mathbf{E}(t') \\ &= \sigma(t) \frac{\mathbf{A}}{c} \end{aligned}$$

since

$$(558) \quad E = \frac{A}{c} \delta(t)$$

when the potential vector is switched off (we take the derivative of $-\theta(t)$). From this it immediately follows that

$$(559) \quad \sigma(t) = \frac{1}{V k_B T} \iint d^d r d^d r' \langle j(\mathbf{r}, 0) j(\mathbf{r}', t) \rangle$$

6. The Liouville equation

It will be useful for the following (linear response theory in the general case) to recall some definitions. The dynamics of a classical systems is governed by Hamilton's equations (or equivalent)

$$(560) \quad \dot{p} = -\frac{\partial H}{\partial q} \quad \dot{q} = \frac{\partial H}{\partial p}$$

We are often interested in how functions of coordinates and momentum change in time. This the case for the probability density in phase space which is a function of p and q . If the quantity of interest is A , then

$$(561) \quad \frac{dA}{dt} = \frac{\partial A}{\partial t} + \dot{p} \frac{\partial A}{\partial p} + \dot{q} \frac{\partial A}{\partial q}$$

or

$$(562) \quad \frac{dA}{dt} = \frac{\partial A}{\partial t} + \{A, H\}$$

where we have defined the Poisson bracket

$$(563) \quad \{A, B\} = \frac{\partial B}{\partial p} \frac{\partial A}{\partial q} - \frac{\partial A}{\partial p} \frac{\partial B}{\partial q}$$

Eq. (562) strongly resembles the Heisenberg form for the time dependence of a quantum mechanical operator, the main change being the replacement of the Poisson bracket by a commutator. Specifically,

$$(564) \quad \{ \quad , \quad \} \rightarrow \frac{[\quad , \quad]}{i\hbar}$$

So we define the Liouville operator

$$(565) \quad iL(t)A = \begin{cases} \{A, H(t)\}, & \text{classical} \\ \frac{[A, H(t)]}{i\hbar}, & \text{quantum.} \end{cases}$$

If A does not explicitly depend on time, the general (formal) solution of the equation of motion is

$$(566) \quad A(t) = A(t=0)e^{iLt}$$

where

$$(567) \quad e^{iLt} = \sum_n \frac{i^n L^n}{n!} t^n$$

As a last point, recall the Liouville theorem: One starts with a phase space in which values of momentum p and position q specify a phase point. The number density of systems at the location (p, q) at time t is $f(p, q, t)$. For example, $f(p, q, t)d^3pd^3q$ gives the number of particles with positions within d^3q of q and momenta within d^3p of p . From the distribution f , one can compute things like the particle current J , and the energy current J_e :

$$(568) \quad \begin{aligned} J(q, t) &= \int d^d p f(q, p, t) \frac{p}{m} \\ J_e(q, t) &= \int d^d p f(q, p, t) \epsilon(p) \frac{p}{m} \end{aligned}$$

Systems, particles or molecules cannot be neither created or destroyed, so the probability density f satisfies a conservation law, in which $\partial f / \partial t$ is minus the divergence of a flux vector:

$$(569) \quad \frac{\partial f}{\partial t} = -\nabla \cdot \mathbf{J} = -\frac{\partial J_p}{\partial p} - \frac{\partial J_q}{\partial q}$$

The six-dimensional flux vector $\mathbf{J} = (J_p, J_q)$ is the product $f\dot{u}$ of the number density f and a velocity u in a six dimensional space:

$$(570) \quad u = (\dot{x}, \dot{y}, \dot{z}, \dot{p}_x, \dot{p}_y, \dot{p}_z)$$

and ∇ is also a six-dimensional phase space vector

$$(571) \quad \nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}, \frac{\partial}{\partial p_x}, \frac{\partial}{\partial p_y}, \frac{\partial}{\partial p_z} \right)$$

From this continuity equation and from the Hamilton equations, it is easy to show that f is constant, i.e.

$$(572) \quad \frac{df}{dt} = 0 \text{ or } \frac{\partial f}{\partial t} = -iL(t)f(t)$$

7. Divertimento : The Schmoluchowsky equation

It is interesting to use the continuity equation (569) to recover Boltzmann's law in two lines. We consider the case where we apply an external potential $\phi(x)$, so that the force on a brownian particle is $-\nabla\phi$. To go further, we also assume that we are not interested in the momenta of the particles, so that we work with the distribution $f(x)$ alone. In other words, we work with

$$(573) \quad f(x) = \int dp f(x, p)$$

where, for simplicity, the system is one-dimensional.

If this force derive from a potential $\phi(x)$, the current is the sum of the usual drift term and a mobility term

$$(574) \quad J = -\mu f(x)\nabla\phi - D\nabla f$$

where the mobility μ is yet undetermined. Eq. (574) is a constitutive equation in the sense that it is an approximation valid in the linear regime. It says that the current is the sum of two terms: one to remove all density fluctuations in space (by diffusion) and an other one which tells us that things move if we apply a field.

As before, conservation of probability requires

$$(575) \quad \frac{\partial f}{\partial t} = \nabla \cdot J$$

and translates into

$$(576) \quad \frac{\partial f}{\partial t} = \frac{\partial}{\partial x} [-\mu f(x) \nabla \phi - D \nabla f]$$

Assuming stationarity

$$(577) \quad \begin{aligned} -\mu f(x) \nabla \phi - D \nabla f &= 0 \\ \text{or } \frac{df}{dx} &= -\frac{\mu}{D} \frac{d\phi}{dx} f(x) \end{aligned}$$

whose solution is given by

$$(578) \quad f(x) = \frac{1}{Z} e^{-\frac{\mu}{D} \phi(x)}$$

where Z is some normalization constant. Remark that we have made no statement concerning equilibrium and we have only hypothesized that the process is stationary. If the process at equilibrium, we recover the Boltzmann's distribution if the Einstein relation holds

$$(579) \quad \frac{\mu}{D} = \frac{1}{kT}$$

Although this derivation is general, it is interesting to state clearly the hypotheses tacitly made to get (576). Since the probability $f(x, t)$ does depend only on the position and not on the speed, we have tacitly assumed that the speed relaxes very fast to some local equilibrium. Actually, (576) is only valid in the strong friction limit.

8. Time-dependent perturbation

We focus on the distribution function $f(p, q)$ (or the density matrix). For what follows, we write the Hamiltonian as

$$(580) \quad H(t) = H_0 + H_1(t)$$

and the Liouville operator becomes:

$$(581) \quad L(t) = L_0 + L_1(t)$$

where H_0 is the time independent part of the Hamiltonian which governs the equilibrium part and where $H_1(t)$ is responsible for taking the system out of equilibrium, and as such, is time-dependent. In addition, we make two assumptions:

(1) We start from equilibrium in the distant past:

$$(582) \quad \text{As } t \rightarrow -\infty, H_1(t) \rightarrow 0 \quad f(t) \rightarrow \propto e^{-\beta H_0}$$

(2) $H_1(t)$ is always small enough such that perturbation is valid.

The perturbation is switched on adiabatically (meaning in a very smooth way), so that the system is stationary $df/dt = 0$. This means:

$$(583) \quad \frac{\partial f}{\partial t} = -iL(t)f(t)$$

with solution:

$$(584) \quad f(t) = f_{eq} - \int_{-\infty}^t ds e^{-iL_0(t-s)} iL_1(s) f(s)$$

This can be checked by direct substitution. Eq. (584) is an integral equation for $f(t)$, since $f(t)$ appears on both sides. To find the solution as a series, we iterate this equation

$$(585) \quad f(t) = f_{eq} - \int_{-\infty}^t ds e^{-iL_0(t-s)} iL_1(s) \left[f_{eq} - \int_{-\infty}^s ds_1 e^{-iL_0(t-s_1)} iL_1(s_1) \right]$$

and so on. Iterating one more time, we see that we get a power series in $L_1(t)$. In particular, stopping at the linear order

$$(586) \quad f(t) = f_{eq} - \int_{-\infty}^t ds e^{-iL_0(t-s)} iL_1(s) f_{eq}(s)$$

9. Kubo relationship

To compute the conductivity as a correlation function, we shall use the quantum mechanical approach. In quantum mechanics, the average of an operator is computed by taking the trace

$$(587) \quad \langle B(t) \rangle = Tr(Bf(t))$$

Hence,

$$(588) \quad \langle B(t) \rangle - \langle B \rangle_{eq} = - \int_{-\infty}^t \frac{ds}{i\hbar} Tr(B e^{-iH_0(t-s)/\hbar} [f_{eq}, H_1(s)] e^{iH_0(t-s)/\hbar})$$

where we have expressed the quantum mechanical Liouville operator, $e^{-iL_0 t}$, in terms of the quantum mechanical operators, $e^{-iH_0 t/\hbar}$.

The trace is invariant to cyclic permutations

$$(589) \quad Tr(ABC) = Tr(BCA) = Tr(CAB)$$

and we use the Heisenberg representation

$$(590) \quad B(t) = e^{iL_0 t} B = e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}$$

It follows that

$$(591) \quad \langle B(t) \rangle - \langle B \rangle_{eq} = - \int_{-\infty}^t \frac{ds}{i\hbar} (B(s-t) [f_{eq}, H_1(s)])$$

$$(592) \quad = \int_{-\infty}^t ds \frac{\langle [B(s-t), H_1(s)] \rangle_{eq}}{i\hbar}$$

In order to proceed, we have to specify the form of the perturbation. A general form is

$$(593) \quad H_1(t) = - \int d^d r A(r) F(r, t)$$

where A represents things like particle densities, charge densities etc. $F(t)$ represents fields like electrical, gravitational or magnetic fields. To simplify our notations, we write

$$(594) \quad H_1(t) = -A \star F$$

to get rid of the volume integral.

We have

$$(595) \quad \langle B(t) \rangle - \langle B \rangle_{eq} = \int_{-\infty}^t ds \frac{i}{\hbar} \langle [B(s-t), A] \rangle_{eq} \star F(s)$$

Again, we can make the standard correspondence

$$(596) \quad \frac{1}{i\hbar} [\dots, \dots] \rightarrow \{\dots, \dots\}$$

$$(597) \quad \langle B(t) \rangle - \langle B \rangle_{eq} = - \int_{-\infty}^t ds \langle \{B(s-t), A\} \rangle_{eq} \star F(s)$$

$$(598) \quad = -\beta \int_{-\infty}^t ds \langle \{B(s-t), H_0\} A \rangle_{eq} \star F(s)$$

$$(599) \quad = -\beta \int_{-\infty}^t ds \langle \dot{B}(s-t) A \rangle_{eq} \star F(s)$$

which means that the dynamical susceptibility is a correlation function .

10. Time-inversion symmetry

Under time-inversion symmetry:

$$(600) \quad I(p, q) = (-p, q)$$

and observable have symmetries:

$$(601) \quad A(I(x)) = \epsilon_A A(x) \quad \epsilon_A = \pm 1$$

If the Hamiltonian is time-reversal symmetric, then

$$(602) \quad C_{BA}(t) = \langle \delta B(t) \delta A(0) \rangle_{eq} = \epsilon_B \epsilon_A \langle \delta B(-t) \delta A(0) \rangle_{eq} = \epsilon_B \epsilon_A C_{BA}(-t)$$

11. Quantum linear response theory

The quantum case is more technical. Operators, however, do not commute. For this reason, correlation functions are defined through a commutator

$$(603) \quad \chi''_{BA}(t) = \frac{1}{2} \langle [B(t), A(0)] \rangle$$

and the dynamical susceptibility is

$$(604) \quad \chi_{BA}(t) = -i\theta(t) \langle B(t), A(0) \rangle$$

where $A(t)$ is written on the Heisenberg picture

$$(605) \quad A(t) = e^{iHt/\hbar} A(0) e^{-iHt/\hbar}$$

Averages are taken with respect the Hamiltonian by taking the trace.

The relationship between the dissipation and the correlation function is different from the classical case

$$(606) \quad \tilde{\chi}''_{BA}(\omega) = \frac{1}{2\hbar} (1 - e^{-\hbar\omega/(k_B T)}) \langle B(t) A(0) \rangle_c$$

EXERCICE 8.4. A Green-Kubo formula is a relationship between a transport coefficient and a correlation function at equilibrium. Time correlation functions play the same role as the equilibrium partition function, meaning that we can calculate the transport coefficients if we know how to calculate the auto-correlation functions. This may me difficult, but we know how to start. Correlation functions are measurable in experiments and in numerical simulations, see Fig. 2.

- (1) Consider Fig. 2. Draw on the same figure the velocity auto-correlation function for a perfect gaz.
- (2) Consider a Brownian particle. We define the diffusion coefficient from the second moment of the displacement as

$$(607) \quad D = \lim_{\Delta t \rightarrow 0} \frac{1}{6} \frac{\langle \Delta \mathbf{R}^2 \rangle}{\Delta t}$$

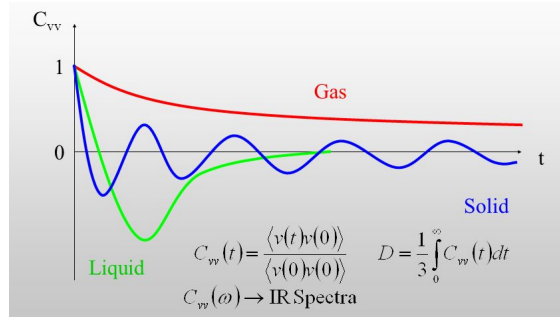


FIGURE 2. Velocity auto-correlation functions for a gaz, a liquid and solid.

Replace the displacement by a time integral of the velocity

$$(608) \quad \Delta \mathbf{R} = \int_0^{\Delta t} ds \mathbf{v}(s)$$

- (3) Change the variable $\tau = s - s'$. Do one of the integral and show that the diffusion coefficient is

$$(609) \quad D = \frac{1}{3} \int_0^{\Delta t} ds \langle \mathbf{v}(0) \cdot \mathbf{v}(s) \rangle$$

EXERCICE 8.5. Diffusion noise refers to the resistance fluctuations caused by a diffusion process and is measured through voltage fluctuations in the presence of a constant applied current (or Vice versa), i.e., in the configuration where $1/f$ noise is usually observed. The measured quantity is proportional to

$$(610) \quad S(\omega) = \int_0^{\infty} dt \cos(\omega t) \frac{\langle \Delta N(t) \Delta N(0) \rangle}{N^2}$$

where N^2 is the square of the number of carriers enclosed within the electrodes, while $\Delta N(t)$ is the fluctuation of diffusing quantities averaged over sites enclosed by the electrodes. Assume that the region of interest has size L and define densities as

$$(611) \quad N(t) = \int d^d \mathbf{x} n(\mathbf{x}, t)$$

For the fluctuations $\delta n(\mathbf{x}, t)$, we define the Fourier transforms in the usual way

$$(612) \quad \delta \tilde{n}(\mathbf{k}, \omega) = \int d^d \mathbf{x} dt e^{-i\mathbf{k} \cdot \mathbf{x}} \delta n(\mathbf{x}, t)$$

- (1) Assuming that the field $n(\mathbf{x}, t)$ is a diffusing field with diffusion constant D , show that

$$(613) \quad \delta \tilde{n}(\mathbf{k}, \omega) = -\frac{1}{i\omega + Dk^2}$$

- (2) Assume that the auto correlation function obeys ³

$$(614) \quad \langle \delta n(\mathbf{x}, t) \delta n(\mathbf{x}', t') \rangle = k_B T \chi \delta^{(d)}(\mathbf{x} - \mathbf{x}')$$

What is $\langle \delta \tilde{n}(\mathbf{k}, t) \delta \tilde{n}(\mathbf{k}', t) \rangle$?

- (3) Assume stationarity. What is $\langle \delta \tilde{n}(\mathbf{k}, \omega) \delta \tilde{n}(\mathbf{k}', \omega') \rangle$?

³Remember $\delta^{(d)}(\mathbf{x} - \mathbf{x}') = \delta(x - x') \delta(y - y') \delta(z - z')$. Since δ -functions do not exist nature, $\delta(x - x')$ means a peaked function with a width much smaller than other length scale in the problem.

(4) Show that

$$(615) \quad S(\omega) = \int \frac{d^d k}{(2\pi)^d} |g(k)|^2 \frac{k^2 D}{\omega^2 + Dk^2}$$

and determine $g(k)$.

EXERCICE 8.6. Following our discussion, we have found that the response function $\chi_{AB}(t)$ in terms of the fluctuating quantities δA and B is

$$(616) \quad \chi_{AB}(t) = -\beta \frac{d}{dt} \langle B(0) \delta A(t) \rangle_0$$

where $\langle \rangle_0$ refer to thermodynamic average to the unperturbed equilibrium system. Here we prove this relation in a simple case.

Consider the motion of a particle in a viscous fluid. Here, the perturbing field can be taken to be an external force applied to the particle. The response of the system is to develop a drift velocity v . Assume that the system is one-dimensional in the direction of the force (say x).

(1) What is the perturbed hamiltonian ?

(2) What is the most general expression for the ensemble average drift velocity $v(t)$ in terms of susceptibility $\chi_{vx}(t)$?

(3) From time translation symmetry, we know that

$$(617) \quad \langle x(0)v(t) \rangle_0 = \langle x(t')v(t+t') \rangle_0$$

which cannot depend on t' . Use this to show that

$$(618) \quad \frac{d}{dt} \langle x(t')v(t+t') \rangle_0 = - \langle v(t')v(t+t') \rangle_0$$

(4) We will see in the next chapter that $D = \mu kT$, where μ is the mobility. Use a Green-Kubo formula and prove (616).

CHAPTER 9

NON-EQUILIBRIUM THERMODYNAMICS

1. The Onsager regression principle

The Lars Onsager's regression hypothesis states the regression of microscopic thermal fluctuations at equilibrium follows the macroscopic law of relaxation of small non-equilibrium disturbances¹.

In order to understand this hypothesis, consider an observable A for a system in thermal equilibrium. The instantaneous value of A fluctuate in time with spontaneous microscopic fluctuations:

$$(619) \quad \delta A(t) = A(t) - \langle A \rangle$$

The average correlation between $\delta A(t)$ and the instantaneous fluctuation at time zero $\delta A(0)$ is described by the correlation function

$$(620) \quad C(t) = \langle \delta A(t) \delta A(0) \rangle = \langle A(t) A(0) \rangle - \langle A \rangle^2$$

where $\langle \dots \rangle$ represents the equilibrium average. For large t , $C(t)$ vanishes

$$(621) \quad \lim_{t \rightarrow \infty} C(t) = 0$$

since $\delta A(t)$ becomes uncorrelated to $\delta A(0)$.

To formulate the Onsager hypothesis, we apply an external force f which acts during the time interval $t < 0$ but becomes identically zero for $t > 0$.

For $t \leq 0$, the ensemble average (assume $\langle A \rangle = 0$ for $f = 0$) of ΔA

$$(622) \quad \Delta A = \frac{\langle A e^{-\beta(H-fA)} \rangle}{\langle e^{-\beta(H-fA)} \rangle} \simeq \beta f [\langle A(0) A(0) \rangle - \langle A(0) \rangle^2] = \beta f C(0)$$

where $\langle \rangle$ means doing all the appropriate integrals in phase space.

For $t > 0$, the system evolves according to H instead of $H - fA$, so δA acquires a time dependence

$$(623) \quad \Delta A(t) = \frac{\langle A e^{-\beta(H-fA)} \rangle}{\langle e^{-\beta(H-fA)} \rangle} \simeq \beta f [\langle A(t) A(0) \rangle - \langle A(0) \rangle^2] = \beta f C(t)$$

This decays of correlations is the regression of microscopic thermal fluctuations referred to as the Onsager's hypothesis. Therefore, Onsager's regression hypothesis can be formulated as follows

$$(624) \quad \frac{\Delta A(t)}{\Delta A(0)} = \frac{C(t)}{C(0)}$$

¹There is no such hypothesis in the quantum case. This section applies only to the classical case

x_i	E	V	N	M
X_i	-1	$-p$	μ	B

TABLE 1. Examples of extensive variables - generalized force pairs, i.e. conjugate variables.

This property which derives from linear response theory was conjectured some twenty years (1931) before it was proven to be true is referred as the Onsager regression principle.

To show this property in more details, we will need two things:

- (1) An equation for the regression of the fluctuations. This equation is equivalent to the Langevin equation we will see in the next chapter. A short summary is as follows. Given a set of EXTENSIVE variables $\{a_i\}_{i=1,2,\dots}$, the return to equilibrium of these extensive variables is given by phenomenological laws:

$$(625) \quad \frac{da_i}{dt} + \sum_j G_{ij} a_j = 0$$

where $G_{i,j}$ is the regression matrix. Then we reinterpret (625) as regression equations for the average behaviour

$$(626) \quad \frac{d\langle a_i \rangle}{dt} + \sum_j G_{ij} \langle a_j \rangle = 0$$

The microscopic fluctuations of the a_i 's are described by the stochastic equations

$$(627) \quad \frac{da_i}{dt} + \sum_j G_{ij} a_j = F_i(t)$$

where the random Gaussian forces are determined from the condition of equilibrium.

- (2) The assumption of time reversal symmetry, see next paragraph.

2. Entropy production and generalized current and force

In non-equilibrium systems, entropy is produced. The question is to relate this entropy production to gradients in thermodynamic parameters (temperature, chemical potential). As before, we will limit ourselves to non-equilibrium systems that are sufficiently close to equilibrium and that the macroscopic intensive variables (pressure, temperature, chemical potential, scalar and vector potentials) are well defined quantities locally. In equilibrium these variables are constant throughout the system. We will consider a situation where a spatial gradient in these quantities is maintained resulting in currents of the appropriate density variables.

Intensive variables are conjugate to extensive variables (densities) through the differential form of the entropy:

$$(628) \quad ds = \frac{1}{T} de - \frac{1}{T} \sum_i X_i d\xi_i - \frac{1}{T} \sum_j \mu_j dn_j = \sum_k \phi_k d\rho_k$$

where e is the energy density, X_i a generalized force and μ_j the chemical potential of species j (see table 1. For example, if \mathbf{l} is a specific deformation vector, elasticity gives a term of the form $\mathbf{f} \cdot d\mathbf{l}$ in (628) to represent the rate of doing reversible work.

A key assumption in irreversible thermodynamics is to assume that the relationship between the entropy s and the extensive variables ρ_k is locally the same as for an equilibrium system, see (628). To derive a model for this, we divide the system into elementary cells of size λ . In a gas, λ is of the order of the mean free path. Each elementary cell interacts with its environment, but we can define within each cell a uniform temperature or a uniform density, so that a local entropy can be defined in the usual way, see (628). This assumption is generally valid if changes in extensive quantities due to gradients in conjugates forces are less than changes due a typical fluctuation.

What happens if we vary spatially the ϕ_k 's? We assume that there is a conservation law for each density ρ_k so that:

$$(629) \quad \frac{\partial \rho_k}{\partial t} = -\nabla \cdot \mathbf{j}_k$$

For what follows, it will be useful to define an entropy current density as:

$$(630) \quad j_s = \sum_k \phi_k \mathbf{j}_k$$

where the ϕ_k 's are the same as in (628) and where the sum runs over all extensive variables.

The rate of change in entropy density is the sum of the changes due to the currents and due to the time varying variables:

$$(631) \quad \frac{ds}{dt} = \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{J}_s$$

where

$$(632) \quad \frac{\partial s}{\partial t} = \sum_k \phi_k \frac{\partial \rho_k}{\partial t}$$

is the key concept of RATE OF ENTROPY PRODUCTION.

Therefore, using (629), the total rate of change in entropy is

$$(633) \quad \frac{ds}{dt} = \sum_k \mathbf{j}_k \cdot \nabla \phi_k$$

which allows to identify the current densities and the force fields $\nabla \phi_k$. Note that the rate of entropy production is proportional to the gradient in the ϕ_k 's. This can be understood if we interpret the gradient in ϕ_k as the discrete difference in ϕ_k . To get a current through a cell, we must apply a voltage drop, i.e. a difference in voltage between the two sides. If we define the affinities \mathcal{F}_k , this relation can be rewritten as

$$(634) \quad \frac{ds}{dt} = \sum_k \mathbf{j}_k \cdot \mathcal{F}_k$$

where the affinities are gradients of local intensive variables (affinity is a term one finds in the literature, this is why we define it here).

To go further, we must assume a relationship between the current and the generalized force. As for Ohm's law (electrical conductivity) and Fick's law (diffusion), we assume as in linear response theory that this relationship is linear

$$(635) \quad j_i(\mathbf{r}, t) = \sum_k L_{ik} \nabla \phi_k(\mathbf{r}, t) + O(\phi_k^2)$$

These equations are said to be constitutive equations and the set of L_{ik} are kinetic coefficients. Note that this is the same linear relation as in the linear response theory and that this is the most general relation: We retain direct effects $\phi_i(\mathbf{r}, t) \rightarrow j_i(\mathbf{r}, t)$ as well as indirect effects $\phi_k(\mathbf{r}, t) \rightarrow j_i(\mathbf{r}, t)$, $k \neq i$.

The assumption of microscopic reversibility proposed by Onsager leads to Onsager reciprocity relations

$$(636) \quad L_{ik}(\mathbf{B}, \boldsymbol{\Omega}) = L_{ki}(-\mathbf{B}, -\boldsymbol{\Omega})$$

with \mathbf{B} being the magnetic field (odd under time reversal) and $\boldsymbol{\Omega}$ being the angular velocity. The proof of these relations rest on the principle of microscopic reversibility we detail in the following.

3. Symmetries and Onsager Relations

The Onsager symmetry relationships are remarkable. If we apply temperature gradients to a three-dimensional sample ($\partial T/\partial x_1, \partial T/\partial x_2, \partial T/\partial x_3$), then we will observe an electrical current with components

$$(637) \quad J_i = - \sum_{k=1,3} L_{i,k} \frac{\partial T}{\partial x_k}$$

There are a priori 9 independent coefficients $L_{i,k}$. One may think as usual that the crystallographic symmetries may reduce the number of independent components to a smaller number. The symmetry relations $L_{i,k} = L_{k,i}$ have however nothing to do with these symmetries. There are due to time reversal symmetry.

4. Phenomenological equations

It is useful to consider simple cases. In the absence of matter flow, temperature diffuses according to Fourier's law

$$(638) \quad J_u = -\kappa \nabla T$$

where κ is the thermal conductivity. This relation applies to insulating materials where heat conduction corresponds to the movement of phonons. In this case the number of phonons is not conserved and $\mu = 0$. This may be written as

$$(639) \quad J_u = \kappa T^2 \nabla(1/T)$$

so that

$$(640) \quad \kappa = \frac{1}{T^2} L_{u,u}$$

In the absence of heat flow, Fick's law for diffusion is usually written as

$$(641) \quad J_n = D \nabla n$$

where n is the density. This relation can just be written as

$$(642) \quad J_n = L_{n,n} \nabla \mu / T$$

where D' is a function of state parameter, but not of their gradient. To see this, assume a uniform system at uniform temperature. To linear order

$$(643) \quad \nabla \mu = \left. \frac{\partial \mu}{\partial n} \right|_T \nabla n$$

so that

$$(644) \quad D = \frac{1}{T} \left. \frac{\partial \mu}{\partial n} \right|_T L_{n,n}$$

In the general case where we have both a temperature gradient and an electrical current, we write for the energy current and for the electrical current

$$(645) \quad \begin{aligned} J_u &= L_{u,u} \nabla(1/T) + L_{u,n} \nabla(-\mu/T) \\ J_n &= L_{n,u} \nabla(1/T) + L_{n,n} \nabla(-\mu/T) \end{aligned}$$

with the symmetry relation

$$(646) \quad L_{u,n} = L_{n,u}$$

as experimentally demonstrated by Thomson in 1854. In (645), the chemical potential includes the electrostatic potential $\phi(\mathbf{r})$ (charge q)

$$(647) \quad \mu = \mu(\phi = 0) + q\phi(\mathbf{r})$$

so that at constant temperature for a uniform distribution of particles

$$(648) \quad J_n = L_{n,n} \nabla\left(-\frac{\mu}{T}\right)$$

We conclude that the electrical conductivity σ is related to the kinetic coefficient

$$(649) \quad \sigma = \frac{q^2}{T} L_{n,n}$$

where we have used the fact that the current density j is related to particle current j_n by $j = qj_n$ with $j = \sigma E$.

Using now the continuity equations, the rate of entropy production may now be written:

$$(650) \quad \frac{\partial s}{\partial t} = J_u \cdot \nabla(1/T) + J_\rho \cdot \nabla(-\mu/T) = \sum_{\alpha} J_{\alpha} \nabla \phi_{\alpha}$$

or equivalently

$$(651) \quad \frac{\partial s}{\partial t} = \sum_{\alpha, \beta} L_{\alpha, \beta} (\nabla \phi_{\alpha}) \cdot (\nabla \phi_{\beta}) > 0$$

5. Microscopic reversibility

Let us consider the fluctuations in two extensive variables, i.e. densities, we will note α_1 and α_2 . The principle of microscopic reversibility states that the condition probability distribution obeys the following rule:

$$(652) \quad P(\alpha_1, t + \Delta t | \alpha_2, t) = P(\alpha_2, t + \Delta t | \alpha_1, t)$$

Since conditional probabilities are equivalent to correlation functions, an equivalent assumption is

$$(653) \quad \langle \alpha_1(t + \Delta t) \alpha_2(t) \rangle = \langle \alpha_2(t + \Delta t) \alpha_1(t) \rangle$$

To see that this is very plausible, assume with Onsager² an abstract process where the $\alpha_{1,2}$'s are related to the moments of the energy density which fluctuate in time (d is the dimension of space)

$$(654) \quad \alpha_i = \int d^d r r_i \epsilon(r) \quad i = 1, \dots, d$$

and the α_i 's measure the spatial asymmetry of a given distribution of energy density. For an homogeneous crystal, the α_i 's will fluctuate in time, but their mean is zero. For symmetry reasons their variance are equal:

$$(655) \quad \langle \alpha_1^2 \rangle = \langle \alpha_2^2 \rangle \quad \langle \alpha_1 \alpha_2 \rangle = 0$$

The principle of microscopic reversibility demands that a displacement α_1 in the r_1 direction at time t followed τ seconds later by a displacement α_2 in the r_2 direction occurs with the same probability that a displacement α_2 at time t followed by α_1 , τ second later. Energy being quadratic in the velocity, we see that this principle makes sense if we think that going from one process to the other amounts reversing the velocities, i.e. making the change $t \rightarrow -t$.

6. Onsager's relations follows from the principle microscopic reversibility

As before, we suppose that the state of the system is given by a complete set of extensive variables $\alpha_1(t), \alpha_2(t), \dots, \alpha_n(t)$. We follow the original paper of Onsager and Machlup¹⁴, so that we are forced to change notations (the α_i 's where denoted ρ_i 's before to emphasize the fact that one can define densities for extensive variables). As before, close to equilibrium, the entropy is given by the first two terms in the Taylor expansion of S :

$$(656) \quad S(\dots, \alpha_i, \dots) = S(\dots, \alpha_i = 0, \dots) + \frac{1}{2} \sum_{l, m} \frac{\partial^2 S}{\partial \alpha_l \partial \alpha_m} \Big|_{\forall \alpha_j = 0} \alpha_l \alpha_m$$

²Phys. Rev **15**, 405, 1931.

where we assume $\alpha_i = 0, \forall i$ at equilibrium with

$$(657) \quad \partial S / \partial \alpha_i \Big|_{\alpha_i=0} = 0$$

According to Einstein fluctuation theory (see previous chapter), the probability for the system to be in a state with specific values of these variables is

$$(658) \quad P(\alpha_1, \alpha_2, \dots, \alpha_n) = A \exp\{[S(\alpha_1, \alpha_2, \dots, \alpha_n)] / k_B T\}$$

where A is a normalization factor. We may expand $S(\alpha_1, \alpha_2, \dots, \alpha_n)$ to second order to get the probability to observe a set of fluctuations $\alpha_1, \alpha_2, \dots, \alpha_n$:

$$(659) \quad P(\alpha_1, \alpha_2, \dots, \alpha_n) = C \exp \left\{ \left[+ \frac{1}{2} \sum_{l,m} \frac{1}{k_B T} \frac{\partial^2 S}{\partial \alpha_l \partial \alpha_m} \Big|_{\forall \alpha_j=0} \alpha_l \alpha_m \right] \right\}$$

where the first equality follows from the Taylor expansion of S .

As before, the conjugated forces are defined as the derivatives with respect to the extensive variables

$$(660) \quad X_i = \frac{\partial S}{\partial \alpha_i} = \sum_j \frac{\partial^2 S}{\partial \alpha_i \partial \alpha_j} \Big|_{\alpha_i=0} \alpha_j \quad \text{with} \quad \frac{\partial^2 S}{\partial \alpha_i^2} \Big|_{\alpha_i=0} < 0$$

Averaging the gaussian probability distribution leads to

$$(661) \quad \langle \alpha_i X_j \rangle = -k_B T \delta_{i,j}$$

Assume now that the principle of microscopic reversibility holds, i.e.

$$(662) \quad \langle \alpha_i(t) \alpha_j(t + \tau) \rangle = \langle \alpha_j(t) \alpha_i(t + \tau) \rangle$$

We define as before the coefficients $L_{i,j}$ (i.e. we assume that the changes in density are linearly related to the forces). For our simple theory, there is no spatial gradients and the "fluxes" of matter, heat, electricity are measured here by the time derivatives of the α_i 's: $J_i = \dot{\alpha}_i$, so that

$$(663) \quad \frac{d\alpha_i}{dt} = \sum_j L_{i,j} X_j(t)$$

The philosophy is the same as before and the rate of changes in quantities is linearly proportional to the forces which cause them. In this simple theory, there is no spatial gradient, since the system is supposed to be spatially homogeneous, and the equation for the conservation of the current should be replaced by (663). We will assume that the L_{ij} 's define this way agree with the previous definition.

Expanding to first order, we have

$$(664) \quad \alpha_j(t + \tau) = \alpha_j(t) + \tau \frac{d}{dt} \alpha_j(t) = \alpha_j(t) + \tau \sum_k L_{j,k} X_k(t)$$

where τ is an hydrodynamic time scale (larger than all microscopic time scales, but smaller than the characteristic time scale of macroscopic averages). We get:

$$(665) \quad \langle \alpha_i(t) \alpha_j(t + \tau) \rangle = \langle \alpha_i(t) \alpha_j(t) \rangle - \tau k_B T L_{j,i}$$

Similarly, $\langle \alpha_i(t) \alpha_j(t + \tau) \rangle$ is given by

$$(666) \quad \langle \alpha_i(t) \alpha_j(t + \tau) \rangle = \langle \alpha_j(t) \alpha_i(t) \rangle - \tau k_B T L_{i,j}$$

Comparing the two time correlation functions, we obtain the reciprocal relations

$$(667) \quad L_{i,j} = L_{j,i}$$

from microscopic reversibility.

Conclusion: For small deviations from equilibrium, where the system is in the linear response regime, the state variables α_i 's evolve according to the equation

$$(668) \quad \dot{\alpha}_i = \sum_j L_{i,j} X_j$$

Or, equivalently

$$(669) \quad X_i = \sum_j R_{i,j} \dot{\alpha}_j$$

where (with a magnetic field \mathbf{B})

$$(670) \quad L_{i,j}(\mathbf{B}) = L_{j,i}(-\mathbf{B}) \quad R_{i,j}(\mathbf{B}) = R_{j,i}(-\mathbf{B})$$

Entropy production and symmetry properties are the key concepts in the theory of irreversible processes.

7. The principle of least production of energy

This principle is essentially equivalent to the principle of least production of entropy. As seen before, the rate of production of entropy (for a closed system) is

$$(671) \quad \sigma = \frac{dS}{dt} = \sum_i \frac{\partial S}{\partial \alpha_i} \dot{\alpha}_i$$

Thus

$$(672) \quad \sigma = \sum_i \dot{\alpha}_i X_i(\alpha) = \sum_{i,j} L_{ij} X_i X_j$$

Next, for the purpose of the demonstration, define the function P

$$(673) \quad P = 2 \sum_i \dot{\alpha}_i X_i - \sum_{ij} L_{ij} X_i X_j$$

The extremum of this function for given fluxes $\dot{\alpha}_i$, and with respect to variations of the thermodynamic forces is determined by the conditions

$$(674) \quad \dot{\alpha}_i - \frac{1}{2} \sum_j (L_{ij} + L_{ji}) X_j = 0$$

We conclude : From an extremum principle, we recover the macroscopic laws $\dot{\alpha}_i = \sum_j L_{ij} X_j$ if $L_{ij} = L_{ji}$. It should, however, be remarked that this statement breaks down when a magnetic field is present. For this reason, the principle of microscopic reversibility is more fundamental.

8. Experimental verification

9. The Boltzmann equation

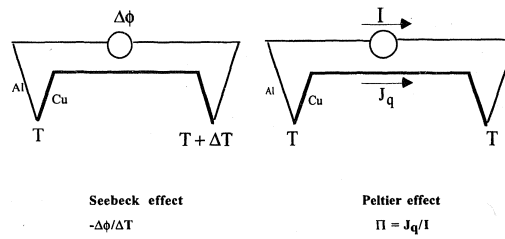


FIGURE 1. After¹¹: The thermoelectric effect is a "cross effect" between thermodynamic forces and flows. (a) In the Seebeck effect, two dissimilar metal wires are joined and the junctions are maintained at different temperatures. As a result an EMF is generated. The EMF generated is generally of the order of 10^{-5} V per Kelvin of temperature difference. (b) In the Peltier effect, the two junctions are maintained at the same temperature and a current is passed through the system. The current flow drives a heat flow Jq from one junction to the other.

CHAPTER 10

PATH INTEGRALS AND QUANTUM DISSIPATION

1. Introduction

In classical mechanics dissipation can often be adequately described by including a velocity dependent damping term into the equation of motion. Such a phenomenological approach is no longer possible in quantum mechanics where the Hamilton formalism implies energy conservation for time-independent Hamiltonians. How do we deal with dissipation in quantum mechanics? We will follow Refs.^{5;10} with the help of Refs.^{7;23}

Such a question arises in macroscopic quantum phenomena where dissipation is connected to the problem of quantum decoherence. Consider, for example, the canonical problem of decay from a metastable state, see Fig. 1. In the high temperature regime, decay will process by the classical thermal activated process we have studied so far. If the temperature is low enough, however, decay will process through quantum tunneling. What is the cross-over temperature? Do quantum dissipation help or suppress tunneling?

A suitable model for dissipative quantum systems should both incorporate the idea of a coupling between the system and its environment. The total Hamiltonian is

$$(675) \quad H = H_S + H_B + H_{SB}$$

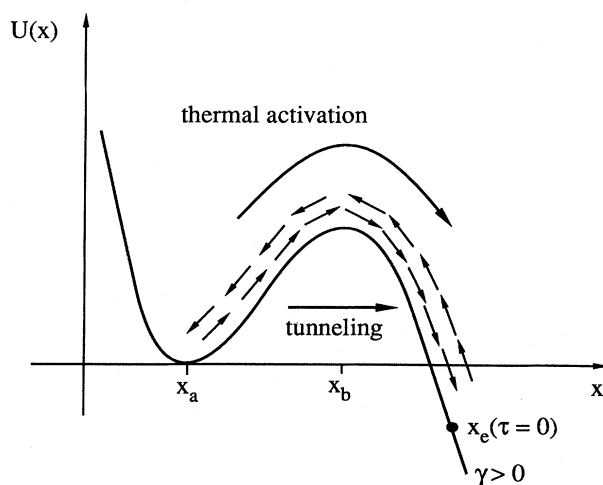


FIGURE 1. Potential used for the decay from a metastable state. If the temperature is low enough, the decays will process through tunneling and not from thermal activation.

and its consists of three contributions. First, the Hamiltonian of the system degree of freedom

$$(676) \quad H_S = \frac{p^2}{2m} + V(q)$$

models a particle of mass m moving in a potential $V(q)$. Here, we denote the coordinate by q to facilitate the distinction from the environmental coordinates x_n .

The Hamiltonian of the environmental degrees of freedom

$$(677) \quad H_B = \sum_{n=1,N} \left(\frac{p_n^2}{2m_n} + \frac{m_n}{2} \omega_n^2 x_n^2 \right)$$

describes a collection of harmonic oscillators.

The coupling defined by the Hamiltonian

$$(678) \quad H_{SB} = -q \sum_{n=1,N} c_n x_n + q^2 \sum_{n=1,N} \frac{c_n^2}{2m_n \omega_n^2}$$

is bilinear in the position operators of system and environment (the c_n 's are positive coefficients). As was first pointed out by Caldeira and Leggett, an infinite number of degrees of freedom still allows for strong damping even if each environmental oscillator couples only weakly to the system.

For such a system, Ref.¹³ has shown (see exercise 10.1) that the equation of motion for the system can be cast into the form:

$$(679) \quad m\ddot{q} + m \int_0^t ds \gamma(t-s) \dot{q}(s) + \frac{\partial V}{\partial q} = \xi(t)$$

where the quantities characterizing the environment may be expressed in terms of the spectral density

$$(680) \quad J(\omega) = \pi \sum_{n=1,N} \frac{c_n^2}{m_n \omega_n} \delta(\omega - \omega_n)$$

This derivation is valid in all cases: The variables can be either operators (quantum case) or fields (classical case). Eliminating the environmental degrees of freedom leads to an effective dissipation for the equation of motion of the system.

$$(681) \quad \gamma(t) = \frac{1}{m} \sum_{n=1,N} \frac{c_n^2}{m_n \omega_n^2} \cos(\omega_n t) = \frac{2}{m} \int_0^\infty \frac{d\omega}{\pi} \frac{J(\omega)}{\omega} \cos(\omega t)$$

EXERCICE 10.1.

- (1) Write down the equations of motion for the environmental degrees of freedom x_n, p_n .
- (2) The trick for solving the environmental equations of motion consists in treating the system coordinate $q(t)$ as if it were a given function of time. Using the result above, show

$$(682) \quad x_n(t) = x_n(0) \cos(\omega_n t) + \frac{p_n(0)}{m_n \omega_n} \sin(\omega_n t) + \frac{c_n}{m_n \omega_n} \int_0^t ds \sin(\omega_n(t-s)) q(s)$$

- (3) Insert this result into the equation of motion for the system variable $q(t)$ and show:

$$(683) \quad \gamma(t) = \frac{1}{m} \sum_{n=1,N} \frac{c_n^2}{m_n \omega_n^2} \cos(\omega_n t)$$

with

$$(684) \quad \xi(t) = \sum_{n=1,N} c_n \left[\left(x_n(0) - \frac{c_n}{m_n \omega_n^2} q(0) \right) \cos(\omega_n t) \frac{p_n(0)}{m_n \omega_n} + \sin(\omega_n t) \right]$$

2. The picture

From ref.⁵. We regard the system and its environment as together forming a closed system (the universe, as we shall denote it for present purposes) which can be described by a Lagrangian or Hamiltonian, to solve (in principle!) for the motion of the whole and to derive from this solution a description of the properties of the system (which, of course, would now more properly be called a subsystem). In this picture the phenomenon of dissipation is simply the transfer of energy from the single degree of freedom characterising the system to the very complex set of degrees of freedom describing the environment; it is implicitly assumed that the energy, once transferred, effectively disappears into the environment and is not recovered within any time of physical interest (i.e., one treats the mathematical existence of Poincare recurrences as physically irrelevant). Formally, one assumes that the number of degrees of freedom of the environment tends to infinity; this assumption is implicit in the replacement of sums by integrals which we shall carry out without further comment at appropriate stages in the calculation.

3. Path integral and Brownian motion

Let us rewrite the Langevin equation as

$$(685) \quad \xi(t) = \gamma \frac{dx}{dt} + \frac{dV}{dx}$$

The probability that we observe a trajectory $x(t)$ can be calculated by finding the random force $\xi(t)$ which was needed to generate this trajectory, and then calculating the probability of this force. We know that the random forces come from a Gaussian distribution,

$$(686) \quad P[\xi(t)] \propto \exp\left\{-\frac{1}{4\gamma k_B T} \int dt \xi^2(t)\right\}$$

where the integral sum is a shorthand notation for discrete sums. The prefactor in the exponential allows the retrieve the equal correlation for the noise:

$$(687) \quad \langle \xi(t)\xi(t') \rangle = 2\gamma k_B T \delta(t-t')$$

This can be seen as the joint probability to get $P(\xi_1, \xi_2, \dots, \xi_n)$ at times t_1, t_2, \dots, t_n . So its tempting to say that the probability of observing the trajectory $x(t)$ is

$$(688) \quad P[x(t)] \propto \exp\left\{-\frac{1}{4\gamma k_B T} \int dt \left(\gamma \frac{dx}{dt} + \frac{dV}{dx}\right)^2\right\}$$

and this is almost correct. What is missing the the Jacobian \mathcal{J} . Remember that for any two variables connected by the transformation $y = f(x)$

$$(689) \quad P_x(x) = P_y(y) \frac{dy}{dx}$$

and, here, the time t plays the role of the function $f(x)$ with $\mathcal{J} = dy/dx$.

So if \mathcal{J} is the Jacobian between $x(t)$ and the random force $\xi(t)$, we have

$$(690) \quad P[x(t)] \propto \exp\left\{-\frac{1}{4\gamma k_B T} \int dt \left(\gamma \frac{dx}{dt} + \frac{dV}{dx}\right)^2\right\} \mathcal{J}$$

The calculation of the Jacobian is a rather difficult task. But we don't need to do it. We work in the limit of low temperature. We remark that \mathcal{J} is temperature independent, so that the dominant contribution comes from the integral $\sim \exp\{-1/T\}$. We shall, therefore, ignore the Jacobian and write (688) as the probability the observe a trajectory in the limit $T \rightarrow 0$.

4. Principe variationnel

Nous désirons "démontrer" l'équation de Schrödinger à partir d'un principe plus général qui est une propriété des équations aux dérivées partielles. Cette démonstration nous permettra de faire un parallèle entre un problème spécifiquement quantique et une situation classique.

Nous supposons deux choses :

- (1) La fonction d'onde obéit à une propriété de propagation. Soit $K(x_2, t_2|x_1, t_1)$ l'amplitude pour que la particule initialement localisée en x_1 à t_1 soit observée en x_2 à t_2 . Nous avons la définition de cette amplitude de probabilité.

$$(691) \quad \psi(x_2, t_2, x_1, t_1) = K(x_2, t_2|x_1, t_1)\psi(x_1, t_1)$$

Fixons l'origine des temps à t_1 . Pour que la particule soit observée en t_2 quelque soit x_1

$$(692) \quad \psi(x_2, t_2 - t_1) = \int K(x_2, t_2|x_1, t_1)\psi(x_1, t_1)dx_1$$

Où $K(\dots)$ est un propagateur. L'Éq. (692) est linéaire, ce qui permet les interférences. Pour avoir une probabilité d'amplitude d'observer la particule en x_2 à t_2 , il faut bien qu'elle se trouvait quelque part en t_1 !

Une fois connu le propagateur K , l'équation (692) est une équation intégrale pour la fonction d'onde. Nous verrons que c'est l'équation de Schrödinger.

- (2) Le propagateur est la somme sur toutes les trajectoires $x(t)$ possibles de l'action fois i/\hbar

$$(693) \quad K(x_2, t_2|x_1, t_1) = \int_{x(t_1)=x_1}^{x(t_2)=x_2} e^{\frac{i}{\hbar} \int_{t_1}^{t_2} L(x, \dot{x}, t) dt} \mathcal{D}[x(t)]$$

Cette définition met sur le même pied tous les chemins, car $K(\dots)$ est une amplitude de probabilité. En prenant le module au carré de l'intégrand, on démontre que tous les chemins ont même poids. La constante \hbar intervient, car l'argument de l'exponentielle doit être un nombre sans dimension.

L'intégrale porte sur tous les chemins possibles. On n'essaiera pas de donner une définition rigoureuse ni de savoir si une telle somme existe. Elle peut-être a priori définie comme suit : tous les chemins $x(t)$ sont décomposables en série de Fourier. Intégrer sur les chemins revient donc à intégrer sur les coefficients de Fourier, ce que l'on sait faire. Bien sûr, cette définition ne démontre pas que l'intégrale existe.

POURQUOI ? Reprenons l'image classique d'une particule classique dont la position est $x(t)$ à l'instant t . Cette trajectoire correspond à une courbe dans le plan (x, t) . Pour aller du point $A(x_1, t_1)$ au point $B(x_2, t_2)$, nous savons que la particule a choisi une trajectoire très particulière. Cette trajectoire rend l'action extrémale. Pour chaque trajectoire Γ , nous pouvons associer une action

$$(694) \quad S(\Gamma) = \int_{t_1}^{t_2} L(x, \frac{dx}{d\tau})d\tau$$

L'amplitude pour aller de A à B par le chemin Γ est noté $\phi_\Gamma(B|A)$. Le propagateur est la somme de toutes ces amplitudes

$$(695) \quad K(B|A) = \int \phi_\Gamma(B|A)D[\Gamma]$$

Dans la pratique, rien ne permet de distinguer un chemin plutôt qu'un autre. Nous postulons que tous les chemins pour aller de A à B sont égaux pour les probabilités. Autrement dit, les

$\phi_{\Gamma}(B|A)$ différent d'un chemin à un autre par un facteur de phase. Nous exigeons que ce facteur de phase dépende de l'action et nous renormalisons par \hbar pour avoir un nombre sans dimension

$$(696) \quad \phi_{\Gamma}(B|A) = e^{\frac{i}{\hbar}S(\Gamma)}$$

Dans (695), le signe \int est synonyme du signe \sum . Deux trajectoires Γ_1 et Γ_2 ne contribuent pas au propagateur si leur action diffère d'un facteur de phase $i\pi\hbar$ car

$$(697) \quad e^{\frac{i}{\hbar}S(\Gamma_1)} + e^{\frac{i}{\hbar}S(\Gamma_2)} = 0$$

La somme sur tous les chemins fait donc que les chemins vont presque tous se télescoper par interférences destructrices. Seuls vont subsister les chemins pour lesquels il est difficile que faire varier l'action d'un facteur de $\hbar\pi$. Mais en perturbant un chemin par une petite variation $x(t) \rightarrow x(t) + \delta x(t)$, nous faisons varier l'action. Autrement dit, le chemin qui va principalement contribuer au propagateur est le chemin pour lequel l'action ne varie pas quand la trajectoire est perturbée et tous les chemins situés dans un voisinage de cette trajectoire classique donnent des processus d'interférences constructives.

Deux cas se présentent suivant la largeur de la région des processus d'interférences constructives.

- (1) Seuls les chemins proches du chemin classique conduisent à des interférences constructives. La situation est dite CLASSIQUE.
- (2) Des chemins très différents du chemin classique conduisent à des interférences constructives. La situation est alors QUANTIQUE.

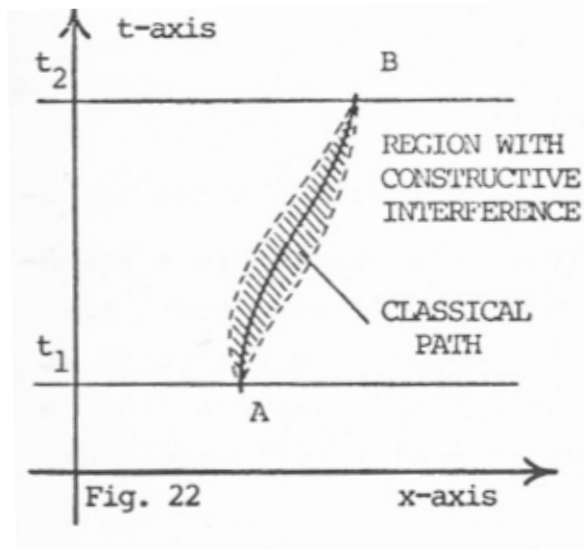


FIGURE 2. Seuls les chemins dans un voisinage du chemin rendant l'action extrémale contribuent au propagateur. Le tout est de savoir si ce voisinage est étroit ou large ...

Calculus

Rappelons ici un théorème utile pour évaluer le comportement asymptotique des intégrales. Il s'agit d'évaluer:

$$(698) \quad I = \int_{\Omega} dx e^{-\lambda f(x)} \text{ avec } \lambda \rightarrow \infty$$

Lorsque $f(x)$ possède un minimum en $x = x_{min}$, le développement limité de $f(x)$ est suffisant:

$$(699) \quad I \approx e^{-\lambda f(x_{min})} \int_{-\infty}^{+\infty} dx e^{-\frac{\lambda}{2}(x-x_{min})^2 f''(x_{min})} \text{ avec } \lambda \rightarrow \infty$$

Cette approximation est souvent appelée l'approximation du point de selle.

Lorsque l'intégrand est complexe :

$$(700) \quad I = \int_{\Omega} dx e^{-i\lambda f(x)} \text{ avec } \lambda \rightarrow \infty$$

nous avons aussi à l'ordre le plus bas :

$$(701) \quad I \approx e^{-i\lambda f(x_{min})} \int_{-\infty}^{+\infty} dx e^{-i\frac{\lambda}{2}(x-x_{min})^2 f''(x_{min})} \text{ avec } \lambda \rightarrow \infty$$

car les parties oscillantes donnent une contribution négligeable sauf au voisinage du minimum où les oscillations sont les plus faibles. Dans ce cas, l'approximation est appelée approximation de la phase stationnaire.

CONSÉQUENCE. La valeur de la constante \hbar est faible devant 1 et elle va servir d'étalon pour savoir si une situation est classique ou quantique. Nous faisons $\lambda = 1/\hbar$. Si l'intégrale (693) est bien approximée par le développement limité autour du chemin qui rend l'action

$$(702) \quad \int_{t_1}^{t_2} L(x, \dot{x}, t) dt$$

extrémale, on dira que la situation est classique. La seule trajectoire qui importe est celle qui rend l'action extrémale et nous retrouvons les équations de Newton. Dans le cas contraire, la situation est quantique.

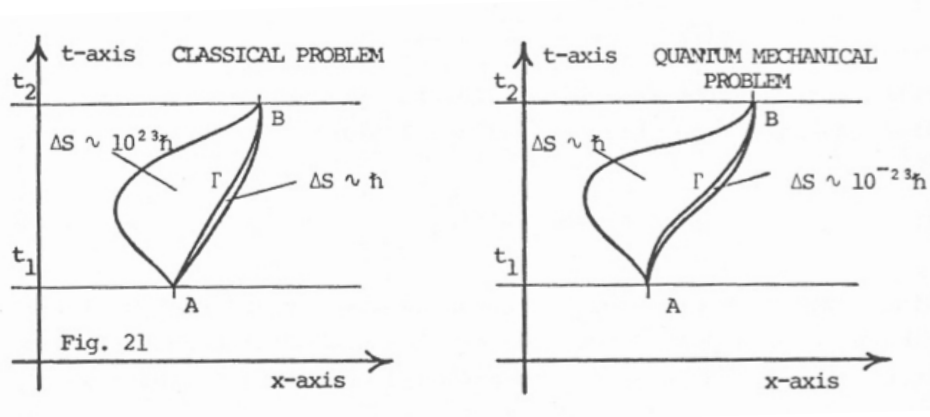


FIGURE 3. Différence entre une situation classique et quantique.

Équation de Schrödinger

Nous posons $t_2 = t_1 + \Delta t$ et nous travaillerons dans la limite $\Delta t \rightarrow 0$. Nous supposons donc:

$$(703) \quad \psi(x, t + \Delta t) = \int K(x, t + \Delta t, y, t) \psi(y, t) dy$$

où:

$$(704) \quad K(x, t + \Delta t, y, t) = \int_{\eta(t)=y}^{\eta(t+\Delta t)=x} \mathcal{D}\eta e^{\frac{i}{\hbar} \int_t^{t+\Delta t} [\frac{m}{2} \dot{\eta}^2 - V(\eta)]}$$

Lorsque $\Delta t \rightarrow 0$, cette équation intégrale pour ψ (K est connue) devient une équation différentielle. Seuls les chemins réguliers donnent une contribution physique. Aussi, lorsque $\Delta t \rightarrow 0$, y diffère peu de x dans (704) et:

$$(705) \quad \dot{\eta} = \frac{x - y}{\Delta t}$$

D'où:

$$(706) \quad \frac{i}{\hbar} \int_t^{t+\Delta t} \left[\frac{m}{2} \dot{\eta}^2 - V(\eta) \right] \approx \frac{i}{\hbar} \frac{m}{2} \frac{(x-y)^2}{\Delta t} - \frac{i}{\hbar} V(x) \Delta t$$

Soit

$$(707) \quad K(x, t + \Delta t | y, t) = e^{\frac{i}{\hbar} \left[\frac{m}{2} \frac{(x-y)^2}{\Delta t} - V(x) \Delta t \right]} \int_{\eta(t)=y}^{\eta(t+\Delta t)=x} \mathcal{D}[\eta]$$

Comme nous ne savons pas calculer la dernière intégrale, nous posons :

$$(708) \quad A[\Delta t] = \int_{\eta(t)=y}^{\eta(t+\Delta t)=x} \mathcal{D}[\eta]$$

ce qui ne permet pas de résoudre la difficulté, mais permet de la cacher sous une notation.

Au risque de tuer le suspens, nous montrerons néanmoins que la limite $\Delta t \rightarrow 0$ donne :

$$(709) \quad \lim_{\Delta t \rightarrow 0} (\Delta t)^{1/2} A[\Delta t] = \left(\frac{m}{2\pi i \hbar} \right)^{1/2}$$

Pour la fonction d'onde

$$(710) \quad \psi(x, t + \Delta t) = \int dy A[\Delta t] e^{\frac{i}{\hbar} \left[\frac{m}{2} \frac{(x-y)^2}{\Delta t} - V(x) \Delta t \right]} \psi(y, t)$$

Comme $\Delta t \rightarrow 0$ et que les trajectoires sont régulières, la contribution principale de cette intégrale vient des y voisins de x (la particule n'a pas eu le temps de bouger beaucoup). Posons $y = x + \epsilon$:

$$(711) \quad \psi(x, t + \Delta t) = \int d\epsilon A[\Delta t] e^{\frac{i}{\hbar} \left[\frac{m}{2} \frac{\epsilon^2}{\Delta t} - V(x) \Delta t \right]} \psi(x + \epsilon, t)$$

avec le développement de Taylor :

$$(712) \quad \psi(x + \epsilon, t) = \psi(x, t) + \epsilon \frac{d\psi}{dx} + \frac{1}{2} \epsilon^2 \frac{d^2\psi}{dx^2} + O(\epsilon^3)$$

Les intégrales sur ϵ sont maintenant des intégrales gaussiennes ! On a :

$$(713) \quad \int_{-\infty}^{+\infty} dx e^{-ax^2} = \left(\frac{\pi}{a} \right)^{1/2} \quad \text{et} \quad \int_{-\infty}^{+\infty} dx x^2 e^{-ax^2} = \frac{1}{2a} \left(\frac{\pi}{a} \right)^{1/2}$$

D'où, utilisant (711)

$$(714) \quad \psi(x, t + \Delta t) = A[\Delta t] e^{-\frac{i}{\hbar} V(x) \Delta t} \left(\frac{2\pi i \hbar \Delta t}{m} \right)^{1/2} \left[\psi(x) + \frac{1}{4} \left(\frac{2i \hbar \Delta t}{m} \right) \frac{\partial^2 \psi}{\partial x^2} \right]$$

Cette équation permet de calculer $A[\Delta t]$. En effet, $A[\Delta t]$ est indépendant de $V(x)$. Donc, on peut prendre $V(x) = 0$ et $\Delta t = 0$ dans (714). D'où :

$$(715) \quad \lim_{\Delta t \rightarrow 0} (\Delta t)^{1/2} A[\Delta t] = \left(\frac{m}{2\pi i \hbar} \right)^{1/2}$$

Soit

$$(716) \quad \psi(x, t + \Delta t) = e^{-\frac{i}{\hbar} V(x) \Delta t} \left[\psi(x) + \frac{i \hbar \Delta t}{2m} \frac{\partial^2 \psi}{\partial x^2} \right]$$

En se limitant au premier ordre en Δt , nous avons donc :

$$(717) \quad \frac{\partial \psi}{\partial t} = \lim_{t \rightarrow 0} \frac{\psi(x, t + \Delta t) - \psi(x, t)}{\Delta t} = \frac{i \hbar}{2m} \frac{\partial^2 \psi}{\partial x^2} - \frac{i}{\hbar} V(x) \psi(x)$$

qui n'est autre que l'équation de Schrödinger.

États stationnaires. Pour un système isolé dans un potentiel indépendant du temps, les états propres sont de la forme

$$(718) \quad \psi(r, t) = \psi_\alpha(r) e^{-iE_\alpha t/\hbar}$$

avec

$$(719) \quad H\psi_\alpha(r) = E_\alpha\psi_\alpha(r)$$

ψ_α est donc une fonction propre de l'opérateur H associé à la valeur propre E_α . Si ψ_n , $n \in N$, désigne une base orthonormée, la théorie des équations différentielles aux dérivées partielles permet d'obtenir le propagateur comme:

$$(720) \quad K(x_2, t_2|x_1, t_1) = \sum_n \psi_n^*(x_1)\psi_n(x_2)e^{-i/\hbar E_n(t_2-t_1)}$$

$K(x_2, t_2|x_1, t_1)$ est la solution unique de l'équation élémentaire

$$(721) \quad i\hbar \frac{\partial}{\partial t_2} K() = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x_2^2} + V(x_2) \right] K()$$

avec la condition initiale

$$(722) \quad K(x_2, t_1|x_1, t_1) = \delta(x_2 - x_1)$$

En d'autres mots, K est une fonction de Green.

This representation of the Green function allows to calculate the K in a few cases.

EXAMPLE 4.1. FREE PARTICLE: The corresponding Hamiltonian

$$(723) \quad H = \frac{p^2}{2m}$$

has *momentum* eigenstates

$$(724) \quad \psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} \exp\left\{ \left(\frac{i}{\hbar} px \right) \right\}$$

Inserting these eigenstates into the representation of the propagator, one finds by virtue of

$$(725) \quad \int_{-\infty}^{+\infty} dx \exp\{(-iax^2)\} = \sqrt{\frac{\pi}{ia}} = \sqrt{\frac{\pi}{a}} \exp\left\{ \left(-i\frac{\pi}{4} \right) \right\}$$

the result

$$(726) \quad \begin{aligned} K(x_2, t_2|x_1, t_1) &= \frac{1}{2\pi\hbar} \int dp \exp\left\{ \left(-\frac{i}{\hbar} \frac{p^2}{2m} t \right) \right\} \exp\left\{ \left(\frac{i}{\hbar} p(x_2 - x_1) \right) \right\} \\ &= \sqrt{\frac{m}{2\pi i\hbar t}} \exp\left\{ \left(\frac{i}{\hbar} \frac{m(x_2 - x_1)^2}{2t} \right) \right\} \end{aligned}$$

EXAMPLE 4.2. DRIVEN HARMONIC OSCILLATOR: As an example, we will consider the driven harmonic oscillator which is simple enough to allow for an exact solution. In addition, the propagator will be of use in the discussion of damped quantum systems in later sections.

Our starting point is the Lagrangian

$$(727) \quad L = \frac{m}{2} \dot{x}^2 - \frac{m}{2} \omega^2 x^2 + x f$$

of a harmonic oscillator with mass m and frequency ω . The force $f(t)$ may be due to an external field, e.g. an electric field coupling via dipole interaction to a charged particle. In the context of dissipative quantum mechanics, the harmonic oscillator could represent a degree of freedom of the environment under the influence of a force exerted by the system.

We will admit that the propagator is

$$(728) \quad K(x_2, t_2|x_1, t_1) = \sqrt{\frac{m\omega}{2\pi\hbar|\sin(\omega t)|}} e^{iS_{cl} - i\left(\frac{\pi}{4} + n\frac{\pi}{2}\right)}$$

where n is the integer part of $\omega t/\pi$. The classical path is solution of the equation of motion

$$(729) \quad m\ddot{x}_{cl} + m\omega^2 x_{cl} = f(s)$$

and S_{cl} is the classical action

$$(730) \quad S_{cl} = \int_0^t ds \left(\frac{m}{2} \dot{x}_{cl}^2 - \frac{m}{2} \omega^2 x_{cl}^2 + x_{cl} f(s) \right)$$

5. Density matrices

The equilibrium density matrix is defined as

$$(731) \quad \rho = \frac{1}{Z} \sum_n e^{-\beta E_n} |n\rangle \langle n|$$

where $|n\rangle$ are eigenstates of H . The normalization is provided by the partition function

$$(732) \quad Z = \text{tr}\{e^{-\beta H}\}$$

We can write this density matrix in the coordinate representation

$$(733) \quad \rho(q, q') = \frac{1}{Z} \langle q | e^{-\beta H} | q' \rangle$$

which looks like a propagator. In order to write this density matrix as a path integral, recall that the action is given by

$$(734) \quad S[q, t] = \int_0^t ds \left[\frac{m}{2} \left(\frac{dq}{ds} \right)^2 - V(q) \right]$$

where we have specified the final time t for clarity. Replacing t by $-i\hbar\beta$ and substituting s by $i\tau$, one obtains

$$(735) \quad S[q, -i\hbar\beta] = iS^E[q, \hbar\beta]$$

where we have introduced the euclidean action

$$(736) \quad S^E[q, \hbar\beta] = \int_0^{\hbar\beta} ds \left[\frac{m}{2} \left(\frac{dq}{d\tau} \right)^2 + V(q) \right]$$

which describes the movement of a particle in an inverted potential $-V(q)$. From this, one obtains the path-integral representation of the density matrix

$$(737) \quad \rho(q, q') = \frac{1}{Z} \int \mathcal{D}q \exp\left(-\frac{1}{\hbar} S^E(q)\right)$$

Since we are taking the $\text{tr}\{\}$, all paths start and end at the same point and we integrate over this point to get thermal averages.

EXERCICE 10.2. We want to calculate²³

$$(738) \quad \mathcal{Z}(\beta, f) = \int \mathcal{D}q \exp\left(-\frac{1}{\hbar} S_G(q, f)\right)$$

where the Gaussian action is defined as

$$(739) \quad S_G(q, f) = \int_{-\tau/2}^{\tau/2} dt \left[\frac{1}{2} m \dot{q}(t)^2 + \frac{1}{2} m \omega^2 q(t)^2 - f(t)q(t) \right]$$

with periodic boundary conditions : $q(\tau/2) = q(-\tau/2)$ (taking periodic boundary conditions is a pure convenience).

- (1) Make the change of variable $q(t) = q_c(t) + r(t)$, where $q_c(t)$ is determined below.
- (2) Integrate by parts if necessary and show that the linear term in $r(t)$ cancels out if $q_c(t)$ is solution of

$$(740) \quad -\ddot{q}_c(t) + \omega^2 q_c = f(t)/m$$

(3) Show that the solution of this equation can be written as

$$(741) \quad q_c(t) = \frac{1}{m} \int_{-\tau/2}^{\tau/2} du \Delta(t-u) f(u)$$

where $\Delta(t)$ is solution of the equation

$$(742) \quad -\ddot{\Delta} + \omega^2 \Delta = \delta(t)$$

(4) By Fourier transforming (use residue theorem), show that

$$(743) \quad \Delta(t) = \frac{1}{2\omega \sinh(\omega\tau/2)} \cosh(\omega(\tau/2 - |t|))$$

which is the Fourier transform of $1/(s^2 + \omega^2)$ with appropriate boundary conditions at infinity.

(5) Show

$$(744) \quad \Delta(t) = \frac{1}{2\omega} e^{-\omega|t|}, \text{ as } t \rightarrow \infty$$

(6) By integrating by parts, show

$$(745) \quad \begin{aligned} S_G(q, f) &= -\frac{1}{2} \int_{-\tau/2}^{\tau/2} dt q_c(t) f(t) \\ &= -\frac{1}{2m} \iint_{-\tau/2}^{\tau/2} dt du f(t) \Delta(t-u) f(u) \end{aligned}$$

(7) Conclude

$$(746) \quad \mathcal{Z}(\beta, f) = \mathcal{Z}(\beta, f=0) \exp\left(\frac{1}{2m\hbar} \iint_{-\tau/2}^{\tau/2} dt du f(t) \Delta(t-u) f(u)\right)$$

which is nothing but the continuous analog of (912). The net result of introducing a driving force is, therefore, to introduce correlations through the kernel $\Delta(t-u)$.

The partition function for a single quantum oscillator is easily obtained as

$$(747) \quad \mathcal{Z}(\beta, f=0) = \sum_n e^{\beta\hbar\omega(n+\frac{1}{2})} = \frac{1}{2 \sinh(\hbar\beta\omega/2)}$$

This property will be useful when we will analyze the tunneling under the influence of dissipation, since this equation connects the calculation of the partition function in the presence of dissipation to the same partition function but for an isolated system.

6. Effective equilibrium density matrix

Recall that the coupling Hamiltonian for the particle with the bath is given by

$$(748) \quad H_{SB} = -q \sum_{n=1, N} c_n x_n + q^2 \sum_{n=1, N} \frac{c_n^2}{2m_n \omega_n^2}$$

where the ω_n 's are the eigenfrequencies for the path oscillators of position coordinates x_n and coupling strength c_n . To compare with the driven oscillator studied in the preceding section, we define the effective force $f(t)$ by

$$(749) \quad f(t) = \sum_{n=1, N} c_n x_n$$

as in (727). The second term in (748) ...

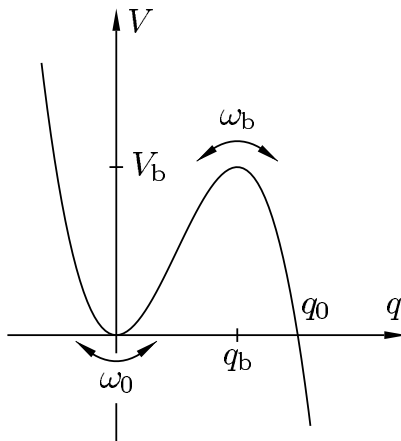


FIGURE 4. Sketch of a cubic potential.

To obtain the effective density matrix for the system, we trace out the bath degrees of freedom. In representation coordinates, the matrix elements are

$$(750) \quad \begin{aligned} \rho(q_i, q_f) &= \text{tr}_B \rho(q, x_i, q', x'_f) \\ &= \frac{1}{\mathcal{Z}(\beta, f)} \int \mathcal{D}\bar{q} \int \prod_i dx_i \oint \mathcal{D}\bar{x} \exp\left(-\frac{1}{\hbar} S^E(\bar{q}, \bar{x})\right) \end{aligned}$$

where

- (1) $\int \mathcal{D}\bar{q}$ means that we integrate over all paths \bar{q} with $q_{i,f}$ as start and end points;
- (2) $\oint \mathcal{D}\bar{x}$ means that all path for the bath variables have the same start and end points (we take the trace, so $x_i = x'_f$);
- (3) We integrate overall possible start (or end) points for the bath variables $\rightarrow \int \prod_i dx_i$.

As a rule, tracing out internal degrees freedom introduce correlation between the variable characterizing the system. The process is strictly the same as for the driven oscillator in Problem 10.2 and we need only to quote the result:

$$(751) \quad \rho(q_i, q_f) = \frac{1}{\mathcal{Z}(\beta)} \int \mathcal{D}q \exp\left(-\frac{1}{\hbar} S_S(q, f)\right) F[\bar{q}]$$

where

$$(752) \quad F[\bar{q}] = \prod_i \mathcal{Z}_i(\beta) \exp\left(\frac{1}{2m\hbar} \iint_{-\hbar\beta/2}^{\hbar\beta/2} dt du \bar{q}(t) \Delta_i(t-u) \bar{q}(u)\right)$$

since, from the point of view of the bath variables x_i 's, the system variable q plays the role of the force.

7. Decay of a metastable state

Consider the cubic potential shown in Fig. 4. A convenient formula for $V(q)$ is written as

$$(753) \quad V(q) = \frac{M}{2} \omega_0^2 q^2 \left(1 - \frac{q}{q_0}\right)$$

We look for extrema of the action among arbitrary paths and take into account fluctuations around these extremal paths in a "semiclassical way".

The classical equation of motion for a cubic potential in the presence of dissipation is given by

$$(754) \quad M\ddot{q} - M\omega_0^2 q + \frac{3}{2}M\omega_0^2 \frac{q^2}{q_0} - \int_0^{\hbar\beta} du \Delta(t-u)q(u) = 0$$

where

$$(755) \quad \Delta(s) = \sum_i \Delta_i(s)$$

This equation gives the extremal paths for the action and we may in the semiclassical approximation evaluate the partition function within the saddle point approximation. Quantum fluctuations may be evaluated by expanding around these solutions to quadratic order.

In the absence of dissipation, i.e. for $\Delta = 0$, the evolution of $x(\tau)$ in imaginary time $t = -i\tau$ corresponds to the real-time τ motion in the inverted potential $-U(x)$. As a solace, there are two constant solutions. The one for $q = 0$ corresponds to the metastable state. The other one, at intermediate $q = q_b$ corresponds to the bottom of the well.

To study the fluctuations around these constant solutions, we may use a convenient basis. Since everything is periodic with period $\hbar\beta$ (when we take the trace which sum over paths with equal start and end points, i.e. periodic paths), fluctuations around these paths may be described as a Fourier series

$$(756) \quad \xi(\tau) = \sum_n \xi_n e^{i\nu_n \tau}, \nu_n = 2\pi \frac{n}{\hbar\beta}, n \in \mathbb{Z}^*$$

Near the constant path $q = q_b$, calculus gives

$$(757) \quad S^E = \hbar\beta V_b + \frac{M\hbar\beta}{2} \sum_n (\nu_n^2 + |\nu_n| \tilde{\gamma}(|\nu_n|) - \omega_b^2) |\xi_n|^2$$

where $\tilde{\gamma}(s)$ is the Laplace transform of the friction kernel defined in Eq. (681)

$$(758) \quad \tilde{\gamma}(s) = \int_0^\infty e^{-st} \gamma(t) dt$$

For practical purpose, taking $\gamma(t) \rightarrow 2\gamma_0 \delta(t)$ is enough, so that $\tilde{\gamma}(s) = \gamma_0$. For the cubic potential we have chosen, the barrier frequency ω_b is equal to ω_0 .

For the saddle point approximation to be valid, quantum fluctuations must increase S^E (otherwise, the integral diverges). Since $n = 0$ corresponds to time translational invariance, the first $n = 1$ dangerous mode is unstable when

$$(759) \quad \nu_1^2 + |\nu_1| \gamma_0 - \omega_b^2 + \omega_b^2 = 0$$

This corresponds to the cross-over temperature

$$(760) \quad 2\pi \frac{kT_c}{\hbar} = -\gamma_0 + \sqrt{\gamma_0^2 + \omega_b^2}$$

below which an other solution exists. This solution corresponds to pure quantum tunneling dissipating energy.

CHAPTER 11

PROBLEMS

PROBLEM 1

Define

$$(761) \quad Z(t) = \int_0^t Y(t') dt' \quad t \geq 0$$

Where $Y(t)$ is an Ornstein-Uhlenbeck process with,

$$(762) \quad \langle Y(t) \rangle = 0 \text{ and } \langle Y(t)Y(t-\tau) \rangle = \Gamma \frac{e^{-\beta|\tau|}}{2\beta}$$

(1) Find: $\langle Z(t_1)Z(t_2) \rangle$

(2) Calculate $\langle \cos [Z(t_1) - Z(t_2)] \rangle$. It will be useful to consider the cumulant expansion of the exponential¹.

Deduce that $Z(t)$ is Gaussian, but neither stationary or Markovian.

PROBLEM 2

Consider the following chemical reaction



with first order kinetics

$$(765) \quad \frac{d\hat{n}_A}{dt} = k_- \hat{n}_B - k_+ \hat{n}_A$$

$$(766) \quad \frac{d\hat{n}_B}{dt} = k_+ \hat{n}_A - k_- \hat{n}_B$$

where $n_A + n_B = n_0$ is constant (the symbol \hat{n} is for the most probable value and n_A is for the instantaneous value). This process is governed by a probability distribution $P(n_A)$, so that n_A fluctuates in time.

(1) Use Onsager's regression principle to compute the correlation function $\langle n_A(t)n_A(t+\tau) \rangle$.

(2) We want to compute the stationary distribution $P(n_A)$. Write down the master equation for this process and show directly that the distribution is binomial with weights $k_{\pm}/(k_- + k_+)$.

¹Recall

$$(763) \quad \langle e^{-i\xi t} \rangle = \exp \left\{ \left[\sum_{m \geq 1} \frac{(-it)^m}{m!} c_m \right] \right\}$$

PROBLEM 3

Let $\xi(t)$ be a stochastic signal, $0 \leq t \leq T$, and define

$$(767) \quad \tilde{\xi}(\omega) = \int_0^T \xi(t) e^{i\omega t} dt$$

The spectral density of $\xi(t)$ is defined as

$$(768) \quad S(\omega) = \lim_{T \rightarrow \infty} \frac{1}{2\pi T} |\tilde{\xi}(\omega)|^2$$

- (1) Show that the spectral density is related to the correlation functions as (Wiener-Khinchin theorem)

$$(769) \quad S(\omega) = \frac{1}{\pi} \int_0^\infty e^{i\omega\tau} \langle \xi(t)\xi(t+\tau) \rangle d\tau$$

- (2) Consider

$$(770) \quad S(\omega) = \frac{1}{2\pi} \int_{-\infty}^\infty e^{i\omega\tau} \langle \xi(t)\xi(t+\tau) \rangle d\tau$$

Using the δ -representation

$$(771) \quad \delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} dt$$

show another version of the theorem

$$(772) \quad \langle \tilde{\xi}(\omega)\tilde{\xi}^*(\omega') \rangle = 2\pi\delta(\omega + \omega')S(\omega')$$

PROBLEM 4

We derive the Green-Kubo relationship.

- (1) Show that the cumulants obey

$$(773) \quad \langle \dot{B}(t)A(0) \rangle_c = - \langle B(t)\dot{A}(0) \rangle_c$$

- (2) Let Ω be the volume of the system. We assume that the particles (position x_i) carry a charge q . We consider

$$(774) \quad A = q \sum_i x_i \quad B = \dot{A} = q \sum_i \dot{x}_i = \Omega j$$

where j is the current density. We assume $j = 0$ at equilibrium and add a perturbation $V(t) = -E(t)A$ to the Hamiltonian (E is the electrical field). Show that the electrical conductivity $\sigma(\omega)$ can be calculated as follows

$$(775) \quad \tilde{\sigma}(\omega) = \beta\Omega \int_0^\infty dt \langle j(0)j(t) \rangle_{|E=0}$$

- (3) Assume

$$(776) \quad \langle \dot{x}_i(t)\dot{x}_k(0) \rangle = \delta_{ik} \frac{kT}{m} e^{-|t|/\tau_c}$$

Show that the conductivity is given by the well-known formula

$$(777) \quad \tilde{\sigma}(\omega) = \frac{nq^2\tau_c}{m(1 - i\omega\tau_c)}$$

PROBLEM 5

Consider a RC electrical circuit where the resistance is in equilibrium with a bath at temperature T . We observe that the net current through the circuit is a fast fluctuation variable.

- (1) Show that the the charge Q in the capacitor obeys a Langevin type equation with a damping coefficient $1/RC$.

- (2) From $\langle Q^2 \rangle / (2C) = kT/2$ (why ?) deduce that the variance of the fluctuations is proportional to the temperature.

PROBLEM 6

We consider the forced harmonic oscillator:

$$(778) \quad \ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{F(t)}{m}$$

with $\langle F(t + \tau)F(t) \rangle = 2A\delta(t)$.

- (1) Use the Wiener-Kinchin's theorem to compute the Fourier transform of $C_{xx}(\tau) = \langle x(t + \tau)x(t) \rangle$
 (2) Show that:

$$(779) \quad C_{xx}(\omega) = \frac{1}{m^2} \frac{2A}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2}$$

- (3) The strong friction limit corresponds to $\gamma \gg \omega_0$. Draw (qualitatively) $C_{xx}(\omega)$ in the strong friction limit. Show that the width is ω_0^2/γ and estimate a characteristic time τ_x .
 (4) Compute the momentum correlation function $\langle p(t + \tau)p(t) \rangle$. Show that $\tau_p \ll \tau_x$.
 (5) Show that making the strong friction limit amounts neglecting the inertial term in the equation of motion. In this way, one recovers the Ornstein-Uhlenbeck equation seen during the lectures.

PROBLEM 7

Consider a RC circuit where the voltage drop obeys the following equation:

$$(780) \quad RI(t) + \frac{Q(t)}{C} = \eta(t) \text{ with } \langle \eta(t)\eta(t') \rangle = \Gamma\delta(t - t')$$

- (1) Show

$$(781) \quad Q(t) = \frac{1}{R} \int_{-\infty}^t d\tau e^{-(t-\tau)/RC}$$

- (2) Show

$$(782) \quad \langle Q(t) \rangle = 0 \text{ and } \langle Q^2(t) \rangle = \frac{\Gamma C}{2R}$$

- (3) From Problem 1, we know that $P(Q)$ is gaussian, $P(Q) \sim \exp\{-Q^2/2kTC\}$. Give Γ as a function of the temperature.
 (4) Show

$$(783) \quad \langle Q(t)Q(t') \rangle = CkTe^{-|t-t'|/RC}$$

- (5) Deduce

$$(784) \quad \langle V(t)V(t') \rangle = \frac{kT}{C} e^{-|t-t'|/RC}$$

- (6) The product RC is characteristic time scale. Show using $\int dt\delta(t) = 1$ that if RC is small compared to the scale where the observations are made

$$(785) \quad \langle V(t)V(t') \rangle = 2kTR\delta(t - t')$$

- (7) Deduce

$$(786) \quad \int_{\omega_1}^{\omega_2} \langle |\tilde{V}(\omega)|^2 \rangle = 4kTR \int_{\omega_1}^{\omega_2} d\omega$$

PROBLEM 8

We have seen that Kubo's theorem gives a relationship between a correlation function and a response function:

$$(787) \quad C_{A,B}(t) = k_B T \int_t^\infty \chi_{A,B}(t') dt'$$

We want to give a straightforward demonstration in the case of a Langevin particle

- (1) Write the Langevin equation with an external force $F(t)$.
- (2) What is the quantity conjugate to the force? What do you take for B and A in (787)?
- (3) Assume $F(t) = 0$. Show

$$(788) \quad \langle v(t)v(t') \rangle = \frac{kT}{m} e^{-\frac{\gamma}{m}|t-t'|}$$

- (4) Deduce ($t > t'$)

$$(789) \quad C_{A,B}(t-t') = \frac{kT}{\gamma} e^{-\frac{\gamma}{m}|t-t'|}$$

- (5) What is $\langle v(t) \rangle$ for small $F(t)$?
- (6) Conclude

$$(790) \quad \chi_{A,B}(t) = \frac{1}{m} e^{-\frac{\gamma}{m}|t|}$$

- (7) Check (787)

PROBLEM 9

We know that there exists a relationship between the response function to an external force and the correlation function at zero force (i.e. at equilibrium). This relation is stated as:

$$(791) \quad C_{AB}(t) = k_B T \int_t^\infty \chi_{A,B}(t') dt'$$

The purpose of this problem is to provide a direct proof of this relation using the Langevin's equation

$$(792) \quad m \frac{dv}{dt} = -\gamma v + \eta(t) + F(t)$$

where, as usual, $\eta(t)$ is the noise and $F(t)$ the external force. Recall $\langle \eta(t)\eta(t') \rangle = \Gamma \delta(t-t')$ with $\Gamma = 2\gamma k_B T$ and $\langle \eta(t) \rangle = 0$.

- (1) For the Langevin's equation, the response function connects the velocity to the force. Therefore, A is the velocity. What is the equivalent of B in our case, i.e. for the Langevin's equation? Why?
- (2) Show (in the stationary regime)

$$(793) \quad \langle v(t)v(t') \rangle = \frac{k_B T}{m} e^{-\frac{\gamma}{m}|t-t'|}$$

and specify if this correlation is calculated at zero force or not.

- (3) If $q(t)$ is the position, show for $t > t'$:

$$(794) \quad \langle v(t)q(t') \rangle = \frac{k_B T}{\gamma} e^{-\frac{\gamma}{m}|t-t'|}$$

- (4) Assume now a non-zero force. Show

$$(795) \quad \langle v(t) \rangle = \frac{1}{m} \int_{-\infty}^t e^{-\frac{\gamma}{m}(t-t')} F(t') dt'$$

(5) Deduce $\chi_{A,B}(t)$ and check relationship (844).

PROBLEM 10

The general form of a master equation is

$$(796) \quad \dot{p}_n = \sum_{n'} [w_{nn'} p_{n'} - w_{n'n} p_n]$$

We consider a process for which the transition matrices are given by

$$(797) \quad w_{n+1,n} = g \quad \text{and} \quad w_{n-1,n} = rn$$

(1) Show that the master equation reads

$$(798) \quad \partial_t p_n = -(g_n + r_n) p_n + g_{n-1} p_{n-1} + r_{n+1} p_{n+1}$$

and give g_n and r_n as a function of n .

(2) Discuss qualitatively what represent the four terms in Eq. (851).

(3) In what follows, we will be interested in the large number of molecules limit, $n \gg 1$, where a change of 1 molecule can be treated as a small change. Then $g_n p_n$ becomes a function $g(n)p(n)$ (and $r_n p_n$ becomes $r(n)p(n)$). Under this approximation, the function $f(n) = g(n)p(n)$, or $f(n) = r(n)p(n)$, can be expanded to second order as

$$(799) \quad f(n \pm 1) = f(n) \pm \partial_n f(n) + \frac{1}{2} \partial_n^2 f(n)$$

Show that this approximation turns the master equation into something that looks more like a Fokker-Plank equation. What is the effective potential in which the 'coordinate' n is diffusing ?

(4) Introduce the current of probability

$$(800) \quad j(n) = v(n)p(n) - \frac{1}{2} \partial_n [D(n)p(n)]$$

and give $v(n)$ and $D(n)$ as a function of n . Can you guess the value of current in equilibrium ?

(5) Compute the steady state distribution within a constant normalization factor.

(6) Show:

$$(801) \quad p(n) = \frac{A}{g} \left(1 + \frac{n}{g}\right)^{4g-1} e^{-2n}$$

where A is a normalization factor.

(7) Show that the mean value $\langle n \rangle = \sum_n n p_n$ obeys the kinetic equation

$$(802) \quad \frac{d\langle n \rangle}{dt} = g - r\langle n \rangle$$

PROBLEM 11

Consider the situation schematized in Fig. 1. Assume that the concentration at $r \rightarrow \infty$ is maintained at c_0 ². The sphere of radius a is covered by sensors with surface density σ . The rate of uptake of solute molecules per unit surface is given by

$$(803) \quad \frac{dn}{dt} = \sigma k_{on} c(a)$$

This equation defines k_{on} as the usual kinetic rate in chemical reaction.

²The concentration is often expressed in Molars M with 1 Molars = 1000 moles / m³

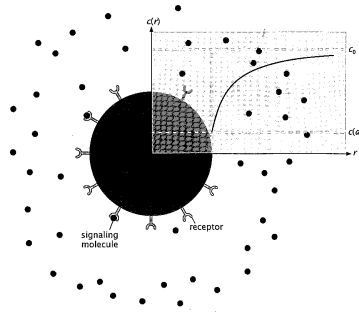


FIGURE 1. An absorbing sphere for a solute diffusing in the bulk. The concentration of solute decreases in the vicinity of the sphere. This depletion zone is characteristic of problem controlled by diffusion.

(1) Show that solution of the 3-*d* Fokker-Planck equation with symmetry of revolution is given by $c(r) = \beta + \alpha/r$.

(2) Using mass conservation, show

$$(804) \quad -4\pi r^2 J(r) = Mk_{on}c(a)$$

(3) Use the last equation to compute the concentration as

$$(805) \quad c(r) - c(a) = \frac{Mk_{on}c(a)}{4\pi D} \left(\frac{1}{a} - \frac{1}{r} \right)$$

(4) Show

$$(806) \quad c(a) = \frac{c_0}{1 + Mk_{on}/(4\pi Da)}$$

(5) Plot $c(r)$.

(6) Deduce that the net adsorption rate is

$$(807) \quad k = \frac{4\pi DaMk_{on}}{4\pi Da + Mk_{on}}$$

(7) Investigate the two limits of a perfect adsorber, $k_{on} \rightarrow \infty$, and of a bad adsorber, $k_{on} \rightarrow 0$. Conclude that the net adsorption rate can be written as

$$(808) \quad \frac{1}{k} = \frac{1}{Mk_{on}} + \frac{1}{k_D}$$

where $1/k_D$ is a diffusion time which depends on the diffusion constant. Thus, our boundary condition together with the diffusion equations set two characteristic time scales. This is in contrast with the usual condition of perfect adsorption with only one time scale.

Non-equilibrium statistical physics exam February, 8 2016

Problem 1

We consider the problem of ligand molecules binding to a single site of a sensor molecule. Ignoring fluctuations, the fractional occupancy of the site, $n(t)$, evolves according to the first-order kinetic equation

$$(809) \quad \frac{dn}{dt} = k_+c[1 - n(t)] - k_-n(t)$$

where c is the background concentration of the ligand (considered as constant in this problem) and k_{\pm} are rate constants.

- (1) Give the equilibrium concentration \bar{n} . Let F be the free energy associated with binding. Use detailed balance to give the ratio k_+c/k_- as a function of F .
- (2) Suppose that thermal noise induces small fluctuations in the binding energy δF . Show

$$(810) \quad \frac{\delta k_+}{k_+} - \frac{\delta k_-}{k_-} = \frac{\delta F}{k_B T}$$

- (3) Linearize (809) about the equilibrium solution, $n = \bar{n} + \delta n$, and show that the fluctuations δn obey the linear equation

$$(811) \quad \gamma \frac{d\delta n}{dt} = -\kappa \delta n + \delta F$$

where γ and κ are effective damping and spring constants. Give γ and κ .

- (4) Eq. (811) is analogous to a known equation. Which one ?
- (5) Solve Eq. (811) and give the Fourier transform of the dynamical susceptibility $\tilde{\chi}(\omega)$.
- (6) Using the lecture notes, show that the power spectrum

$$(812) \quad S_n(\omega) = \int_{-\infty}^{+\infty} dt \langle \delta n(0)\delta n(t) \rangle e^{i\omega t}$$

is given by

$$(813) \quad S_n(\omega) = \frac{2k_B T}{\omega} \text{Im} [\tilde{\chi}(\omega)]$$

- (7) Conclude that the power spectrum has a Lorentzian form

$$(814) \quad S_n(\omega) = \frac{2k_+c(1 - \bar{n})}{\omega^2 + (k_+c + k_-)^2}$$

- (8) Conclude

$$(815) \quad \langle \delta n(t)\delta n(0) \rangle = \langle \delta n^2 \rangle e^{-|t|/\tau_c}$$

and give the characteristic time τ_c .

- (9) Obtain the same result using a principle that we have studied during the lectures.

Problem 2 : Bownian motion in a gravitational field

We know that the Langevin equation for a particle

$$(816) \quad \frac{dy}{dt} = A(y) + c\eta(t),$$

with $\langle \eta(t)\eta(t') \rangle = \Gamma\delta(t - t')$, is equivalent to the Fokker-Planck equation for the probability

$$(817) \quad \frac{\partial P}{\partial t} = -\frac{\partial [A(y)P]}{\partial y} + \frac{c^2\Gamma}{2} \frac{\partial^2 P}{\partial y^2}$$

irrespective of the function $A(y)$.

Let x be the variable for the height variable for a Brownian particle with a mass m in a gravitational field g with friction coefficient γ .

- (1) What is the Langevin equation for this particle ?
- (2) Work in the large friction limit and neglect inertial effects. What is the equivalent Fokker-Planck equation ?
- (3) Assume stationarity. Solve this equation in the general case.
- (4) As usual, solutions of differential equations depend on the boundary conditions. Give the solution when the probability current is 0 at $x = 0$ and when $x \geq 0$.

Problem 3

We consider again the situation of Problem 1. From now on, the concentration of ligands is NOT considered as homogenous and we consider small deviations with respect to the background value

$$(818) \quad c = \bar{c} + \delta c$$

Taking the sensor molecule at position $\mathbf{x}_0 = 0$ and setting $c(\mathbf{x}, t)$, we assume that

$$(819) \quad \frac{dn}{dt} = k_+ c(\mathbf{x}, t) [1 - n(t)] - k_- n(t)$$

$$(820) \quad \frac{\partial c(\mathbf{x}, t)}{\partial t} = D \Delta c(\mathbf{x}, t) - \delta(\mathbf{x} - \mathbf{x}_0) \frac{dn}{dt}$$

where the last term accounts for the transfer of a molecule when a ligand binds the receptor.

- (1) By linearizing these equations of motions about the uniform steady state (\bar{n}, \bar{c}) and using detailed balance show that

$$(821) \quad \gamma \frac{d\delta n}{dt} = -\kappa \delta n + k_+ [1 - \bar{n}] \gamma \delta c(\mathbf{x} = \mathbf{0}, t) + \delta F$$

with

$$\gamma = kT / [k_+ \bar{c} (1 - \bar{n})] \quad \text{and} \quad \kappa = (k_+ \bar{c} + k_-) \gamma$$

and

$$(822) \quad \frac{\partial \delta c(\mathbf{x}, t)}{\partial t} = D \Delta c(\mathbf{x}, t) - \delta(\mathbf{x} - \mathbf{x}_0) \frac{d\delta n(t)}{dt}$$

- (2) Define the Fourier transforms as

$$(823) \quad \delta \tilde{c}(\mathbf{k}, \omega) = \int_{-\infty}^{+\infty} dt \int d^3 x e^{i\omega t} e^{i\mathbf{k} \cdot \mathbf{x}} \delta c(\mathbf{x}, t) \quad \delta \tilde{n}(\omega) = \int_{-\infty}^{+\infty} dt e^{i\omega t} \delta n(t)$$

Show that

$$(824) \quad \delta c(\mathbf{x}, \omega) = i\omega \Sigma_0(\omega) \delta \tilde{n}(\omega), \quad \Sigma_0(\omega) = \int \frac{d^3 k}{(2\pi)^3} \frac{1}{Dk^2 - i\omega}$$

- (3) The last integral diverges. We impose a cut-off $|\mathbf{k}| < \pi/a$. What does a correspond to ?

- (4) Hence derive the result for the generalized susceptibility

$$(825) \quad \frac{\delta \tilde{n}(\omega)}{\delta \tilde{F}(\omega)} = \frac{1}{\gamma - i\omega [1 + \Sigma(\omega)] + k_+ \bar{c} + k_-}$$

- (5) We make the approximation $\Sigma(\omega) = \Sigma(0)$ in (824). Conclude

$$(826) \quad S_n(\omega) = \bar{n}(1 - \bar{n}) \frac{2\tau_c}{1 + (\omega\tau_c)^2}$$

and give τ_c .

Non-equilibrium statistical physics exam
January, 15 2017
Write this exam in your native language

1. Problem 1

In chemical kinetics, a chemical reaction occurring between species A_i , $1 \leq i \leq N$, is represented as



with the rate equation for the concentration c_i

$$(828) \quad \frac{dc_i}{dt} = \gamma_i (\omega_r^+ - \omega_r^-) \quad \gamma_i = \beta_i - \alpha_i$$

where the subscript r stands for reaction. The reaction rates are defined as :

$$(829) \quad \begin{aligned} \omega_r^+ &= \omega_{eq} \exp \left\{ \left[\sum_i \alpha_i (\mu_i - \mu_i^{eq}) / kT \right] \right\} \\ \omega_r^- &= \omega_{eq} \exp \left\{ \left[\sum_i \beta_i (\mu_i - \mu_i^{eq}) / kT \right] \right\} \end{aligned}$$

where the μ_i 's are the chemical potentials (per unit volume). For ideal solutions:

$$(830) \quad \mu_i(c_i, T) = kT \ln c_i + \mu_i^\theta(T)$$

where $\mu_i^\theta(T)$ is the chemical potential in a reference state for species i (here $\mu_i^\theta(T)$ is a parameter).

(1) As a special case, consider



Follow recipe (828) and give dc_1/dt and dc_2/dt as a system of two ordinary differential equations. What the first principle seen in the lectures that Eqs. (829) obey ?

(2) From now on, $1 \leq i \leq N$. Remember that the free energy for an ideal solution of concentration c is

$$(832) \quad F(c) = kT c (\ln c - 1 + \mu^\theta(T)/kT)$$

Calculate the rate dF_{total}/dt of the total free energy change per unit time as a function of ω_r^+ and ω_r^- .

(3) Conclude. To answer to this question, we will use the properties of function $(\ln x - \ln y)(x - y)$ as studied during the lectures.

(4) If we consider R reactions of type (827) instead of 1, meaning $1 \leq r \leq R$, the same type of calculation leads to

$$(833) \quad \frac{dc_i}{dt} = - \sum_j \left[\sum_r w_r^{eq} \gamma_{r,j} \gamma_{r,i} \right] \frac{\mu_j - \mu_j^{eq}}{kT}$$

where we have assumed small deviation from equilibrium. In these equations, $\gamma_{r,j} = \beta_{r,j} - \alpha_{r,j}$. What kind of reciprocity relations does these equations correspond to ? What kind of symmetry do they possess ?

Problem 2

We consider a particle moving along a one-dimensional periodic track. This particle is subjected to:

- (1) A periodic potential $V(x)$ with $V(x+l) = V(x)$, where l is the periodicity.
- (2) A force, i.e. a load F .

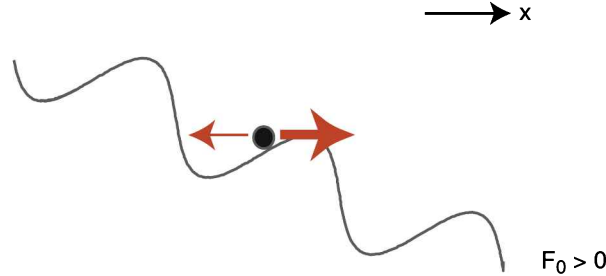


FIGURE 2.

We want to compute the velocity of the particle under the load F .

- (1) Show that there exists an effective potential $V_e(x)$ depending on the force F such that the Fokker-Planck equation can be written as

$$(834) \quad \frac{\partial p}{\partial t} = D_0 \left[\frac{1}{kT} \frac{\partial [V_e(x)p(x)]}{\partial x} + \frac{\partial^2 p}{\partial x^2} \right]$$

- (2) To study the averages motion of the particle under the force F , we define the average quantities:

$$(835) \quad \begin{aligned} \hat{P}(x, t) &= \sum_n p(x + nl, t) \\ \hat{J}(x, t) &= \sum_n j(x + nl, t) \end{aligned}$$

where n runs on a sufficiently large number of sites. Show that

$$(836) \quad \hat{J}(x, t) = -D_0 \left[\frac{1}{kT} V_e'(x) \hat{P}(x) + \frac{\partial \hat{P}}{\partial x} \right]$$

- (3) What are the boundary conditions for $\hat{P}(x, t)$, $\hat{J}(x, t)$ at $x = 0, l$?
- (4) Assume a stationary state with current \hat{J}_0 and show that $p_0(x)$ is solution of

$$(837) \quad \frac{d}{dx} \left[e^{V_e(x)/kT} \hat{p}_0(x) \right] = -\frac{\hat{J}_0}{D_0} e^{V_e(x)/kT}$$

- (5) Integrate this equation and show

$$(838) \quad \hat{p}_0(x) = \frac{J_0}{1 - e^{-Fl/kT}} \mathcal{N}(x)$$

where

$$(839) \quad \mathcal{N}(x) = \frac{1}{D_0} e^{-V_e(x)/kT} \int_x^{x+l} e^{V_e(y)/kT} dy$$

- (6) Assume that the mean velocity of the particle is equal to the ensemble averaged current

$$(840) \quad v = \int_{-\infty}^{+\infty} j(x, t) dx = \int_0^L \hat{J}(x, t) dx$$

and give v as a function of F

- (7) Using the periodic boundary conditions, show that the average velocity is zero when $F = 0$.
- (8) Does this result hold for a non-symmetric potential such as in Fig. 3 ?



FIGURE 3.

- (9) Now consider the same problem as before but for a motor protein with two internal states $i = 1, 2$. How can we generalize (834) in this case ? Hint. Introduce two parameters ω_1 and ω_2 .

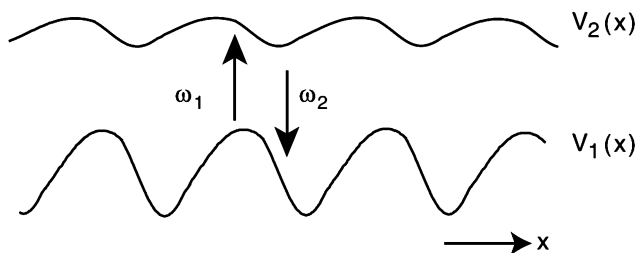


FIGURE 4.

- (10) What is the relation between these two parameters if you assume detailed balance ?

Problem 3

Consider a master equation. the Master equation. We consider the process for which

$$(841) \quad W_{m,n} = \begin{cases} \lambda & \text{if } m = n + 1 \\ 0 & \text{if } m \neq n + 1 \end{cases}$$

- (1) Write the master equation for P_n
- (2) Introduce the generating function $P(z, t) = \sum_{n \geq 0} z^n P_n(t)$ with the initial condition $P_n(0) = \delta_{n,0}$. Show:

$$(842) \quad P(z, t) = \exp\{[(z - 1)\lambda t]\}P(z, 0)$$

- (3) Deduce

$$(843) \quad P_n(t) = \frac{((\lambda t))^n}{n!} e^{-\lambda t}$$

- (4) Do you know this distribution ?

Non-equilibrium statistical physics exam

January 25, 2019

PROBLEM 1

We know that there exists a relationship between the response function to an external force and the correlation function at zero force (i.e. at equilibrium). This relation is stated as:

$$(844) \quad C_{AB}(t) = k_B T \int_t^\infty \chi_{A,B}(t') dt'$$

The purpose of this problem is to provide a direct proof of this relation using the Langevin's equation

$$(845) \quad m \frac{dv}{dt} = -\gamma v + \eta(t) + F(t)$$

where, as usual, $\eta(t)$ is the noise and $F(t)$ the external force. Recall $\langle \eta(t)\eta(t') \rangle = \Gamma \delta(t-t')$ with $\Gamma = 2\gamma k_B T$ and $\langle \eta(t) \rangle = 0$.

- (1) For the Langevin's equation, the response function connects the velocity to the force. Therefore, A is the velocity. What is the equivalent of B in our case, i.e. for the Langevin's equation? Why?
- (2) Show (in the stationary regime)

$$(846) \quad \langle v(t)v(t') \rangle = \frac{k_B T}{m} e^{-\frac{\gamma}{m}|t-t'|}$$

and specify if this correlation is calculated at zero force or not.

- (3) If $q(t)$ is the position, show:

$$(847) \quad \langle v(t)q(t') \rangle = \frac{k_B T}{\gamma} e^{-\frac{\gamma}{m}|t-t'|}$$

- (4) Assume now a non-zero force. Show

$$(848) \quad \langle v(t) \rangle = \frac{1}{m} \int_{-\infty}^t e^{-\frac{\gamma}{m}(t-t')} F(t') dt'$$

- (5) Deduce $\chi_{A,B}(t)$ and check relationship (844).

PROBLEM 2

The general form of a master equation is

$$(849) \quad \dot{p}_n = \sum_{n'} [w_{nn'} p_{n'} - w_{n'n} p_n]$$

We consider a process for which the transition matrices are given by

$$(850) \quad w_{n+1,n} = g \quad \text{and} \quad w_{n-1,n} = rn$$

- (1) Show that the master equation reads

$$(851) \quad \partial_t p_n = -(g_n + r_n) p_n + g_{n-1} p_{n-1} + r_{n+1} p_{n+1}$$

and give g_n and r_n as a function of n .

- (2) Discuss qualitatively what represent the four terms in Eq. (851).
- (3) In what follows, we will be interested in the large number of molecules limit, $n \gg 1$, where a change of 1 molecule can be treated as a small change. Then $g_n p_n$ becomes

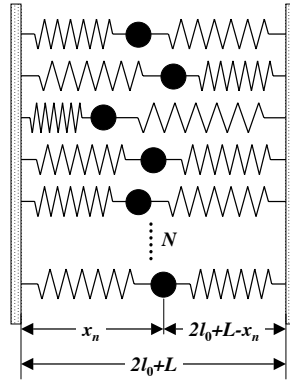


FIGURE 5. System under consideration with N particles of mass m connected by harmonic springs to two walls.

a function $g(n)p(n)$ (and $r_n p_n$ becomes $r(n)p(n)$). Under this approximation, the function $f(n) = g(n)p(n)$, or $f(n) = r(n)p(n)$, can be expanded to second order as

$$(852) \quad f(n \pm 1) = f(n) \pm \partial_n f(n) + \frac{1}{2} \partial_n^2 f(n)$$

Show that this approximation turns the master equation into something that looks more like a Fokker-Plank equation. What is the effective potential in which the 'coordinate' n is diffusing?

(4) Introduce the current of probability

$$(853) \quad j(n) = v(n)p(n) - \frac{1}{2} \partial_n [D(n)p(n)]$$

and give $v(n)$ and $D(n)$ as a function of n . Can you guess the value of current in equilibrium?

(5) Compute the steady state distribution within a constant normalization factor.

(6) Show:

$$(854) \quad p(n) = \frac{A}{g} \left(1 + \frac{n}{g}\right)^{4g-1} e^{-2n}$$

where A is a normalization factor.

(7) Show that the mean value $\langle n \rangle = \sum_n n p_n$ obeys the kinetic equation

$$(855) \quad \frac{d\langle n \rangle}{dt} = g - r\langle n \rangle$$

PROBLEM 3

Consider the system of Fig. 5. The particles are in equilibrium with a reservoir at temperature T . We imagine that at $t = 0$ the right wall is moved with uniform velocity V , so that $L(t) = (L_0 + Vt)\theta(t)$, where $\theta(t)$ is the Heaviside function. Let ΔF the free energy difference between the final state L_1 and the initial state L_0 .

What is your prediction for the total work done on all individual particles (2 lignes)? Discuss the large particle number limit (2 lignes).

Non equilibrium Statistical Mechanics
Université Grenoble Alpes
Year 2019-2020

(1) PROBLEM 1

Consider an electrical RC-circuit with capacity C and a resistance R . The charge on the capacitor is denoted $Q(t)$. From the formulae $U = RI$ and $Q = CU$ the macroscopic equation can be found to be

$$(856) \quad \dot{Q}(t) = -\frac{Q}{RC} = -\gamma Q \text{ with } \gamma = 1/(RC)$$

The electrostatic energy of a capacitor is $Q^2/(2C)$.

- (a) Assuming that the electrical current I fluctuates as $\Gamma\eta(t)$ ($\eta(t)$ is the normal Gaussian white noise), what is the Langevin equation for this macroscopic problem ?
- (b) Given that $Q(t=0) = Q_0$, find $Q(t)$ ³
- (c) Give $\langle Q^2(t) \rangle$. What is the mean energy stored in the capacitor in the stationary regime ? How do you adjust Γ to recover known results from equilibrium statistical mechanics ?
- (d) Correction: The equivalent Langevin equation is

$$(857) \quad R \frac{dQ}{dt} = -\frac{Q}{C} + \eta(t)$$

where $\eta(t)$ is a white noise due to thermal effects

$$(858) \quad \langle \eta(t)\eta(t') \rangle = \Gamma\delta(t-t')$$

As in the lecture, one can calculate

$$(859) \quad Q(t) = \frac{1}{R} \int_{-\infty}^t d\tau \exp\left\{-\frac{t-\tau}{RC}\right\} \eta(\tau)$$

This gives

$$(860) \quad \langle Q \rangle = 0 \quad \langle Q^2 \rangle = \frac{\Gamma C}{2R}$$

The energy stored in the capacitor is given by the Boltzmann law

$$(861) \quad P(Q) \propto \exp\left\{\left[-\frac{Q^2}{2CkT}\right]\right\}$$

which gives

$$(862) \quad \frac{\langle Q^2 \rangle}{2C} = \frac{kT}{2}$$

(2) PROBLEM 2

Consider an isolated system consisting of two parts. A left part and a right part (these parts communicate arbitrarily). Let $N_R(t)$ be the number of particles in the right part of the system and we consider the following total energy

$$(863) \quad E = E_0 - V(t)N_r(t)$$

³Recall that the solution to $\dot{y}(t) - \gamma y(t) = a(t)$ can be found by posing $y(t) = f(t)e^{-\gamma t}$.

if the potential $V(t)$ varies over time, this leads to a variation in the number of particles $N_R(t)$ in the right part of the system. Recall the fluctuation dissipation theorem

$$(864) \quad C_{AB}(t) = kT \int_t^{+\infty} \chi_{AB}(t') dt'$$

Assume that the system is in equilibrium for $t < 0$ with $V(t = 0)$ and that $V(t)$ is suddenly increased at $t = 0$ to a constant value V

$$(865) \quad V(t) = \begin{cases} 0 & \text{for } t < 0 \\ V & \text{for } t > 0 \end{cases}$$

- (a) Apply linear response theory and give a general expression for $\langle N_R(t) \rangle_V - \langle N_R(t) \rangle_0$.
 (b) By computing the difference

$$(866) \quad \int_0^\infty \chi(t') dt' - \int_t^\infty \chi(t') dt'$$

show

$$(867) \quad \langle N_R(t) \rangle_V - \langle N_R(0) \rangle_V = \frac{\beta V}{2} \langle (N_R(t) - N_R(0))^2 \rangle_0$$

- (3) Correction: the response of the particle number to a change in potential is

$$(868) \quad \langle N_R(t) \rangle_V = \langle N_R(t) \rangle_0 + V \int_0^t \chi(t') dt'$$

The fluctuation dissipation theorem gives

$$(869) \quad \int_t^\infty \chi(t') dt' = \beta [\langle N_R(t) N_R(0) \rangle_0 - \langle N_R(t) \rangle_0 \langle N_R(0) \rangle_0]$$

In particular

$$(870) \quad \int_0^\infty \chi(t') dt' = \beta [\langle N_R(0)^2 \rangle_0 - \langle N_R(0) \rangle_0 \langle N_R(0) \rangle_0]$$

Taking the difference between these two expressions gives

$$(871) \quad \langle N_R(t) \rangle_V - \langle N_R(0) \rangle_0 = \beta V [\langle N_R(0)^2 \rangle_0 - \langle N_R(t) N_R(0) \rangle_0]$$

We have :

$$(872) \quad \langle N_R(0) \rangle_V = \langle N_R(0) \rangle_V$$

since at $t = 0$, N_R cannot not depend on V . We also have

$$(873) \quad \langle N_R(t)^2 \rangle_0 = \langle N_R(0)^2 \rangle_0$$

because of time translational invariance of equilibrium systems.

- (4) PROBLEM 3

Consider a molecule walking along a one-dimensional filament (without leaving it). The trajectory is described as $X(t) = dN(t)$ where d is the step length defined by the length of the binding sites. The rules are as follows: The stepper can only makes step to right or stay at the same place. He cannot go the left. The probability to make a step to right during Δt is $\alpha \Delta t$. For Δt small, the stepper can only stay or make one step (i.e. he cannot make two or more steps).

- (a) Show that the master equations can be written as

$$(874) \quad \begin{aligned} \frac{d}{dt} p_n(t) &= w_{n,n-1} p_{n-1}(t) - w_{n+1,n} p_n(t) \\ \frac{d}{dt} p_0(t) &= -w p_0(t) \end{aligned}$$

and give the w_{\dots} as a function of α .

(b) Define

$$(875) \quad G(z, t) = \sum_n p_n(t) z^n$$

By using Eqs. (874) show

$$(876) \quad \frac{\partial}{\partial t} G(z, t) = \alpha(z - 1)G(z, t)$$

(c) The initial condition is $p_n(0) = \delta_{n,0}$ What is $G(z, t)$?

(d) Taylor expanding this result, give $p_n(t)$.

(e) Correction. All w 's are equal to α . From

$$(877) \quad \frac{\partial G}{\partial t} = \sum_n z^n (\alpha p_{n-1} - \alpha p_n) = \alpha z \sum_n z^{n-1} p_{n-1} - \alpha \sum_n z^n p_n$$

we find

$$(878) \quad G(z, t) = G(z, t = 0) \exp\{\alpha(z - 1)t\}$$

Using $p_n(t = 0)$ we find $G(z, t = 0) = 1$. Taylor expanding:

$$(879) \quad p_n(t) = (z - 1)^n \frac{\alpha^n}{n!}$$

(5) PROBLEM 4

Let x be the variable of the height of a brownian particle (mass m , gravity constant g , friction parameter γ , diffusion constant D). In the stationary state, the Fokker-Planck equation is

$$(880) \quad \frac{mg}{\gamma} P(x) + D \partial_x P(x) = 0$$

(a) Using the boundary condition that the surface of the earth reflects the particle (zero current) give $P(x)$.

(b) What is the relationship between D and γ you can infer from statistical mechanics ?

(c) Correction : Using the boundary condition that the surface reflects the particle, meaning $j(x = 0, t) = 0$, one obtains

$$(881) \quad P_S(x) = \frac{C}{2D} \exp\left\{\left[-\frac{mg}{D\gamma}x\right]\right\}$$

and comparing this with statistical mechanics, we find $D\gamma = k_B T$, which is the Einstein relation.

Non-equilibrium Statistical Mechanics
Université Grenoble Alpes
May, 29 2020

(1) PROBLEM 1

We consider a molecule diffusing on a one-dimensional track with position coordinate x . Let D be the diffusion coefficient of this molecule. If T is the temperature, the thermal energy is denoted by kT .

- (a) Assuming that this molecule is subjected to thermal noise, what is the Fokker-Planck equation for the probability $P(x, t)$ to find the molecule at position x at time t ?
- (b) We assume from now on that the molecule experiences along the track a position-dependent potential $V_0(x)$. What is the Fokker-Planck equation in this case ?
- (c) Using a laser, we can also apply an external load F (independent of the position) on the particle. What is the Fokker-Planck equation when $V_0(x) \neq 0$? It will be useful to define an effective potential $V_{eff}(x)$ as a function of the force.
- (d) We assume that $V_0(x)$ is periodic with periodicity l , i.e. :

$$(882) \quad V_0(x + l) = V_0(x)$$

To study the average motion of this molecule, we introduce the quantity

$$(883) \quad P_a(x, t) = \sum_n P(x + nl, t)$$

where $P(x, t)$ is the probability of question (c). Define an average current $J_a(x, t)$ in the same way and show:

$$(884) \quad J_a(x, t) = -D \left[\frac{1}{kT} V'_{eff}(x) P_a(x, t) + \frac{\partial P_a}{\partial x} \right]$$

- (e) What is the equivalent Fokker-Planck equation for $P_a(x, t)$?
- (f) We consider from now on the stationary regime where $P_a(x)$ is time independent. Show that there is a constant C such that:

$$(885) \quad \frac{d}{dx} [e^{V_{eff}(x)/kT} P_a(x)] = -\frac{C}{D} e^{V_{eff}/kT}$$

(2) PROBLEM 2

We consider again a molecule moving on a one-dimensional track with position coordinate x . This molecule has two conformational states \uparrow and \downarrow . The rate per unit time for the molecule to pass from the state \downarrow to the state \uparrow is $k_{\uparrow, \downarrow}$ ($k_{\downarrow, \uparrow}$ for the reverse process, respectively). Let $P_{\uparrow}(x)$ the probability to find the molecule in \uparrow at position x (with $P_{\downarrow}(x)$, respectively). Assuming that the particle can only diffuse in the \uparrow state with diffusion coefficient D (and not in the \downarrow state where $D = 0$), write two coupled Fokker-Planck equations for $P_{\uparrow}(x)$ and $P_{\downarrow}(x)$.

(3) PROBLEM 3

Fisher showed that the fertility of a population increases on average as the variance of fertility increases. This theorem shows that the fertility of a population increases even in the absence of mutations. To prove this assertion, the starting point is to consider a model where the number of individuals n_i with fertility σ_i obeys the following equation:

$$(886) \quad \frac{dn_i}{dt} = \sigma_i n_i$$

We are interested in the average fertility

$$(887) \quad \langle \sigma \rangle = \frac{\sum_i n_i \sigma_i}{\sum_i \sigma_i}$$

Show:

$$(888) \quad \frac{d\langle \sigma \rangle}{dt} = \langle \sigma^2 \rangle - \langle \sigma \rangle^2$$

Conclude.

Université Grenoble-Alpes
Année 2020-2021

Nonequilibrium Statistical Mechanics

Note : It may be helpful to read the entire problem set. You can use either English, French or German.

(1) Problem 1

Suppose the system being investigated is a single rigid spherical bead. We will consider rotational diffusion constrained in the $x - y$ plane and it will be convenient to represent the orientational vector $\hat{n}(t)$ by the polar angle $\theta(t)$.

- (a) By analogies with the translational movement of a bead with velocity v and mass m , the rotational movement of the bead is described by an angular velocity Ω , a drag force $-\zeta\Omega$ and an inertial moment I . Give the Langevin equation corresponding to the rotational movement of the bead.
- (b) Give $\langle\theta(t)^2\rangle_{\text{eq.}}$ as a function of time.
- (c) The orientational time correlation function is

$$(889) \quad C(t) = \langle e^{-i\theta(t=0)} e^{i\theta(t)} \rangle_{\text{eq.}}$$

What is the probability density you expect for $\Delta\theta(t)$? Why ?

- (d) Give $C(t)$ for large t .
- (e) Instead of considering the Brownian motion of a sphere, we consider from now on the Brownian motion of an ellipsoid (translational AND rotational). A uniaxial anisotropic particle is characterized by two translational hydrodynamic friction coefficients, γ_a and γ_b , respectively, for motion in directions parallel and perpendicular to its long axis. Consider a particle with a given initial angle. Will it diffuse more rapidly along its long axis than along its short axis ?
- (f) Using a camera, the experiment gives access to the position $(x(t), y(t))$ of the ellipsoid, so that one can compute the averages

$$(890) \quad \langle\Delta x(t)^2\rangle_{\theta_0}/(2t) \quad \text{and} \quad \langle\Delta y(t)^2\rangle_{\theta_0}/(2t)$$

at fixed starting angle $\theta_0(t=0)$. Consider Fig. 6 where the instantaneous diffusion coefficient is plotted as a function of time. Can you comment this figure in 3 lines?

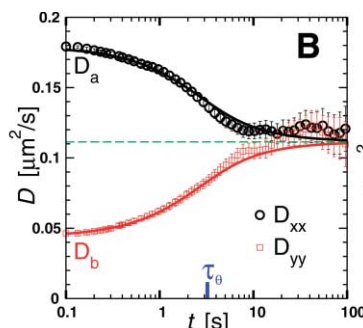


FIGURE 6. Diffusion coefficients D . The initial orientation of each trajectory was chosen to be along the x -axis or along the y -axis. See Y. Han et al., Brownian motion of an Ellipsoid, *Science*, **314**, 626, 2006.

(2) Problem 2

We consider an isolated system composed of two parts, a left part and a right part.

This system contains two types of particles free to move. We call N_1 and N_2 the number of particles of type 1 or 2 in the right part. We consider the following energy

$$(891) \quad E - V_1(t)N_1 - V_2(t)N_2$$

and we recall the F.D. (fluctuation-dissipation) theorem ($\beta = 1/kT$)

$$(892) \quad C_{AB}(t) = 1/\beta \int_{-\infty}^t \chi_{AB}(t-t')F(t')$$

(a) We choose $V_1(t) = 0$ for all t and

$$(893) \quad V_2(t) = \begin{cases} 0 & \text{for } t < 0 \\ V_2 & \text{for } t > 0 \end{cases}$$

Therefore, we have :

$$(894) \quad \langle N_1(t) \rangle_{V_2} - \langle N_1 \rangle_0 = V_2 \int_0^t \chi_{N_1, N_2}(t') dt'$$

Using the F.D. theorem, calculate $\int_0^t \chi_{N_1, N_2}(t) dt$ as :

$$(895) \quad \int_0^t \chi_{N_1, N_2}(t) dt = \int_0^\infty \chi_{N_1, N_2}(t) dt - \int_t^\infty \chi_{N_1, N_2}(t) dt$$

(b) Deduce

$$(896) \quad \langle N_1(t) \rangle_{V_2} - \langle N_1(0) \rangle_{V_2} = \beta V_2 [\langle N_1(0)N_2(0) \rangle_0 - \langle N_1(t)N_2(0) \rangle_0]$$

(c) Give a similar equation for

$$(897) \quad \langle N_2(t) \rangle_{V_2} - \langle N_2(0) \rangle_{V_2} = ?$$

(d) From now on, we choose the more general perturbation

$$(898) \quad (V_1(t), V_2(t)) = \begin{cases} (0, 0) & \text{for } t < 0 \\ (V_1, V_2) & \text{for } t > 0 \end{cases}$$

and we write

$$(899) \quad \begin{aligned} \langle N_1(t) - N_1(0) \rangle_{V_1, V_2} &= L_{11}V_1 + L_{12}V_2 \\ \langle N_2(t) - N_2(0) \rangle_{V_1, V_2} &= L_{21}V_1 + L_{22}V_2 \end{aligned}$$

Generalize the previous calculation and give the coefficients L_{ij} .

(e) What is the symmetry you expect for the L_{ij} 's and why is this symmetry valid ?

(3) Problem 3

Consider the process schematized in Fig. 7.

(a) What is then the work W_g provided to the system ?

(b) What is the work W_e extracted from the system ?

(c) With the chosen protocol, can the work fluctuate ? Compute $\langle e^{-\beta W} \rangle$ where you have to choose for W either 1) or 2).

(d) Do your result seem to contradict a basic thermodynamic principle and-or does it contradict an inequality we have derived during the lectures ?

(e) This exercise shows that one can extract work from a system at thermal equilibrium if some information is available. What information is available to you in this case ?

(4) Hints:

We recall that for Brownian particle (1-D)

$$(900) \quad m \frac{dv}{dt} = -\zeta v + \delta F(t) \quad \text{with} \quad \langle \delta F(t) \delta F(t') \rangle = 2B\delta(t-t')$$

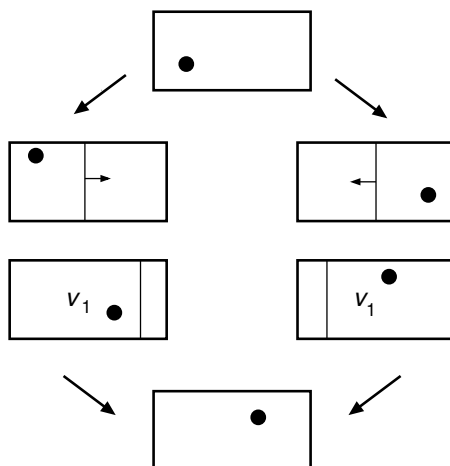


FIGURE 7. Initially, there is only one particle in a volume v . A piston is inserted in the middle. If the particle is on the left, the piston is pushed to the right. If the particle is on the right, the piston is pushed to the left. In both cases $v_{final} = v_1 = v$.

we have

$$(901) \quad \langle \Delta x(t)^2 \rangle_{\text{eq.}} = 2 \frac{kT}{\zeta} \left[t - \frac{m}{\zeta} + \frac{m}{\zeta} e^{-\zeta t/m} \right]$$

We also have for a well-known distribution

$$(902) \quad \langle e^{iax} \rangle = e^{ia\bar{x} - \frac{1}{2}a^2 \langle (x-\bar{x})^2 \rangle}$$

Université Grenoble-Alpes
Year 2021-2022

No lecture notes allowed, only 1 handwritten page.

Non equilibrium Statistical Mechanics

Note : It may be helpful to read the entire problem set. You can use either English, French or German.

(1) **Problem 1**

Answering this problem takes 2 lines. Let I , θ , Ω be the moment of inertia, the angular variable and the angular velocity of a single rigid dipolar molecule which rotates in a plane. Following classical mechanics, the equations of motion are

$$(903) \quad \frac{d\theta}{dt} = \Omega \quad I \frac{d\Omega}{dt} = -\zeta\Omega$$

- (a) Give the Langevin equation for this problem.
 (b) Show that this problem is equivalent to a simple problem we have seen during the lectures. Using this analogy, what is (without calculation)

$$(904) \quad \langle \delta\theta(t)^2 \rangle$$

(2) **Problem 2**

Consider the following Fokker-Planck equation in one space dimension

$$(905) \quad \frac{\partial P}{\partial t} = \frac{\alpha}{\gamma} \frac{\partial}{\partial x} xP + D \frac{\partial^2}{\partial x^2} P$$

- (a) What does this equation describe ? (1 line)
 (b) We define the moments $\langle x^n(t) \rangle$ as

$$(906) \quad \langle x^n(t) \rangle = \int_{-\infty}^{+\infty} dx x^n P(x, t)$$

and assume that the first two moments exist. If $x(t=0) = x_0$, show by integrating by parts:

$$(907) \quad \frac{d \langle x(t) \rangle}{dt} = -\frac{\alpha}{\gamma} \langle x(t) \rangle$$

and deduce $\langle x(t) \rangle$.

- (c) Specializing to $x(t=0) = 0$ for all processes, show in the same way

$$(908) \quad \langle x^2(t) \rangle = \frac{D\gamma}{\alpha} \left[1 - \exp\left\{ \left(-\frac{2\alpha t}{\gamma} \right) \right\} \right]$$

and comment your result (2-3 lines).

(3) **Problem 3**

Master equations are sometimes used to model chemical reaction. Consider the following reaction:



where the number of A molecule is n_A and the number of B molecules is n_B . Let N be the total number of molecules.

- (a) What is the relation between N , n_A and n_B ?

- (b) A state of the system is specified by the pair (n_A, n_B) . Transitions are made only to neighboring states, for example, (n_A, n_B) to $(n_A + 1, n_B - 1)$ and the transition rate for this process is the forward rate constant times the number n_A of A molecules times the concentration of B molecules

$$(910) \quad w(n_A, n_B \rightarrow n_A + 1, n_B - 1) = k_1 n_A \frac{n_B}{V}$$

For the other reaction in (909), complete the formula

$$(911) \quad (n_A, n_B) \rightarrow (?, ?)$$

- (c) Give $w(n_A, n_B \rightarrow ?, ?)$ for the reaction (909) as a function of k_2 .
- (d) Let $P_{n_A}(t)$ be the probability to find the system with n_A molecule (because of question 1, we don't need to specify the number of B molecules). What are the three types of events which can take place during a small time interval Δt ?
- (e) What is the probability for each event to occur ?
- (f) By writing $P_{n_A}(t + \Delta t)$ as a function of $P_{n_A \pm 1}(t)$ and $P_{n_A}(t)$, give the Master equation for $P_{n_A}(t)$.

CHAPTER 12

APPENDIX

1. Gaussian integrals

(912)

$$Z(\mathbf{A}, \mathbf{b}) = \int d^n x \exp\left(-\frac{1}{2} \sum_{i,j} x_i A_{i,j} x_j + \sum_i b_i x_i\right) = (2\pi)^{n/2} (\det \mathbf{A})^{-1} \exp\left(-\frac{1}{2} \sum_{i,j} b_i \Delta_{i,j} b_j\right)$$

where

(913)
$$\Delta = \mathbf{A}^{-1}$$

Voir ici :²²

BIBLIOGRAPHY

- [1] Christopher Battle, Chase P Broedersz, Nikta Fakhri, Veikko F Geyer, Jonathon Howard, Christoph F Schmidt, and Fred C MacKintosh. Broken detailed balance at mesoscopic scales in active biological systems. *Science*, 352(6285):604–7, Apr 2016.
- [2] Nils B Becker, Andrew Mugler, and Pieter Rein Ten Wolde. Optimal prediction by cellular signaling networks. *Phys Rev Lett*, 115(25):258103, Dec 2015.
- [3] H C Berg and E M Purcell. Physics of chemoreception. *Biophys J*, 20(2):193–219, Nov 1977.
- [4] W Bialek. *Biophysics: Searching for Principles*. Princeton University Press, 2012.
- [5] A.O. Caldeira and A.J. Leggett. Quantum tunneling in a dissipative system. *Annals of Physics*, 140:374–456, 1983.
- [6] T. M. Cover and J.A. Thomas. *Elements of information theory*. John Wiley & Sons Inc., 1991.
- [7] Bjoern Felsager. *Geometry, Particles, and Fields*. Springer-Verlag, 1997.
- [8] E. Frey and K. Kroy. Brownian motion: a paradigm of soft matter and biological physics. *Annalen der Physik*, 14(1,Ä3):20–50, 2005.
- [9] Thai M. Hoang, Rui Pan, Jonghoon Ahn, Jaehoon Bang, H. T. Quan, and Tongcang Li. Experimental test of the differential fluctuation theorem and a generalized jarzynski equality for arbitrary initial states. *Phys. Rev. Lett.*, 120:080602, Feb 2018.
- [10] Gert-Ludwig Ingold. Path integrals and their application to dissipative quantum systems. *Lecture Notes in Physics*, pages 1–53, 2002.
- [11] D Kondepudi and I. Prigigine. *Modern Thermodynamics. Frome heat engines to dissipatives structures*. John Wiley & Sons Ltd, 1998.
- [12] Pavel L. Krapivsky, Sidney Redner, and Eli. Ben-Naim. *A kinetic View of Statistical Mechanics*. Cambridge Univeristy Press, 2010.
- [13] Magalinskiĕ. Dynamical model in the theory of the brownian motion. *Sov. Phys. JETP*, 9:1381, 1959.
- [14] L. Onsager and S. Machluo. Fluctuations and irreversible processes. *Phys. Rev.*, 6:1505–1512, 1953.
- [15] Yves Pomeau and Jarosław Piasecki. The langevin equation. *Comptes Rendus Physique*, 18(9):570 – 582, 2017. Science in the making: The Comptes rendus de l’Académie des sciences throughout history.
- [16] F Ritort. Single-molecule experiments in biological physics: methods and applicatios. *J. Phys.: Cond. Matter*, 18:R531–R583, 2006.
- [17] Sheldon M. Ross. *Stochastic Processes*. John Wiley & Sons Inc., 1986.
- [18] I Z Steinberg. On the time reversal of noise signals. *Biophys J*, 50(1):171–9, Jul 1986.
- [19] Gašper Tkačik and Aleksandra M Walczak. Information transmission in genetic regulatory networks: a review. *J Phys Condens Matter*, 23(15):153102, Apr 2011.

- [20] G.E. Uhlenbeck and L.S. Ornstein. On the theory of brownian motion. *Phys. Rev.*, 36:823–841, 1930.
- [21] N.G. Van Kampen. *Stochastic Processes in Physics and Chemistry*. North-Holland, 1981.
- [22] Eric Woillez, Yariv Kafri, and Nir S Gov. Active trap model. *Phys Rev Lett*, 124(11):118002, Mar 2020.
- [23] J. Zinn-Justin. *Intégrale de chemin en mécanique quantique: Introduction*. CNRS Editions, 2003.