

Nonequilibrium and Active Systems

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The goal of these lecture notes, inspired by a lecture series given over earlier years by Julien Tailleur, is to support the live lectures by giving specific references to the actual scientific literature, which is an almost impossible thing to achieve when writing on the board. They are of course riddled with mistakes, typos, *etc*, but they should provide the reader with a minimal back-up in case a lecture was missed. Curious readers will also find additional material going somewhat beyond the live lectures. Beware, these lecture notes are not allowed during the exam. Only your handwritten notes are.

Chapter 1

Equilibrium Statistical Mechanics

1.1 Basic postulates

If we quickly review classical statistical mechanics the starting point is quite simply Hamilton's equations of motion for the phase space coordinates $\Gamma = \{q, p\}$, where q refers to the positions of the particles making up the system (and possibly rotational degrees of freedom, or else), and p stand for the conjugate momenta $p = \frac{\partial L}{\partial \dot{q}}$, where L is the Lagrangian of the system. The Hamiltonian $H(q, p) = \dot{q}p - L(q, \dot{q})$ (with $\dot{q}(q, p)$ being the implicit solution of $p = \frac{\partial L}{\partial \dot{q}}$) is then used to write the equations of motion:

$$\dot{q} = \frac{\partial H}{\partial p}, \dot{p} = -\frac{\partial H}{\partial q} \quad (1.1)$$

which are, in simple notations, Newton's equations of motion.

In statistical mechanics, a key concept is that of Gibbs ensemble: this is a collection of $M \gg 1$ systems that are, from a macroscopic point of view, prepared in an identical manner. While from one system to another the positions of the particles may differ, some macroscopic quantities are the same. Some Gibbs ensembles have specific names. For instance, the micro-canonical ensemble refers to a collection of systems sharing in common the same total energy, the same number of particles, and the same volume.

Out of this collection of M identically prepared systems, we call $n(\Gamma, t)d\Gamma$ the number of systems whose phase space coordinates are between Γ and $\Gamma + d\Gamma$. Of course, this Γ notation is a short cut for a large dimensional vector

$$\Gamma = \{\mathbf{r}_i, \mathbf{p}_i\}_{i=1, \dots, N}, d\Gamma = d^d r_1 \dots d^d r_N d^d p_1 \dots d^d p_N \quad (1.2)$$

where d is the embedding space dimension ($d = 1, 2$ or 3 depending on the physical context), N is the number of particles, and the \mathbf{p}_i 's are the momenta conjugate to the positions \mathbf{r}_i of the particles making up the system.

Very often, one considers $\frac{1}{M}n d\Gamma$, and this quantity is the probability to find one of the M systems with its phase space coordinates between Γ and $\Gamma + d\Gamma$, and one works with $\rho = n/M$

as ρ (which then becomes a probability density over the collection of M systems).

Because systems are neither created nor destroyed, the systems can be viewed as the M particles of a locally conserved fluid flowing in phase space, with the continuity equation

$$\partial_t \rho + \partial_\Gamma \cdot (\dot{\Gamma} \rho) = 0 \quad (1.3)$$

involving the local current $\dot{\Gamma} \rho$ in phase space (and again, $\dot{\Gamma}$ is a short notation for $\{\dot{\mathbf{r}}_i, \dot{\mathbf{p}}_i\}$ while the divergence $\partial_\Gamma \cdot$ is a divergence in phase space with respect to the $2dN$ coordinates $\mathbf{r}_1, \dots, \mathbf{p}_N$). This conservation equation simply expresses that the M systems are independent.

However, due to Hamilton's equations of motion, the fluid of systems is actually incompressible. Indeed the velocity of the fluid is

$$\dot{\Gamma} = \{\dot{\mathbf{r}}_i, \dot{\mathbf{p}}_i\} \quad (1.4)$$

and it is divergenceless

$$\begin{aligned} \partial_\Gamma \cdot \dot{\Gamma} &= \sum_i \partial_{\mathbf{r}_i} \cdot \dot{\mathbf{r}}_i + \sum_i \partial_{\mathbf{p}_i} \dot{\mathbf{p}}_i \\ &= \sum_i \partial_{\mathbf{r}_i} \cdot \left[\frac{\partial H}{\partial \mathbf{p}_i} \right] + \sum_i \partial_{\mathbf{p}_i} \cdot \left[-\frac{\partial H}{\partial \mathbf{r}_i} \right] \\ &= 0 \end{aligned} \quad (1.5)$$

another way of phrasing this property is to look at the evolution of $\rho(t) = \rho(\Gamma(t), t)$ in a Lagrangian way, namely along the motion, by considering the total derivative of ρ :

$$\begin{aligned} \frac{d\rho}{dt} &= \partial_t \rho + (\dot{\Gamma} \cdot \partial_\Gamma) \rho \\ &= \underbrace{\partial_t \rho + \partial_\Gamma \cdot (\dot{\Gamma} \rho)}_{=0 \text{ by the continuity equation}} - \rho \underbrace{\partial_\Gamma \cdot \dot{\Gamma}}_{=0 \text{ due to incompressibility}} \\ &= 0 \end{aligned} \quad (1.6)$$

Hence the phase space density is a constant along the motion. This tells us that

$$\begin{aligned} 0 &= \partial_t \rho + (\dot{\Gamma} \cdot \partial_\Gamma) \rho \\ &= \partial_t \rho + \sum_i \dot{\mathbf{r}}_i \cdot \partial_{\mathbf{r}_i} \rho + \sum_i \dot{\mathbf{p}}_i \cdot \partial_{\mathbf{p}_i} \rho \\ &= \partial_t \rho + \sum_i \left[\frac{\partial H}{\partial \mathbf{p}_i} \right] \cdot \partial_{\mathbf{r}_i} \rho + \sum_i \left[-\frac{\partial H}{\partial \mathbf{r}_i} \right] \cdot \partial_{\mathbf{p}_i} \rho \\ &= \partial_t \rho + \partial_p H \partial_q \rho - \partial_q H \partial_p \rho \\ &= \partial_t \rho - \{H, \rho\} \end{aligned} \quad (1.7)$$

where the Poisson brackets notation is defined as

$$\{F(\Gamma = (q, p)), G(\Gamma)\} = \partial_q F \partial_q G - \partial_q G \partial_p F = \sum_i [\partial_{\mathbf{r}_i} F \cdot \partial_{\mathbf{p}_i} G - \partial_{\mathbf{r}_i} G \cdot \partial_{\mathbf{p}_i} F] \quad (1.8)$$

This linear, first order in time, differential equation governing the evolution of $\rho(\Gamma, t)$, namely,

$$\partial_t \rho = \{H, \rho\} = -i\mathcal{L}\rho, \quad -i\mathcal{L} = \{H, \cdot\} \quad (1.9)$$

is also known as the Liouville equation (\mathcal{L} is the Liouvillian). The big question is: can we solve it? And the short answer is: in general, no.

Our goal is indeed to obtain ρ so that we can make averages to determine the properties of the system of interest.

This is where the two postulates of equilibrium statistical mechanics come into play. The first one is that, at large times, when the system has settled in a steady-state, one can equate a time average performed in the course of the evolution of the physical system of interest, with an average over a collection of systems prepared in the same conditions. This is the ergodic hypothesis.

The second postulate is way stronger: if the system is initially closed and isolated, at fixed volume then at large times $\rho(\Gamma, t)$ converges to a constant. This means that in equilibrium, all the microstates Γ that the system can be found in are equally likely to be observed. In the microcanonical Gibbs ensemble characterized by ρ , we have

$$\overline{A(\Gamma)} = \lim_{\tau \rightarrow +\infty} \frac{1}{\tau} \int_0^\tau dt A(\Gamma(t)) \stackrel{\text{ergodic}}{=} \int d\Gamma \rho(\Gamma) A(\Gamma) \stackrel{\text{equiprobability}}{=} \frac{\int d\Gamma A(\Gamma)}{\int d\Gamma} \quad (1.10)$$

The denominator $\Omega = \int d\Gamma$ is finite because one integrates only over phase space coordinates that respect the finite volume and finite energy constraints that are prescribed. The normalization constant Ω (which often incorporates prefactors such as $\frac{1}{N!}$ or h^{-dN} , where h is Planck's constant) is known as the microcanonical partition function.

In practice, and depending on the modeling, instead of phase space coordinates Γ one may be interested in a spin configuration, or in the conformation of a polymer, or *etc.*. To make notations somewhat lighter, we'll henceforth use \mathcal{C} as a generic microstate, and use discrete summation $\sum_{\mathcal{C}}$ instead of integrals over phase space, but depending on context, one should use $\sum_{\mathcal{C}}$ or $\int d\Gamma$ or whatever is appropriate. In this discrete notation, $P(\mathcal{C})$ plays the role of $\rho(\Gamma)$. In the microcanonical ensemble, $\Omega = \sum_{\mathcal{C}} 1$ with fixed energy E .

It turns out that the Shannon entropy $S = -\sum_{\mathcal{C}} P(\mathcal{C}) \ln P(\mathcal{C})$ is the largest when the random variable is uniform, which is the case of interest. It reduces to $S = \ln \Omega$ for our uniform distribution $P(\mathcal{C}) = \frac{1}{\Omega}$, or, better, introducing physical units, $S = k_B \ln \Omega$ so that direct contact with the thermodynamic entropy is achieved.

1.2 The canonical ensemble, and the concept of a thermostat

Once we have our statistical mechanics postulates, we can apply them to a rather common situation: that of a system \mathcal{S} embedded in some much larger system \mathcal{R} (that we shall call a reservoir), while the reunion $\mathcal{S} \cup \mathcal{R}$ is actually isolated with energy E . This is the cartoon of Fig. 1.1.

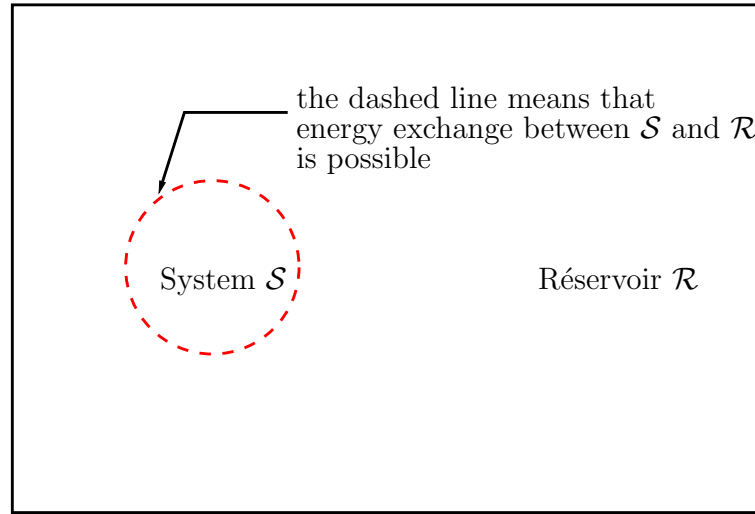


Figure 1.1: The whole system $\mathcal{S} \cup \mathcal{R}$ is isolated and thus the microcanonical postulate applies to it.

Our interest goes only to the system, not to its surrounding environment. Fortunately, it is possible to determine the probability $P(\mathcal{C}_{\mathcal{S}})$ to find the system in state $\mathcal{C}_{\mathcal{S}}$ regardless of the microstate of the environment \mathcal{R} :

$$\begin{aligned}
 P(\mathcal{C}_{\mathcal{S}}) &= \frac{\text{number of configurations of } \mathcal{R} \text{ compatible with state } \mathcal{C}_{\mathcal{S}}}{\text{total number of configurations}} \\
 &= \frac{\Omega_{\mathcal{R}}(\text{with energy } E - E_{\mathcal{S}}(\mathcal{C}_{\mathcal{S}}))}{\Omega_{\mathcal{S} \cup \mathcal{R}}(E)}
 \end{aligned} \tag{1.11}$$

But since the system is much smaller than the reservoir, we can make the following approximation,

$$\begin{aligned}
 P(\mathcal{C}_{\mathcal{S}}) &= \frac{\Omega_{\mathcal{R}}(E - E_{\mathcal{S}}(\mathcal{C}_{\mathcal{S}}))}{\Omega_{\mathcal{S} \cup \mathcal{R}}(E)} \\
 &= \frac{e^{\frac{1}{k_{\text{B}}} S_{\mathcal{R}}(E - E_{\mathcal{S}}(\mathcal{C}_{\mathcal{S}}))}}{\Omega_{\mathcal{S} \cup \mathcal{R}}(E)} \\
 &\simeq \text{a } \mathcal{C}_{\mathcal{S}}\text{-independent constant} \times e^{-\frac{1}{k_{\text{B}}} \frac{\partial S_{\mathcal{R}}}{\partial E} E_{\mathcal{S}}} \\
 &= \frac{1}{Z} e^{-\beta E_{\mathcal{S}}(\mathcal{C}_{\mathcal{S}})}
 \end{aligned} \tag{1.12}$$

where $\beta = \frac{1}{k_B T_{\mathcal{R}}}$ and $T_{\mathcal{R}} = \frac{1}{\partial S_{\mathcal{R}}/\partial E}$ is the temperature of the reservoir. In this formula, Z appears to be a normalization constant,

$$Z = \sum_{\mathcal{C}} e^{-\beta E_{\mathcal{S}}(\mathcal{C}_{\mathcal{S}})} \quad (1.13)$$

and it is remarkable that, in the expression of the Boltzmann distribution $P(\mathcal{C}_{\mathcal{S}}) = \frac{1}{Z} e^{-\beta E_{\mathcal{S}}(\mathcal{C}_{\mathcal{S}})}$, the only place where the reservoir appears is through its inverse temperature β . The reservoir is called a thermostat. Note that the system \mathcal{S} does not have to be a macroscopic system.

Of course, there are some hypotheses that we haven't detailed. One of them is that the interactions between the system and the reservoir must be short-ranged. And needless to say, asserting that Z is merely a normalization constant is a gross understatement, as we know that

$$F = -\frac{1}{\beta} \ln Z \quad (1.14)$$

is the free energy of the system, out of which many physical properties can be extracted (by differentiation with respect to β). Such systems \mathcal{S} that are in contact with a thermostat, and whose energy can thus fluctuate, are said to be prepared in canonical conditions (this is Gibbs' canonical ensemble: a collection of systems with fixed volume and fixed particle number, in contact with a thermostat imposing a fixed temperature).

In a mathematical language, Z is the generating function of the energy of the system (which is a random variable). Forgetting about the \mathcal{S} index, when we write

$$Z = \sum_{\mathcal{C}} e^{-\beta E(\mathcal{C})} \quad (1.15)$$

we see that $\langle E \rangle = -\partial_{\beta} \ln Z$, $\langle E^2 \rangle - \langle E \rangle^2 = \partial_{\beta}^2 \ln Z$, and thus the free energy (or rather $\ln Z = -\beta F$) is the generating function of the cumulants of the energy of the system,

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = U, \quad \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = \beta^{-2} C_v \quad (1.16)$$

where U is the internal energy and C_v the heat capacity. The entropy can be retrieved from $S = -\frac{\partial F}{\partial T}$ and it is a simple exercise to verify that, again,

$$S/k_B = -\sum_{\mathcal{C}} P(\mathcal{C}) \ln P(\mathcal{C}) \quad (1.17)$$

where now $P(\mathcal{C}) = e^{-\beta E(\mathcal{C})}/Z$ is the canonical distribution. Maximizing $S[P] = -\sum_{\mathcal{C}} P(\mathcal{C}) \ln P(\mathcal{C})$ under the constraints that not only $\sum_{\mathcal{C}} P(\mathcal{C}) = 1$ but also that $U = \sum_{\mathcal{C}} E(\mathcal{C})P(\mathcal{C})$ are fixed leads exactly to the canonical distribution, where the coefficient β is an implicit function of U .

All this is the realm of equilibrium statistical mechanics. A particularly dense and to-the-point book is that of Chandler [19] in case refreshing one's memory would be necessary.

The take home message of this section is

- Start from a complex systems whose dynamics can in general not be solved but in some specific conditions invoke two simplifying postulates;
- Postulate that the probability of observing a given microstate has a the microcanonical form (or canonical one if a thermostat can be defined), then all static, one point quantities can in principle be obtained;
- this is remarkable that no information on a reservoir is needed beyond its temperature;
- but be humble, as it may actually be very hard to extract the physics from a partition function, even when all the equilibrium conditions are gathered;
- and, still in equilibrium, we know nothing about relaxation processes, time-correlations, *etc.*. Time doesn't just disappear as a relevant variable just because a system is in equilibrium;
- and realize that equilibrium conditions are the exception rather than the rule.

1.3 Why does it work?

As mentioned above, the equilibrium machinery does have limitations: the number of systems for which one can actually exactly compute Ω or Z is extremely limited (some one-dimensional systems, including the Ising model with an external magnetic field, a few two-dimensional systems including the Ising model without a field) and the whole point of statistical mechanics is to have the Boltzmann formula spit out what it knows on the macroscopic behavior of the system. Beyond exactly-solvable models that are so rare, a zoo of approximations have been invented, and numerical techniques able to efficiently sample the Boltzmann distribution have been designed over the years.

And yet, it is a legitimate question to understand why the equilibrium machinery works so well (beyond technical difficulties). This is a field of mathematical physics of its own known as ergodic theory and dynamical systems. One of the key ingredients is that the dynamics of the system must display chaotic properties, and more precisely, it must display the ability to mix probabilities appropriately. These mixing properties are measured by quantifying the time it takes for the probability distribution to forget its initial distribution. This time must be short enough, which is of course a sloppy statement unless other reference times are specified. Such discussions are taken up in the book by Dorfman [29]. That book is about understanding why these are difficult questions.

1.4 Dynamics in statistical mechanics

1.4.1 Phase space and Liouville equation

A physical system is, at a microscopic level, characterized by its coordinates in phase space, $\Gamma = \{q, p\}$ and its time evolution is entirely contained in the explicit form of its Hamiltonian

$\mathcal{H}(\Gamma)$. Given an initial set of positions and velocities, integrating the equations of motion

$$\dot{p} = -\frac{\partial \mathcal{H}}{\partial q}, \quad \dot{q} = \frac{\partial \mathcal{H}}{\partial p} \quad (1.18)$$

The phase space density $\rho(\Gamma, t)$ evolves according to the Liouville equation. Due to the conservation of probability, we have that

$$\partial_t \rho + \partial_\Gamma \cdot (\dot{\Gamma} \rho) = 0 \quad (1.19)$$

and thus we must have that

$$\begin{aligned} \frac{d\rho}{dt} &= \partial_t \rho + \{\rho, \mathcal{H}\} \\ &= -\rho \partial_\Gamma \cdot (\dot{\Gamma}) \\ &= 0 \end{aligned} \quad (1.20)$$

where $\{f, g\} = \partial_q f \partial_p g - \partial_p f \partial_q g$. The incompressibility of phase space

$$\partial_\Gamma \cdot \dot{\Gamma} = \partial_{q_i} \dot{q}_i + \partial_{p_i} \dot{p}_i = 0 \quad (1.21)$$

reflects the symplectic nature of the Hamiltonian dynamics. Liouville's equation is thus a linear first-order in time evolution equation

$$\partial_t \rho = \{\mathcal{H}, \rho\} = -i\mathcal{L}\rho \quad (1.22)$$

where the Liouvillian \mathcal{L} is by convention defined with a $-i$ prefactor. Of course we know that under some conditions (closed isolated system with a fixed volume), in the long time limit the equilibrium solution is uniform over phase space. We know this is true, but it's in general impossible to prove, and the reasons behind this property are rather subtle (they are to be found in the chaotic and mixing properties of the dynamics). However, in general, ρ is hard to get, and in general, we are simply not interested in ρ . It is only a subset of the degrees of freedom of the system that is of interest to us.

1.4.2 Projection operator at the level of probabilities

There are various ways to implement the Mori-Zwanzig idea of projecting onto relevant degrees of freedom (we refer to [124] for a pedagogical introduction). One of these approaches, proposed by Nakajima and Zwanzig [86, 122, 65], operates directly at the level of probability densities, which we find very convenient, mostly for discussion purposes, at this stage of the lectures. We imagine that the probability of a set of degrees of freedom denoted by c (we shall use discrete summations, but c may as well refer to a set of canonically conjugate phase space variables, and then \mathbf{w} becomes a first order differential operator) evolves according to a linear, first order in time, differential equation (such as the Liouville equation):

$$\partial_t p(c, t) = \sum_{c'} \mathbf{w}_{cc'} p(c', t) \quad (1.23)$$

where \mathbf{w} is some operator (in Hamiltonian dynamics, $\mathbf{w} = -i\mathcal{L}$ is called the Liouvillean). But it turns out that we are only interested in a subset of the degrees of freedom, namely those for which the physical observable $C(c)$ takes the value \mathcal{C} . Our goal is really to study

$$P(\mathcal{C}, t) = \text{Prob}\{C(c(t)) = \mathcal{C}\} = \sum_c \delta_{\mathcal{C}, C(c)} p(c, t) \quad (1.24)$$

Of course, the choice of the observable C depends on context and

- C can refer to the position of a tagged particle;
- C can refer to a collective density mode;
- C can refer to a composite observable such as the kinetic energy of the system.

To proceed, one introduces $\Omega_{\mathcal{C}} = \sum_c \delta_{\mathcal{C}, C(c)}$ which counts how many microstates c have the same value \mathcal{C} of $C(c)$. We also introduce an operator \mathcal{P} that applies to any function $f(c)$ of the microstates c :

$$\mathcal{P}f(c) = \frac{1}{\Omega(C(c))} \sum_{c'} \delta_{C(c'), C(c)} f(c') \quad (1.25)$$

One can verify that $\mathcal{P}^2 = \mathcal{P}$, which means that \mathcal{P} is a projector. It is then used to define both $\bar{p}(c, t) = \mathcal{P}p(c, t)$ and $q = p - \bar{p} = \mathcal{Q}p$. By construction $\bar{p}(c, t) = P(C(c), t)/\Omega_{C(c)}$ but the probability P we are after can *a posteriori* be reconstructed from the knowledge of \bar{p} :

$$P(\mathcal{C}, t) = \sum_c \delta_{\mathcal{C}, C(c)} \bar{p}(c, t) \quad (1.26)$$

The evolution equation for p , $\partial_t p = \mathbf{w}p$ splits into two coupled evolution equations for \bar{p} and for q ,

$$\partial_t \bar{p} = \mathcal{P}\mathbf{w}\bar{p} + \mathcal{P}\mathbf{w}q, \quad \partial_t q = \mathcal{Q}\mathbf{w}\bar{p} + \mathcal{Q}\mathbf{w}q \quad (1.27)$$

hence $q(t) = \int_0^t dt' e^{\mathcal{Q}\mathbf{w}(t-t')} \mathcal{Q}\mathbf{w}\bar{p}(t')$. We have chosen an initial condition such that $q(c, 0) = 0$, namely one in which the value of $C(c)$ is the same. The expression for q can then be substituted into the evolution equation for \bar{p} , thus leading to a linear equation for \bar{p} alone:

$$\partial_t \bar{p} = \mathcal{P}\mathbf{w}\bar{p} + \int_0^t dt' \mathcal{P}\mathbf{w}e^{\mathcal{Q}\mathbf{w}(t-t')} \mathcal{Q}\mathbf{w}\bar{p}(t') \quad (1.28)$$

But we are after $P(C, t)$, not after $\bar{p}(c, t)$, so that one final step is required. We multiply Eq. (1.28) with $\delta_{\mathcal{C}, C(c)}$ and we sum over c :

$$\partial_t P(C, t) = \sum_{c, c'} \delta_{\mathcal{C}, C(c)} (\mathcal{P}\mathbf{w})_{cc'} \bar{p}(c', t) + \int_0^t dt' \sum_{c, c'} \delta_{\mathcal{C}, C(c)} (\mathcal{P}\mathbf{w}e^{\mathcal{Q}\mathbf{w}(t-t')} \mathcal{Q}\mathbf{w})_{cc'} \bar{p}(c', t') \quad (1.29)$$

Then we use the trick that

$$\sum_{c'} \dots = \sum_{C'} \sum_{c'} \delta_{\mathcal{C}, C'} \dots \quad (1.30)$$

to finally arrive at

$$\partial_t P(C, t) = \sum_{C'} \left[\sum_{c, c'} \delta_{\mathcal{C}, C(c)} (\mathcal{P}^{\mathbf{w}})_{cc'} \right] P(C', t) + \int_0^t dt' \sum_{C'} \left[\sum_{c, c'} \sum_{c, c'} \delta_{\mathcal{C}, C(c)} (\mathcal{P}^{\mathbf{w}} e^{\mathcal{Q}^{\mathbf{w}}(t-t')} \mathcal{Q}^{\mathbf{w}})_{cc'} \right] P(C', t') \quad (1.31)$$

The general form of the evolution equation for P is thus

$$\partial_t P(C, t) = \sum_{C'} M_{CC'}^{(1)} P(C', t) + \int_0^t dt' \sum_{C'} M_{CC'}^{(2)}(t-t') P(C', t') \quad (1.32)$$

If the choice of the slow degrees of freedom is appropriate, and in general, then $M^{(2)}$ will exhibit a rapid exponential decay over a typical time scale τ which will justify to replace $M^{(2)}(t-t')$ by an effective $M^{(2)}(0)\tau\delta(t-t')$ operator, and the resulting equation for P reads

$$\partial_t P = \mathbb{W}P, \quad \mathbb{W} \simeq M^{(1)} + \tau M^{(2)}(0) \quad (1.33)$$

This so-called Markov approximation applies when there is a decoupling of the fast and irrelevant degrees of freedom from the physically relevant degrees of freedom whose physics develops over time scales large with respect to that of the fast degrees of freedom. Of course, lots of relevant physical cases do not exhibit a clear-cut decoupling between the slow and the fast degrees of freedom and it may also be that $M^{(2)}(t-t')$ slowly decays as a power law (as for instance in visco-elastic materials where the memory kernel goes by the name of the creep function). All in all, in what follows, we shall always assume that there is a level of description at which an equation of the form $\partial_t \rho = \mathbb{W}\rho$ can be our starting point. In general, except at the microscopic level, \mathbb{W} is a complicated operator (that is certainly not of order one in terms of differentiation with respect to space and momentum). We shall now take such an operator \mathbb{W} for granted.

Note that if the existence of \mathbb{W} is assumed, the conservation of probability at all times forces and the requirement that P remains non-negative force \mathbb{W} to be a master equation matrix.

1.4.3 Projection operator at the level of observables

The Mori-Zwanzig projection technique can be implemented by other means, but beyond the specifics, the method draws on the same idea. Our starting assumption is that a given observable $A(\Gamma(t))$ of interest, depending on phase space coordinates Γ , evolves according to a first-order in time differential equation of the form

$$\frac{dA}{dt} = i\mathcal{L}A \quad (1.34)$$

where \mathcal{L} is the Liouvillean, $-i\mathcal{L} = \{\mathcal{H}, \dots\}$ that also evolves the phase space density, $\partial_t \rho = -i\mathcal{L}\rho$. Formally, and as long as \mathcal{H} does not explicitly depend on time, we have that

$$A(t) = e^{i\mathcal{L}t} A(0) \quad (1.35)$$

In the space of all possible observables, we can choose to introduce a projection operator along A , defined by

$$\mathcal{P}X(\Gamma) = \frac{(A, X)}{(A, A)}A \quad (1.36)$$

where (A, B) denotes a scalar product yet to be specified. One possible choice involves the stationary distribution ρ_{ss} of the Liouville equation, $(A, B) = \int d\Gamma \rho_{\text{ss}}(\Gamma)A(\Gamma)B(\Gamma) = \langle AB \rangle_{\text{ss}}$ and it corresponds to an equal time correlation in the steady-state. At this stage, we invoke the Dyson identity

$$e^{i\mathcal{L}t} = e^{i\mathcal{Q}\mathcal{L}t} + \int_0^t dt' e^{i\mathcal{L}(t-t')} \mathcal{P}\mathcal{L}e^{i\mathcal{Q}\mathcal{L}t'} \quad (1.37)$$

which can be established by differentiating and then integrating the quantity $e^{-i\mathcal{L}t}e^{i\mathcal{Q}t}$ with respect to time. This identity is applied to $i\mathcal{Q}\mathcal{L}A$ and the resulting equation for A reads

$$\frac{dA}{dt} = \Omega A + \int_0^t dt' K(t-t')A(t') + F(t) \quad (1.38)$$

where Ω , K and F are given by:

$$\Omega = \frac{(i\mathcal{L}A, A)}{(A, A)}, F(t) = e^{it\mathcal{Q}\mathcal{L}}\mathcal{Q}i\mathcal{L}A, K(\tau) = \frac{(i\mathcal{L}F(t), A)}{(A, A)} \quad (1.39)$$

The physical interpretation of F as a random force comes from the fact that $\mathcal{P}F = 0$: F involves degrees of freedom orthogonal to A that we do not wish to describe. Note that the same approach can be repeated with a set of several observables A , but then a few adaptations are needed. Further adjustments are needed when \mathcal{H} explicitly depends on time.

Chapter 2

The Langevin Equation

2.1 What is the question?

In order to set the goal of this chapter straight, it's a good idea to have a clear physical picture in mind. Consider a colloidal particle (micron sized) in a bath of water molecules (3.4 Å in size). The whole system is assumed to be in equilibrium. Of course, one is absolutely not

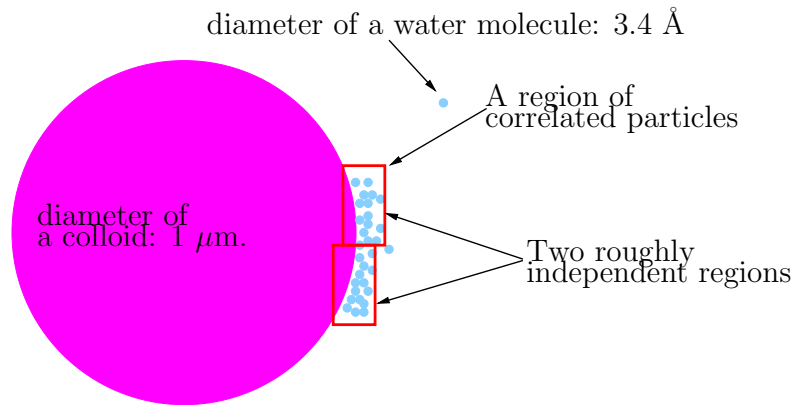


Figure 2.1: The regions of correlated particles are large enough so that they exceed in size the water molecules correlation length (also a few Å), but small enough so that there is a large number of these independent regions. For this to be possible, the separation of length scales between the bath particles and the colloid must be sufficient. Here we have four orders of magnitude.

interested in the properties of the bath of water molecules. What we are after are the statics and dynamics of the colloidal particle. The latter can in addition be subjected to gravity or to some optical laser-induced trapping, or to some electric field (if the colloid is charged). The Hamiltonian of the system has several contributions:

$$\mathcal{H} = \underbrace{\mathcal{H}_0(\mathbf{R}, \mathbf{P})}_{\text{colloid, mass } M} + \underbrace{\mathcal{H}_b(\{\mathbf{r}_i, \mathbf{p}_i\})}_{\text{water molecules}} + \underbrace{\sum_i V_i(\mathbf{R} - \mathbf{r}_i)}_{\text{interaction of the bath with the colloid}} \quad (2.1)$$

and the corresponding equations of motion read

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\mathbf{F}_i - \partial_{\mathbf{r}_i} \mathcal{H}_b, \quad M \frac{d^2 \mathbf{R}}{dt^2} = -\partial_{\mathbf{R}} \mathcal{H}_0 + \sum_i \mathbf{F}_i \quad (2.2)$$

where $\mathbf{F}_i = -\partial_{\mathbf{R}} V(\mathbf{R} - \mathbf{r}_i)$ is the force exerted by water molecule i on the colloid. Regarding the statics, we can rely on equilibrium statistical mechanics to assert that one can actually forget about the molecules of the bath. The bath properties enter through a single number, namely its temperature T ($\beta = T^{-1}$), which is actually remarkable, and

$$P(\mathbf{R}, \mathbf{P}) \propto e^{-\beta \mathcal{H}_0(\mathbf{R}, \mathbf{P})} \quad (2.3)$$

Of course, this is true only if certain conditions are fulfilled (short range interactions, the bath is much bigger than the colloid, *etc.*). Regarding the dynamics, we would like to obtain an evolution equation for \mathbf{R} only, forgetting about the bath molecules, or rather, forgetting about individual water molecules, but still retaining some of the relevant properties of the bath they make up. The last contribution is interesting, because if we sample our initial state from the Boltzmann distribution for the water molecules, then $\sum_i \mathbf{F}_i$ is a random variable. This is the sum of a large number of identically distributed random variables. They are correlated, but given the scale separation between the colloid and the water molecules, we expect that we can group $\sum_i \mathbf{F}_i$ into $\sum_{\text{regions}} \sum_{i \in \text{region}} \mathbf{F}_i$, where within a given **region** the water molecules are indeed correlated, while regions are independent (as shown in Fig. 2.1). This is possible if the correlation length of the water molecules is smaller than the size of the colloid, and if it is sufficiently smaller so that there can be a large number of these independent regions, then the central limit theorem applies and we can write something like

$$\sum_i \mathbf{F}_i = \langle \sum_i \mathbf{F}_i \rangle_b + \text{Gaussian fluctuations} \quad (2.4)$$

where in principle $\langle \sum_i \mathbf{F}_i \rangle_b$ functionally depends on \mathbf{R} . Of course, we know what to expect for this average contribution. If for some external reason (gravity, electric field, pulling the center of the optical trap) the colloid has a net motion, it will have to push the water molecules away, and this will cause a viscous drag, that is a force proportional to $-\frac{d\mathbf{R}}{dt}$. In a much more general fashion, since $\langle \sum_i \mathbf{F}_i \rangle_b$ is a vector it can only be expressed with the available vectors, namely \mathbf{R} , but also $\dot{\mathbf{R}}$, $\ddot{\mathbf{R}}$, and so on and so forth. It is thus possible *a priori* to express it as

$$\langle \sum_i \mathbf{F}_i \rangle_b = \sum_n \lambda_n \frac{d^n \mathbf{R}}{dt^n} \quad (2.5)$$

or,

$$\langle \sum_i \mathbf{F}_i \rangle_b = \int dt' \Gamma(t - t') \frac{d\mathbf{R}}{dt'} \quad (2.6)$$

where Γ is some memory kernel whose expansion is related to the λ_n coefficients. However, obtaining Γ explicitly is of course beyond our reach. In addition, the λ_n or Γ are scalars, but they could also depend on scalars constructed with the function \mathbf{R} .

When we can actually write that $\langle \sum_i \mathbf{F}_i \rangle_b$ is a simple viscous drag $-\gamma \dot{\mathbf{R}}$ that involves a friction coefficient γ , then we can, for large enough colloids, compute γ using hydrodynamics (for a colloid of radius a , $\gamma = 6\pi\eta a$ where η is the viscosity of water). Perhaps memory effects will come into play and the drag force could be a little more complicated, but if the repeated collisions of the water molecules occur at a high enough frequency (10^{13} Hz roughly [95] to be compared with the typical time at which velocity equilibrates, 10^{-9} s), memory effects can be considered irrelevant and $\Gamma(t)$ will be proportional to $\delta(t)$.

The lesson we draw from this discussion is the following: if there is a separation of time and spatial scales, then things seem to simply considerably. But so much more remains to be done:

- Can we actually determine $\langle \sum_i \mathbf{F}_i \rangle_b$ as a functional of \mathbf{R} ? Can the viscous drag term pop out of a calculation in which this average could be explicitly carried out?
- That there are Gaussian fluctuations remains rather vague. Are they colored or memoryless? How does their amplitude depend on \mathbf{R} (if at all)?
- And is there anything generic that can be stated regarding the viscous drag kernel and force fluctuations?

2.2 The Feynman-Vernon-Caldeira-Leggett-Ford-Kac-Mazur approach

2.2.1 The model

The Hamiltonian of the system at $t > 0$ has several contributions:

$$\mathcal{H} = \underbrace{\mathcal{H}_0(\mathbf{R}, \mathbf{P})}_{\text{colloid, mass } M} + \underbrace{\mathcal{H}_b(\{\mathbf{r}_i, \mathbf{p}_i\})}_{\text{water molecules}} + \underbrace{\sum_i V_i(\mathbf{R} - \mathbf{r}_i)}_{\text{interaction of the bath with the colloid}} \quad (2.7)$$

and the corresponding equations of motion read

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = -\mathbf{F}_i - \partial_{\mathbf{r}_i} \mathcal{H}_b, \quad M \frac{d^2 \mathbf{R}}{dt^2} = -\partial_{\mathbf{R}} \mathcal{H}_0 + \sum_i \mathbf{F}_i \quad (2.8)$$

where $\mathbf{F}_i = -\partial_{\mathbf{R}} V(\mathbf{R} - \mathbf{r}_i)$ is the force exerted by water molecule i on the colloid. Regarding the statics, we can rely on equilibrium statistical mechanics to assert that one can actually forget about the molecules of the bath. The bath properties enter through a single number, namely its temperature T ($\beta = T^{-1}$), which is actually remarkable, and

$$P(\mathbf{R}, \mathbf{P}) \propto e^{-\beta \mathcal{H}_0(\mathbf{R}, \mathbf{P})} \quad (2.9)$$

Let us now focus on the following situation. We assume that the bath is for now alone, and that at $t = 0$ it is indeed in thermal equilibrium. We further assume that it is made of an

assembly of harmonic oscillators

$$\mathcal{H}_b + \sum_i V(\mathbf{r}_i) = \sum_i \left[\frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2}k_i \mathbf{r}_i^2 \right] \quad (2.10)$$

Note that, due to equipartition of energy, at $t \leq 0$ we have

$$\langle r_i^\mu(0)r_j^\nu(0) \rangle = \delta_{ij}\delta^{\mu\nu}\frac{k_B T}{k_i}, \quad \langle p_i^\mu(0)p_j^\nu(0) \rangle = \delta_{ij}\delta^{\mu\nu}m_i k_B T, \quad \langle r_i^\mu(0)p_j^\nu(0) \rangle = 0 \quad (2.11)$$

where the $\mu, \nu = 1, \dots, d$ indices refer to the d possible space directions. Then the colloidal particle is placed at the initial time $t = 0$ at location $\mathbf{R}(0) = \mathbf{0}$ and now there is an interaction of the particle with the bath, so that

$$\sum_i V_i(\mathbf{r}_i) \rightarrow \sum_i V_i(\mathbf{R} - \mathbf{r}_i) \quad (2.12)$$

The force \mathbf{F}_i exerted by the bath on the particle is $\mathbf{F}_i = -k_i(\mathbf{R} - \mathbf{r}_i)$ and the equation of motion of a particle of the bath is

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = -\mathbf{F}_i \quad (2.13)$$

which, using the Green's function $G(t, t') = \frac{\sin \omega |t - t'|}{\omega}$ of $\frac{d^2}{dt^2} + \omega^2$ leads to

$$\mathbf{r}_i(t) = \mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t + \omega_i \int_0^t dt' \sin \omega_i(t - t') \mathbf{R}(t') \quad (2.14)$$

so that

$$\begin{aligned} \mathbf{r}_i(t) - \mathbf{R}(t) &= \mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t + \int_0^t dt' \omega_i \sin \omega_i(t - t') \mathbf{R}(t') - \mathbf{R}(t) \\ \mathbf{r}_i(t) - \mathbf{R}(t) &= \mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t - \int_0^t dt' \cos \omega_i(t - t') \frac{d}{dt'} \mathbf{R}(t') \end{aligned} \quad (2.15)$$

$$\begin{aligned} M \frac{d^2 \mathbf{R}}{dt^2} &= -\partial_{\mathbf{R}} H_0 - \sum_i k_i (\mathbf{R} - \mathbf{r}_i) \\ &= -\partial_{\mathbf{R}} H_0 + \sum_i k_i \left[\mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t - \int_0^t dt' \cos \omega_i(t - t') \frac{d}{dt'} \mathbf{R}(t') \right] \\ &= -\partial_{\mathbf{R}} H_0 - \int_0^t dt' M_R(t - t') \frac{d}{dt'} \mathbf{R}(t') + \boldsymbol{\xi}(t) \end{aligned} \quad (2.16)$$

where

$$M_R(\tau) = \theta(\tau) \sum_i k_i \cos \omega_i \tau \quad (2.17)$$

and

$$\boldsymbol{\xi}(t) = \sum_i k_i \left[\mathbf{r}_i(0) \cos \omega_i t + \frac{\mathbf{p}_i(0)}{m_i \omega_i} \sin \omega_i t \right] \quad (2.18)$$

We have used the notation $\omega_i^2 = k_i/m_i$ that characterizes the vibration modes of the bath. The function $\boldsymbol{\xi}$ is random because the initial positions and momenta are drawn from a Boltzmann distribution. The random variables are Gaussian because the energy of the bath is quadratic ($\langle \frac{k_i \mathbf{r}_i(0)^2}{2} \rangle = dT/2$ and $\langle \frac{\mathbf{p}_i(0)^2}{2m_i} \rangle = d\frac{T}{2}$). Hence $\boldsymbol{\xi}$ is a Gaussian variable with correlations

$$\begin{aligned} \langle \xi^\mu(t) \xi^\nu(t') \rangle &= \delta^{\mu\nu} \sum_i k_i T [\cos \omega_i t \cos \omega_i t' + \sin \omega_i t \sin \omega_i t'] \\ &= T \delta^{\mu\nu} \sum_i k_i \cos \omega_i(t - t') \\ &= M_C(t - t') \end{aligned} \quad (2.19)$$

The present derivation has been discussed by several authors [37, 123, 14] and further discussion can be found in L. Cugliandolo's lecture notes, subsection 2.4.2. There a discussion of the various ingredients ω_i and m_i characterizing the bath is carried out. An important conclusion that we can draw from this calculation is that generically, integrating the bath degrees of freedom out leads to a generalized Langevin equation. Another important conclusion is that this purely dynamical approach, which contrasts with the statistical one of the earlier chapters, shows us how to adapt our approach to the quantum world.

2.2.2 The resulting generalized Langevin equation and the Markov limit

Let us summarize our findings: it is possible to mimic the effect of the bath by replacing its degrees of freedom by two ingredients, a friction force and a noise term. These ensure that the statics of \mathbf{R} is identical to the one that would be obtained by explicitly considering the individual bath degrees of freedom. The resulting equation reads

$$M \frac{d^2 \mathbf{R}}{dt^2} = -\partial_{\mathbf{R}} H_0 - \int_0^t dt' M_R(t-t') \frac{d}{dt'} \mathbf{R}(t') + \boldsymbol{\xi}(t) \quad (2.20)$$

with the friction kernel given by

$$M_R(t) = \theta(\tau) \sum_i k_i \cos \omega_i t \quad (2.21)$$

and $\boldsymbol{\xi}$ which has Gaussian statistics

$$\langle \xi^\mu(t) \xi^\nu(t') \rangle = \delta^{\mu\nu} M_C(t - t') \quad (2.22)$$

and quite remarkably we notice that $M_C(\tau) = T(M_R(\tau) + M_R(-\tau))$ (which is often called Kubo's second fluctuation-dissipation theorem). This property is rooted in the equilibrium nature of the dynamics, as we will discuss later. This is of course not a coincidence. We know at large time the degree of freedom of the colloid will be equilibrated, but why this is connected to the equality of M_C and M_R is still unclear. However, we do expect that M_R and M_C must be strongly connected, because whatever energy the colloid loses to the bath through viscous

friction will be reinjected by the bath into the colloid by means of random kicks. At this moment in the lectures, we have however no clue on how to bridge Eq. (2.20) directly to the fact that at large times, \mathbf{R} and \mathbf{P} are sampled according to the Boltzmann distribution $e^{-\beta\mathcal{H}_0(\mathbf{R},\mathbf{P})}$. We will be able to make this technical step in the next chapter. However, we know that this must be true since our starting point is an equilibrium system, each subsystem of which is in equilibrium as well.

What the ω_i 's are exactly is difficult to pinpoint if the analysis is restricted to the present model of oscillators. And in general, for a given bath, there will be a distribution of these frequencies. For instance

$$M_R(t) = \theta(\tau)m \sum_i \omega_i^2 \cos \omega_i t \simeq \theta(\tau)m \int d\omega g(\omega) \cos(\omega t) \quad (2.23)$$

where $g(\omega)d\omega$ is the number of ω_i 's between ω and $\omega + d\omega$. Depending on the density $g(\omega)$, the memory kernel can display a variety of behaviors, from very short-range to slow power-law decay. For instance, for $g(\omega) \propto \frac{1}{\omega^2 + \tau_c^2}$ we see that $M_R(t) \propto \exp(-t/\tau_c)$, where τ_c is a correlation time reflecting the properties of the bath. This means that, for instance

$$M_C(t) = 2T\gamma \frac{1}{2\tau_c} e^{-|t|/\tau_c} \quad (2.24)$$

which defines the constant γ . And if τ_c is much shorter than any other time scale (resulting from the dynamics of \mathbf{R} itself) then we can make the Markov approximation

$$M_C(t) = 2T\gamma\delta(t) \quad (2.25)$$

which consists in neglecting memory effects. Whether one considers a colloid in water or a microvesicle in an oocyte, the approximation is justified, or not. For instance, in [39], M_R is directly measured by microrheology methods and it is not short ranged, as shown in Fig. 2.2. Within the Markov approximation, we can then write

$$M \frac{d^2\mathbf{R}}{dt^2} = -\partial_{\mathbf{R}}\mathcal{H}_0 - \gamma \frac{d\mathbf{R}}{dt} + \boldsymbol{\xi} \quad (2.26)$$

and

$$\langle \xi^\mu(t) \xi^\nu(t') \rangle = 2\gamma T \delta^{\mu\nu} \delta(t-t') \quad (2.27)$$

This is a so-called Gaussian white noise.

2.3 The large damping limit

2.3.1 Underdamped *vs.* Overdamped

In the additional limit where the damping is large, the bath exerting an effective force $\mathbf{F}_b = -\gamma \frac{d\mathbf{R}}{dt} + \boldsymbol{\xi}$ will quickly equilibrate the external forces $\mathbf{F} = -\partial_{\mathbf{R}}\mathcal{H}_0$, and one can then write

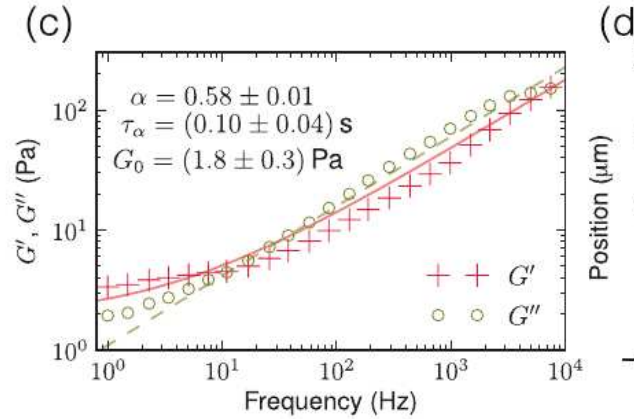


Figure 2.2: Notations wise, the kernel M_R is, basically, and in Fourier transform, $\propto G^{-1}$.

that $\mathbf{F} + \mathbf{F}_b = \mathbf{0}$. To better grasp and quantify the corresponding scaling limit, we introduce make a small detour via a particular case, that of a colloid in a harmonic trap. Then we have $\mathcal{H}_0 = \frac{\mathbf{P}^2}{2M} + \frac{1}{2}m\Omega^2\mathbf{R}^2$, where $\Omega^2 = k/M$ is a characteristic of the trap. The equation of motion

$$M \frac{d^2\mathbf{R}}{dt^2} = -M\Omega^2\mathbf{R} - \gamma \frac{d\mathbf{R}}{dt} + \boldsymbol{\xi} \quad (2.28)$$

which one could rewrite as

$$\frac{d\mathbf{V}}{dt} = -\frac{\gamma}{M} (\mathbf{V} - \mathbf{V}_{\text{ext}}) \quad (2.29)$$

with $\mathbf{V} = \dot{\mathbf{R}}$ and $\mathbf{V}_{\text{ext}} = \frac{1}{\gamma}(\mathbf{F} + \mathbf{F}_b)$. shows that three time scales are competing. These are $\tau_{\text{inertia}} = M/\gamma$, $\tau_0 = \Omega^{-1}$ and $\tau_{\text{relax}} = \frac{\gamma}{M\Omega^2}$. In the regime where $\tau_{\text{inertia}} \ll \tau_0, \tau_{\text{relax}}$ we see that inertia can be forgotten, and the resulting equation reads indeed

$$\mathbf{V} \simeq \mathbf{V}_{\text{ext}}, \quad -\partial_{\mathbf{R}}\mathcal{H}_0 - \gamma \frac{d\mathbf{R}}{dt} + \boldsymbol{\xi} = \mathbf{0} \quad (2.30)$$

It is instructive to have a look at real experimental data, shown in Fig. 2.3, extracted from [71]. The overdamped limit is justified by a separation of more than three orders of magnitude.

2.3.2 Ornstein-Uhlenbeck process, or modeling a colloid in an optical trap

The motion of a colloidal particle in an optical trap is consistent with the Markov small inertia limits. Using one-dimensional notation, the position X of the colloid thus evolves as

$$\dot{X} = -\mu kX + \sqrt{2\mu T}\eta \quad (2.31)$$

where $\mu = 1/\gamma$ is the mobility of the particle, and where η is a Gaussian white noise with correlations $\langle \eta(t)\eta(t') \rangle = \delta(t-t')$. The stiffness of the trap is denoted by k . This is both a

TABLE I. Overview of the characteristic times and frequencies for a Brownian particle in a harmonic potential. τ_p and τ_f are related to the Brownian particle through the properties of the particle with density ρ_p and radius a and of the fluid with density ρ_f and viscosity η . τ_k is connected to the property of the harmonic potential, its spring constant k , also referred to as the trap stiffness. The values are calculated for a polystyrene sphere ($a=0.5 \mu\text{m}$) in water ($\rho_p/\rho_f=1.05$, $\eta=0.001 \text{ Pa s}$). The equivalent values in the frequency domain are ϕ_p , ϕ_f , and ϕ_k . ϕ_k corresponds to the corner frequency of the power spectrum.

Time constant (μs)	Frequency constant (MHz)	Determining factor
$\tau_p = m / (6\pi\eta a) = 0.06$	$\phi_p = 1 / (2\pi\tau_p) = 2.65$	Inertia of the particle
$\tau_f = a^2 \rho_f / \eta = 0.25$	$\phi_f = 1 / (2\pi\tau_f) = 0.68$	Inertia of the surrounding displaced fluid
$\tau_k = 6\pi\eta a / k = 147$	$\phi_k = 1 / (2\pi\tau_k) = 0.001$	Harmonic potential (optical trap) for $k_1 = 64 \mu\text{N/m}$

Figure 2.3: The notations τ_p and τ_k refer, respectively, to τ_{inertia} and τ_{relax} .

pedagogical example, in the sense that this is extremely useful to understand how things work in this simple setting from the beginning to the end, but this is also an example that is at the core of active microrheology and it is thus of great of experimental relevance. What is our goal here? Well, starting from some initial position X_0 the particle will equilibrate after some time, at we know that at large time the probability $p(x, t)dx$ to observe $x \leq X(t) \leq x + dx$ is given by $p(x, t \rightarrow \infty) \sim e^{-\beta k x^2 / 2}$. But we are asking about intermediate times and about dynamical quantities, such as the position auto-correlation function.

First, we integrate Eq. (2.31) and we find that

$$X(t) = X_0 e^{-\mu k t} + \sqrt{2\mu T} \int_0^t dt' e^{-\mu k (t-t')} \eta(t') \quad (2.32)$$

and thus $\tau_{\text{init}} = (k\mu)^{-1}$ is the time it takes to forget about the initial position X_0 . On average, X relaxes to the center of the trap exponentially fast:

$$\langle X(t) \rangle = X_0 e^{-\mu k t} \quad (2.33)$$

because $\langle \eta \rangle = 0$. But by a similar manipulation we can actually determine the auto-correlation $\langle X(t)X(t') \rangle$:

$$\begin{aligned} \langle X(t)X(t') \rangle &= X_0 e^{-\mu k t} X_0 e^{-\mu k t'} + 2\mu T \int_0^t dt_1 \int_0^{t'} dt_2 e^{-\mu k (t-t_1) - \mu k (t'-t_2)} \langle \eta(t_1)\eta(t_2) \rangle \\ &\quad + X_0 e^{-\mu k t} \sqrt{2\mu T} \int_0^{t'} dt_2 e^{-\mu k (t'-t_2)} \langle \eta(t_2) \rangle + X_0 e^{-\mu k t'} \sqrt{2\mu T} \int_0^t dt_1 e^{-\mu k (t-t_1)} \langle \eta(t_1) \rangle \\ &= X_0 e^{-\mu k t} X_0 e^{-\mu k t'} + 2\mu T \int_0^t dt_1 \int_0^{t'} dt_2 e^{-\mu k (t-t_1) - \mu k (t'-t_2)} \delta(t_2 - t_1) \\ &= X_0 e^{-\mu k t} X_0 e^{-\mu k t'} + 2\mu T \int_0^{\min\{t, t'\}} dt_1 e^{-\mu k (t-t_1) - \mu k (t'-t_1)} \\ &= X_0 e^{-\mu k t} X_0 e^{-\mu k t'} + \frac{T}{k} \left(e^{-\mu k |t-t'|} - e^{-\mu k (t+t')} \right) \end{aligned} \quad (2.34)$$

In passing, we thus remark that for $t, t' \gg \tau_{\text{init}}$, the process indeed becomes stationary, as its autocorrelation function depends on the time-difference only:

$$\langle X(t)X(t') \rangle = \frac{T}{k} e^{-\mu k |t-t'|} \quad (2.35)$$

and at equal times, we do recover the expected equipartition result, namely $\langle X(t)^2 \rangle = \frac{T}{k}$ for $t \gg \tau_{\text{init}}$.

It is actually possible to obtain $p(x, t)$ without any additional calculation. It is sufficient to note that, according to Eq. (2.32), X is a linear combination of Gaussian variables, and thus X too is a Gaussian variable. A Gaussian is characterized by its mean and its variance, which we both have,

$$\langle X(t) \rangle = X_0 e^{-\mu k t}, \quad \langle X(t)^2 \rangle - \langle X(t) \rangle^2 = \frac{T}{k} (1 - e^{-2\mu k t}) \quad (2.36)$$

so that we can directly write that

$$p(x, t) = \frac{1}{\sqrt{2\pi \frac{T}{k} (1 - e^{-2\mu k t})}} e^{-\frac{k}{T} \frac{(x - X_0 e^{-\mu k t})^2}{2(1 - e^{-2\mu k t})}} \quad (2.37)$$

Langevin equations for which exact calculations are available are not plentiful, so that this example often serves as a guide when trying to approximate the evolution of a stochastic process.

Chapter 3

Stochastic calculus

3.1 Mathematical trouble ahead

3.1.1 Gaussian processes

This is a seemingly detached subsection on how to manipulate a vectorial Gaussian variable. We use it to properly define a Gaussian process as a large vectorial Gaussian variable with a number of components going to infinity as a discretization time-scale is sent to 0.

We consider a set of M Gaussian variables ξ_m distributed according to

$$P(\boldsymbol{\xi}) = Z^{-1} e^{-\frac{1}{2} \boldsymbol{\xi} \cdot \Gamma \boldsymbol{\xi}} \quad (3.1)$$

where $\Gamma_{mm'}$ is a positive matrix (which we choose to be symmetric without loss of generality). The normalization factor is $Z = (2\pi)^{M/2} / \sqrt{\det \Gamma}$. A known property of the Gaussian distribution is that its generating function has the expression

$$G[\mathbf{h}] = \langle e^{\mathbf{h} \cdot \boldsymbol{\xi}} \rangle = e^{\frac{1}{2} \mathbf{h} \cdot \Gamma^{-1} \mathbf{h}} \quad (3.2)$$

By definition, this means that a Gaussian variable has no cumulant of order greater than or equal to three. There are two straightforward consequences of Eq. (3.2). The first one is that, if one introduces

$$G_{ij} = \left. \frac{\partial^2 \ln G}{\partial h_i \partial h_j} \right|_{\mathbf{h}=0} = (\Gamma^{-1})_{ij} \quad (3.3)$$

then we must have

$$\langle \xi_i \xi_j \rangle = G_{ij} \quad (3.4)$$

The second consequence is Wick's theorem, which states that

$$\langle \xi_1 \dots \xi_{2k} \rangle = \sum' G_{i_1 i_2} \dots G_{i_{2k-1} i_{2k}} \quad (3.5)$$

where the symbol \sum' bears on all the $(2k-1)!!$ distinct pairings $\{i_1, \dots, i_{2k}\}$ of $\{1, \dots, 2k\}$.

We may picture the Gaussian variables as a discrete time process in which $m = 1, \dots, M$ is viewed as a time-slice index. We denote by $t_m = m\Delta t$ and we take the $\Delta t \rightarrow 0$ limit with the ratio $M = t_{\text{obs}}/\Delta t$ going to infinity as t_{obs} is fixed. In this limit, the Gaussian probability can be rewritten

$$\begin{aligned} P[\boldsymbol{\xi}]d^M\xi &= Z^{-1}d^M\xi e^{-\frac{1}{2}\sum_{m,m'=1}^M \xi_m \Gamma_{m,m'} \xi_{m'}} \\ &= Z^{-1}d^M\xi e^{-\frac{1}{2}\int dt dt' \xi(t) \Gamma(t,t') \xi(t')} \end{aligned} \quad (3.6)$$

where $\sum_m \leftrightarrow \int dt/\Delta t$ (in the spirit of a Riemann sum, and if this eventually makes sense), and where

$$\xi(t) = \Delta t^{-1/2} \xi_{t/\Delta t}, \quad \Gamma(t,t') = \Delta t^{-1} \Gamma_{t/\Delta t, t'/\Delta t} \quad (3.7)$$

The noise kernel $\Gamma(t,t')$ has the dimensions of an inverse time. The inverse kernel $G(t,t')$ which verifies

$$\int dt_2 \Gamma(t_1, t_2) G(t_2, t_3) = \delta(t_1 - t_3) \quad (3.8)$$

can of course be viewed as the continuum analog of G_{ij} :

$$\begin{aligned} \sum_{m_2} \Gamma_{m_1, m_2} G_{m_2, m_3} &= \delta_{m_1, m_3} \\ \int dt_2 \Delta t^{-1} \Delta t \Gamma(t_1, t_2) G_{t_2/\delta, t_3/\delta} &= \Delta t \delta(t_1 - t_3) \end{aligned} \quad (3.9)$$

which leads to identifying $G(t_2, t_3) = \Delta t^{-1} G_{t_2/\Delta t, t_3/\Delta t} = \langle \xi(t_2) \xi(t_3) \rangle$.

In terms of notation, we use the path-integral notation

$$\begin{aligned} P[\boldsymbol{\xi}]d^M\xi &= Z^{-1}d^M\xi e^{-\frac{1}{2}\sum_{m,m'=1}^M \xi_m \Gamma_{m,m'} \xi_{m'}} \\ &= P[\xi(t)] \mathcal{D}\xi, \quad P[\xi] = e^{-\frac{1}{2}\int dt dt' \xi(t) \Gamma(t,t') \xi(t')} \end{aligned} \quad (3.10)$$

but this only makes sense as the continuum limit of a discretized version.

In terms of vocabulary, if $\Gamma_{ij} = G_{ij} = \delta_{ij}$ then $\Gamma(t,t') = G(t,t') = \delta(t-t')$ and the resulting limiting process $\xi(t)$ is called a Gaussian white noise. Whenever Γ is not a δ kernel, one refers to ξ as a colored Gaussian process.

At this stage, it is not clear what the process $\xi(t)$ represents, and it is not clear either why, if ξ_m is a perfectly well-behaved Gaussian variable, the $\xi(t) = \xi_m/\sqrt{\Delta t}$ (with $t = m\Delta t$) counterpart would be too. Suppose we want to evaluate, for a given Δt , the quantity

$$x_M = \Delta t^{1/2} \sum_{m=0}^M \xi_m \quad (3.11)$$

then it is clear that $\langle x_M \rangle = 0$ and that

$$\langle x_M^2 \rangle = \Delta t M = t_{\text{obs}} \quad (3.12)$$

without even taking any $\Delta t \rightarrow 0$ limit. This shows that the quantity x_M has a well-defined limit as $\Delta t \rightarrow 0$ (M going to infinity, Δt going to zero, while keeping $t_{\text{obs}} = M\Delta t$ fixed). If we had used the continuous notation, we would have written, with $x(t_{\text{obs}}) = x_M$,

$$x(t_{\text{obs}}) = \Delta t^{1/2} \sum m \xi_m = \int_0^{t_{\text{obs}}} ds \xi(s) \quad (3.13)$$

and similarly

$$\langle x(t_{\text{obs}})^2 \rangle = \int_0^{t_{\text{obs}}} ds_1 \int_0^{t_{\text{obs}}} ds_2 \langle \xi(s_1) \xi(s_2) \rangle = \int_0^{t_{\text{obs}}} ds_1 \int_0^{t_{\text{obs}}} ds_2 \delta(s_1 - s_2) = t_{\text{obs}} \quad (3.14)$$

and we do find the same result. Of course, if the Δt prefactor had, for some reason, been absent from the definition of x_M , we would not have obtained any well defined $\Delta t \rightarrow 0$ limit.

3.1.2 Brownian motion, plain and simple

In the whole chapter our interest will go to Langevin equations in which the memory kernels are well approximated by δ functions expressing the very short range nature in time. This encompasses the underdamped Langevin equation

$$m\ddot{\mathbf{r}} = \mathbf{F} - \gamma\dot{\mathbf{r}} + \sqrt{2\gamma T}\boldsymbol{\eta} \quad (3.15)$$

which can also be cast in the form

$$\frac{d}{dt} \begin{pmatrix} \mathbf{r} \\ \mathbf{v} \end{pmatrix} = \begin{pmatrix} \mathbf{v} \\ \frac{1}{m}(\mathbf{F} - \gamma\mathbf{v} + \sqrt{2\gamma T}\boldsymbol{\eta}) \end{pmatrix} \quad (3.16)$$

or more simply an underdamped Langevin equation

$$\dot{\mathbf{r}} = \mu\mathbf{F} + \sqrt{2\mu T}\boldsymbol{\eta} \quad (3.17)$$

and these equations are all of the form $\dot{x}^\mu = f^\mu + g^{\mu i} \eta_i$, where μ is a label indexing the components of the process of interest (whether (\mathbf{r}, \mathbf{v}) or \mathbf{r} alone), while i is an index labeling the noise components (i runs at most up to the dimension of the variable of interest). In what follows, for simplicity we will always focus on a Langevin process of the form $\dot{x} = f + g\eta$ where f and η are arbitrary. Whatever complication possibly arising from working with vectorial—rather than scalar—variables will be addressed in due time, and none of them will actually prove deep.

Before we actually learn how to manipulate such equations, we want to point some of their intrinsic mathematical issues. To this end we look at a one dimensional Brownian motion

$$\dot{x} = \sqrt{2\mu T}\eta \quad (3.18)$$

where η is a Gaussian white noise with correlations $\langle \eta(t)\eta(t') \rangle = \delta(t - t')$. Then $x(t) - x(0) = \sqrt{2D} \int_0^t dt' \eta(t')$ and we see that $x(t) - x(0)$ has variance

$$\langle (x(t) - x(0))^2 \rangle = 2Dt \quad (3.19)$$