

# Out of equilibrium dynamics of complex systems

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# 1 Introduction

This introduction is much more detailed than what I described in the first lecture and it does not describe quantum problems. Still, it might be useful.

## 1.1 Falling out of equilibrium

In standard condensed matter or statistical physics focus is set on **equilibrium** systems. Microcanonical, canonical or grand canonical ensembles are used depending on the conditions one is interested in. The relaxation of a tiny perturbation away from equilibrium is also sometimes described in textbooks and undergraduate courses.

More recently, attention has turned to the study of the evolution of similar macroscopic systems in **far from equilibrium** conditions. These can be achieved by changing the properties of the environment (e.g. the temperature) in a canonical setting or by changing a parameter in the system's Hamiltonian in a microcanonical one. The procedure of rapidly (ideally instantaneously) changing a parameter is called a **quench**. Right after both types of quenches the initial configuration is not one of equilibrium at the new conditions and the systems subsequently evolve in an out of equilibrium fashion. The relaxation towards the new equilibrium (if possible) could be fast (and not interesting for our purposes) or it could be very slow (and thus the object of our study). There are plenty of examples of the latter. Dissipative ones include systems quenched through a phase transition and later undergoing domain growth, and problems with competing interactions that behave as glasses. Energy conserving ones are of great interest at present due to the rapid growth of activity in cold-atom systems.

Out of equilibrium situations can also be established by **driving** a system, that otherwise would reach equilibrium in observable time-scales, with an external perturbation. In the context of macroscopic systems an interesting example is the one of sheared complex liquids. Yet another interesting case is the one of powders that stay in static metastable states unless externally perturbed by tapping, vibration or shear that drives them out of equilibrium and makes them slowly evolve towards more compact configurations. Such situations are usually called non-equilibrium steady states (NESS). Small systems can also be driven out of equilibrium with external perturbations. Transport in nano-structures is the quantum (small) counterpart phenomenon of these cases, also of special interest at present.

Our interest is, therefore, in **macroscopic complex<sup>1</sup> systems**:

- With out of equilibrium initial condition. These include
  - open dissipative systems;
  - closed systems with energy conserving dynamics.

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<sup>1</sup>Complex simply means here 'not easy to understand'.

- with external driving forces.

A number of questions one would like to give an answer to naturally arise. Among these are:

- Is the (instantaneous) **structure** out of equilibrium similar to the one in equilibrium (at some temperature, pressure, etc.)?
- What **microscopic/mesoscopic relaxation mechanism** takes place after the quench?
- Does the system quickly settle into a stationary state? In more technical terms, is there a **finite relaxation time** to reach a steady state and which are the properties of the system on which it depends?
- What is the **microscopic/mesoscopic** dynamics in non-equilibrium steady states when these are reached?
- Can one describe the states of the system sometime after the quench with some kind of **effective equilibrium-like measure**?
- Are there **thermodynamic concepts**, such as temperature, entropy, free-energy, playing a rôle in the non-equilibrium relaxation? Under which conditions?

One notices that some of these questions apply to the free as well as to the driven dynamics.

In the last 20 years or so a rather complete theory of the dynamics of **classical macroscopic systems evolving slowly in a small entropy production limit** (asymptotic regime after a quench, small drives), that encompasses the situations described above has been developed [1, 2]. This is a **mean-field theory** type in the sense that it applies strictly to models with long-range interactions or in the infinite dimensional limit. It is, however, expected that many aspects of it also apply to systems with short-range interactions although with some caveats. A number of finite dimensional problems have been solved demonstrating this fact.

In several cases of practical interest, **quantum effects** play an important rôle. For instance, glassy phases at very low temperatures have been identified in a large variety of materials (spin-glass like systems, interacting electrons with disorder, materials undergoing super-conductor transitions, metallic glasses, etc.). Clearly, the driven case is also very important in systems with quantum fluctuations. Take for instance a molecule or an interacting electronic system driven by an external current applied via the coupling to leads at different chemical potential. It is then necessary to settle whether the approach developed and the results obtained for the classical dynamics in a limit of small entropy production carry through when quantum fluctuations are included.

In these notes we start by exposing some examples of the **phenomenology** of out of equilibrium dynamics we are interested in. We focus on classical problems and

their precise setting. We introduce nucleation [3], phase ordering kinetics [4], critical dynamics [5] structural glasses [6] and disordered systems [7, 8]. We also discuss some interdisciplinary problems that have many points in common with glassy physics including optimization problems [9], neural networks [10] and active matter [11].

Next we go into the **formalism** used to deal with these problems. The basic techniques used to study classical glassy models with or without disorder are relatively well documented in the literature (the replica trick, scaling arguments and droplet theories, the dynamic functional method used to derive macroscopic equations from the microscopic Langevin dynamics, functional renormalization, Monte Carlo and molecular dynamic numerical methods). On the contrary, the techniques needed to deal with the statics and dynamics of quantum macroscopic systems are much less known in general. I shall briefly discuss the role played by the environment in a quantum system and introduce and compare the equilibrium and dynamic approaches.

Concretely, we recall some features of the Langevin formalism and its generating function. We dwell initially with some emblematic aspects of classical macroscopic systems slowly evolving out of equilibrium. Concerning models, we focus on two, that are intimately related: the  **$O(N)$  model in the large  $N$  limit** that is used to describe **coarsening phenomena**, and the **random manifold**, that finds applications to many physical problems like charge density waves, high-Tc superconductors, etc. Both problems are of **field-theoretical** type and can be treated both **classically and quantum mechanically**. These two models are ideal for the purpose of introducing and discussing formalism and some basic ideas we would wish to convey in these lectures. Before entering the technical part we explain the two-fold meaning of the word **disorder** by introducing the glass problem and some of the numerous questions it raises.

## 1.2 Nucleation

When a system with a **first order phase transition** is taken to a region in the phase diagram in which it is still locally stable but metastable with respect to the new absolute minimum of the free-energy, its evolution towards the new equilibrium state occurs by nucleation of the stable phase. The theory of simple nucleation [3] is well established and the time needed for one bubble of the stable state to conquer the sample grows as an exponential of the free-energy difference between the metastable and the stable states over the thermal energy available,  $k_B T$ . Once the bubble has reached a critical size that also depends on this free-energy difference it very rapidly conquers the full sample and the system reaches the stable state. The textbook example is the one of a magnetic system, *e.g.* an Ising model, in equilibrium under a magnetic field that is suddenly reversed. The sample has to reverse its magnetization but this involves a nucleation process of the kind just explained. Simple nucleation is therefore not very interesting to us but one should notice that as soon as multiple nucleation and competition between different states intervenes the problem becomes

rapidly hard to describe quantitatively and it becomes very relevant to the mean-field theory of fragile structural glasses that we shall discuss.

### 1.3 Phase ordering kinetics

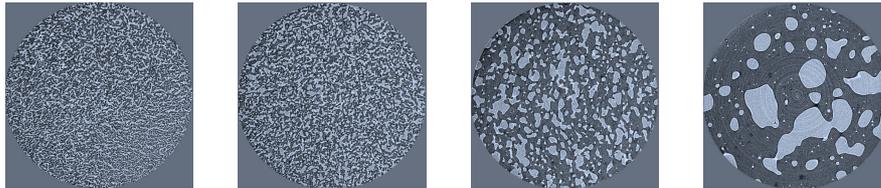


Figure 1: Four images after a quench of a two species mixture (of glasses!) that tends to demix under the new working conditions. Images courtesy of E. Gouillart (St. Gobain), D. Bouttes and D. Vandembroucq (ESPCI).

Choose a system with a well-understood equilibrium phase transition and take it across the critical point (second order phase transition) very quickly by tuning a control parameter. If the system is taken from its disordered (mixed) phase to its ordered (demixed) phase the sample will tend to phase separate in the course of time to approach the ideal equilibrium configuration under the new conditions. Such an example of **phase ordering kinetics** [4], i.e. **phase separation**, is shown in Fig. 1. None of the two species disappears, they just separate. This is such a slow process that the time needed to fully separate the mixture diverges with the size of the sample, as we shall see later on.

Another example of phase ordering kinetics is given by the **crystal grain growth** sketched in the left-most panel in Fig. 2. Grains are formed by pieces of the lattice with the same orientation. Boundaries between these grains are drawn with lines in the figure. The other panels show snapshots of a  $2d$  isotropic ferromagnetic Potts model

$$H_J[\{s_i\}] = -J \sum_{\langle ij \rangle} \delta_{s_i s_j} \quad (1.1)$$

with  $s_i = 1, \dots, q = 8$  quenched below its first order phase transition at the initial time  $t = 0$  from a configuration in equilibrium at infinite temperature. The quench is done well below the region of metastability and the dynamics are the ones of **domain growth**. Indeed, domains of neighboring spin ordered in the same direction grow in the course of time. This is clear from the subsequent snapshots taken at  $t = 128$  MCs and  $t = 1024$  MCs. This model has been used to mimic this kind of physical process when the number of spin components becomes very large,  $q \gg 1$ . Note that the number of spins of each kind is not conserved along the system's evolution.

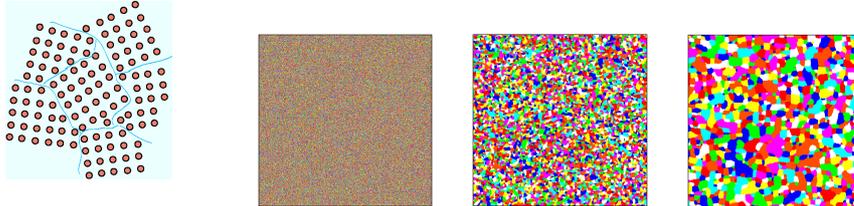


Figure 2: Grain boundaries in crystal growth. Three snapshots of the  $2d$  ferromagnetic Potts model with  $q = 8$  quenched below its (first order) phase transition to  $T = T_c/2$ . The times at which the images were taken are  $t = 0, 128, 1024$  MCs. Data from M. P. Loureiro, J. J. Arenzon, and LFC

These problems are simple in that the systems try to order in configurations that are easy to visualize and to characterize. It is also quite clear from the figures that two kinds of processes coexist: what happens within the domains, far from the interfaces, and what the interfaces do. We shall come back to this very important issue. To conclude phase ordering kinetics are rather well understood qualitatively although a full quantitative description is hard to develop as the problem is set into the form of a non-linear field theory with no small parameter.

#### 1.4 Critical dynamics

In **critical quenches** [5], patches with equilibrium critical fluctuations grow in time but their linear extent never reaches the equilibrium correlation length that diverges. Clusters of neighboring spins pointing in the same direction of many sizes are visible in the figures and the structure is quite intricate with clusters within clusters and so on and so forth. The interfaces look pretty rough too. A comparison between critical and sub-critical coarsening are shown in Figs. 3 and 4.

**Critical slowing down** implies that the relaxation time diverges close to the phase transition as a power law of the distance to criticality

$$\tau \sim (T - T_c)^{-\nu z} \quad (1.2)$$

with  $\nu$  the exponent that controls the divergence of the correlation length and  $z$  the dynamic critical exponent.

#### 1.5 Structural disorder: glassy physics

While the understanding of equilibrium phases, the existence of phase transitions as well as the characterization of critical phenomena are well understood in clean systems, as soon as **competing interactions** or **geometric frustration** are included one faces the possibility of destroying this simple picture by giving way to novel phenomena like **glassy** behavior [6].

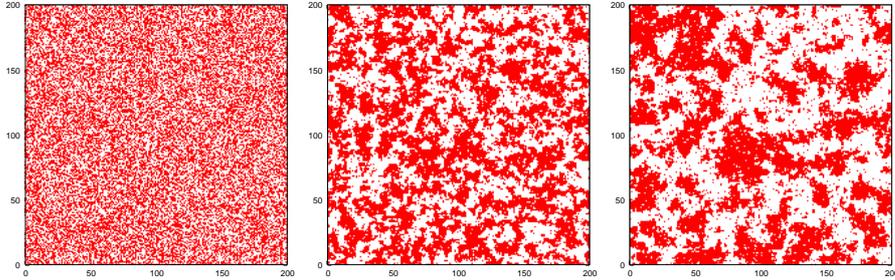


Figure 3: Monte Carlo simulations of a  $2d$  Ising model. Three snapshots at  $t = 1, 3 \times 10^5, 3 \times 10^6$  MCs after a quench to  $T_c$ . Data from T. Blanchard, LFC and M. Picco.

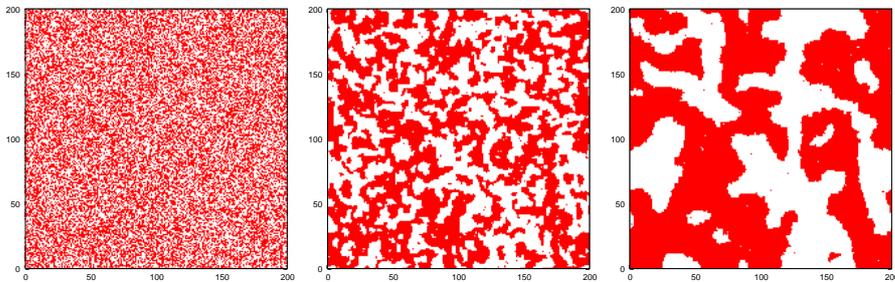


Figure 4: Monte Carlo simulations of a  $2d$  Ising model. Three snapshots at  $t = 1, 3 \times 10^5, 3 \times 10^6$  MCs after a quench to  $0.5 T_c$ . Thermal fluctuations within the domains are visible. Data from T. Blanchard, LFC and M. Picco.

Glassy systems are usually **dissipative**, that is to say in contact with a much larger environment, that has a well defined temperature and with which the systems in question can exchange heat. We deal with open dissipative systems here.

Competing interactions in physical systems can be dynamic, also called **annealed**, or **quenched**. A simple example illustrates the former: the Lennard-Jones potential<sup>2</sup>,

$$V(r) = V_0 [(r_0/r)^a - (r_0/r)^b] \quad (1.3)$$

with usually,  $a = 12$  and  $b = 6$  (see Fig. 7-left) that gives an effective interaction between soft<sup>3</sup> particles in a liquid has a repulsive and an attractive part, depending on the distance between the particles, a set of dynamic variables. In this example,

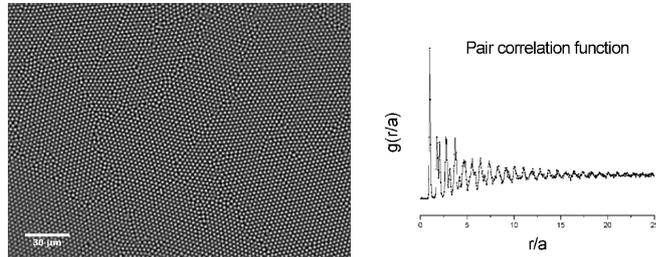


Figure 5: A crystal in a  $2d$  colloidal suspension of hard spheres.

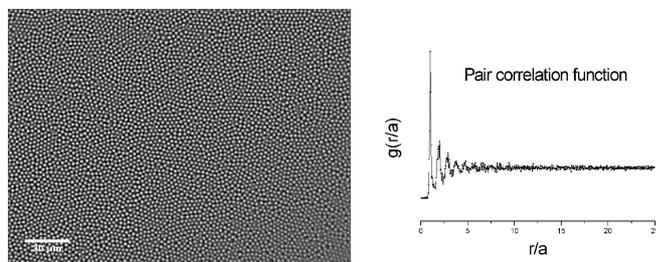


Figure 6: A liquid or a glass in a  $2d$  colloidal suspension of hard spheres.

the interactions depend on the positions of the particles and evolve with them.

When competing interactions are present the low-temperature configurations may look disordered but still have macroscopic properties of a kind of crystalline state. Again, cooling down a liquid to obtain a glass is helpful to exemplify what we mean here: the liquid cannot support stress and flows while the glass has solid-like properties as crystals, it can support stress and does not easily flow in reasonable time-scales (this is why glasses can be made of glass!). However, when looked at a microscopic scale, one does not identify any important structural difference between the liquid and the glass: no simple long-range structural order has been identified for glasses. Moreover, there is no clear evidence for a phase transition between the liquid and the glass. At present one can only talk about a dynamic crossover. The glassy regime is, however, usually called a **glassy phase** and it is sometimes said to be a **disordered phase** due to the lack of a clear structural order – this does not mean that there is

<sup>2</sup>The first term is chosen to take care of a quantum effect due to Pauli repulsion in a phenomenological way, the asymptotically leading attractive term is the van der Waals contribution when  $b = 6$ .

<sup>3</sup>Soft means that the particles can overlap at the price of an energy cost. In the case this is forbidden one works with hard particles.

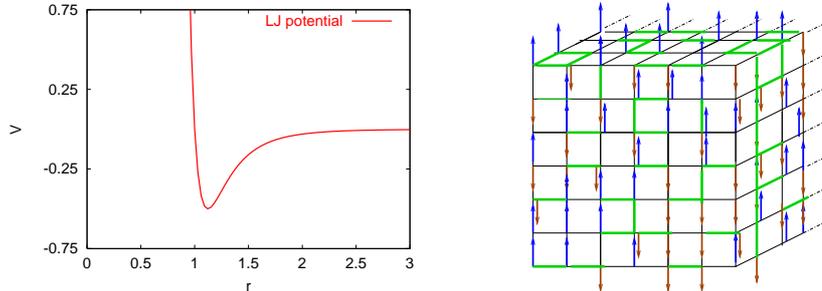


Figure 7: Left: The Lennard-Jones potential. Right: the Edwards-Anderson 3d spin-glass.

no order whatsoever (see Fig. 6 for an example of a system with a liquid, a crystal and a glassy phase). Lennard-Jones binary mixtures are prototypical examples of systems that undergo a glass transition (or crossover) when cooled across the glass temperature  $T_g$  or when compressed across a density  $n_g$  [6].

There are many types of glasses and they occur over an astounding range of scales from macroscopic to microscopic. See Fig. 8 for some images. Macroscopic examples include **granular media** like sand and powders. Unless fluidized by shaking or during flow these quickly settle into jammed, amorphous configurations. Jamming can also be caused by applying stress, in response to which the material may effectively convert from a fluid to a solid, refusing further flow. Temperature (and of course quantum fluctuations as well) is totally irrelevant for these systems since the grains are typically big, say, of  $1\text{mm}$  radius. **Colloidal suspensions** contain smaller (typically micrometre-sized) particles suspended in a liquid and form the basis of many paints and coatings. Again, at high density such materials tend to become glassy unless crystallization is specifically encouraged (and can even form arrested gels at low densities if attractive forces are also present). On smaller scales still, there are atomic and **molecular glasses**: window glass is formed by quick cooling of a silica melt, and of obvious everyday importance. The plastics in drink bottles and the like are also glasses produced by cooling, the constituent particles being long polymer molecules. Critical temperatures are of the order of  $80\text{C}$  for, say, PVC and these systems are glassy at room temperature. Finally, on the nanoscale, glasses are also formed by vortex lines in type-II superconductors. **Atomic glasses** with very low critical temperature, of the order of  $10\text{mK}$ , have also been studied in great detail.

A set of experiments explore the macroscopic **macroscopic** properties of glass formers. In a series of usual measurements one estimates the entropy of the sample by using calorimetric measurements and the thermodynamic relation

$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} dT \frac{C_p(T)}{T}. \quad (1.4)$$

In some cases the specific volume of the sample is shown as a function of temperature.

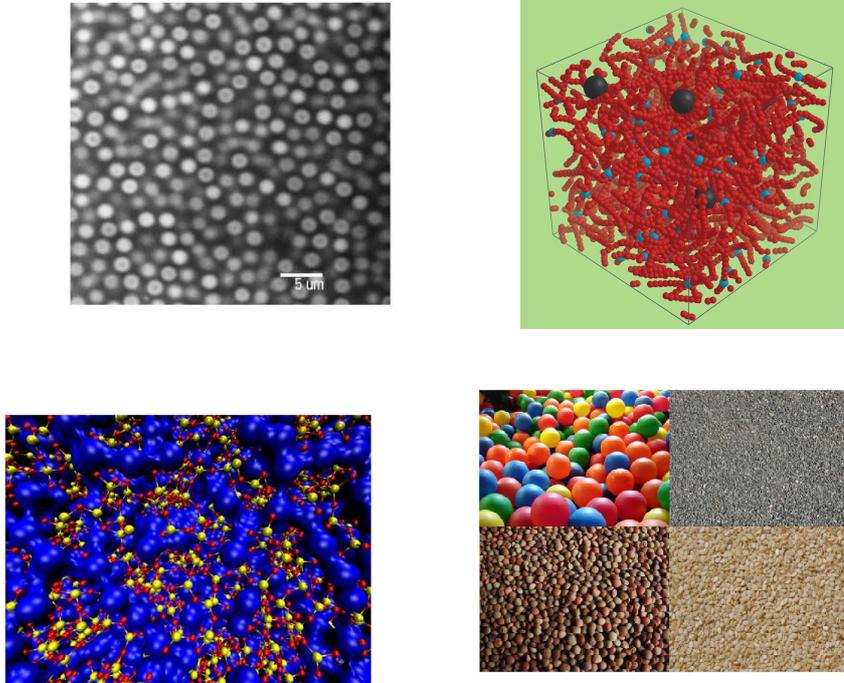


Figure 8: Several kinds of glasses. A colloidal suspension observed with confocal microscopy. A polymer melt configuration obtained with molecular dynamics. A simulation box of a Lennard-Jones mixture. A series of photograph of granular matter.

In numerical simulations the potential energy density can be equally used. Figure 9 shows the entropy of the equilibrium liquid,  $S(T) \simeq cT$  and the jump to the entropy of the equilibrium crystal at the melting temperature  $T_m$ , a first order phase transition. The figure also shows that when the cooling rate is sufficiently fast, and how fast is fast depends on the sample, the entropy follows the curve of the liquid below  $T_m$ , entering a metastable phase that is called a super-cooled liquid. The curves obtained with different cooling rates are reproducible in this range of temperatures. However, below a characteristic temperature  $T_g$  the curves start to deviate from the liquid-like behavior, they become flatter and, moreover, they depend on the cooling rate (red, orange and yellow curves in the figure). The slower the cooling rate the lower the entropy and the closer it comes to the one of the crystal. Typical cooling rates used in the laboratory are 0.1 – 100 K/min. Within these experiments  $T_g$  is defined as the temperature at which the shoulder appears.

The extrapolation of the entropy of the liquid below  $T_g$  crosses the entropy of the

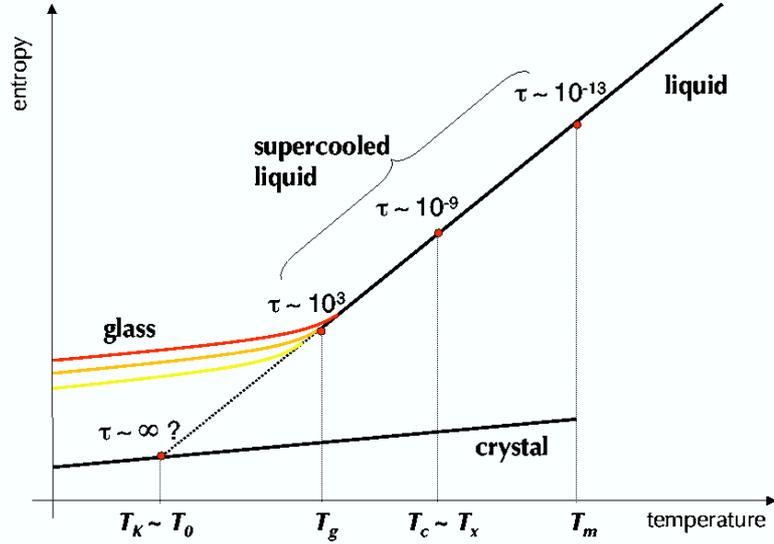


Figure 9: The typical plot showing the four ‘phases’ observed in a cooling experiment: liquid, supercooled liquid, glass and crystal. The characteristic temperatures  $T_m$  (a first order phase transition),  $T_g$  and the Kauzmann temperature  $T_K$  are shown as well as the typical relaxation times in the liquid and super-cooled liquid phases.

crystal at a value of the temperature that was conjectured by Kauzmann to correspond to an actual phase transition. Indeed, at  $T_K$  the entropy of the ‘glass’ is no longer larger than the one of the crystal and the system undergoes an **entropy crisis**. Of course experiments cannot be performed in equilibrium below  $T_g$  and, in principle, the extrapolation is just a theoretical construction. Having said this, the mean-field models we shall discuss later on realize this feature explicitly and put this hypothesis on a firmer analytic ground. If  $T_K$  represents a thermodynamic transition it should be reachable in the limit of infinitely slow cooling rate.

Rheological measurements show that the viscosity of a super-cooled liquid, or the resistance of the fluid to being deformed by either shear or tensile stress, also increases by many orders of magnitude when approaching the glass ‘transition’. One finds – or alternatively defines –  $T_g$  as the temperature at which the viscosity reaches  $\eta = 10^2$  Pa s [Pascal s = k m/s<sup>2</sup> s/m<sup>2</sup> = kg/(m s)]. At this temperature a peak in the specific heat at constant pressure is also observed, but no divergence is measured.

Bulk relaxation times are also given in the figure in units of seconds. In the super-cooled liquid phase the relaxation time varies by 10 orders of magnitude, from  $\tau_\alpha \simeq 10^{-13}$  at the melting point to  $\tau_\alpha \simeq 10^3$  at the glassy arrest. The interval of variation of the temperature is much narrower; it depends on the sample at hand but one can

say that it is of the order of 50 K. We note that the relaxation times remain finite all along the super-cooled liquid phase and do not show an explicit divergence within the temperature range in which equilibrium can be ensured. We discuss below how these relaxation times are estimated and the two classes, i.e. temperature dependences, that are found.

The values of  $T_g$  depend on the sample. In polymer glasses one finds a variation from, say,  $-70$  C in rubber to  $145$  C in polycarbonate passing by  $80$  C in the ubiquitous PVC.

There are many different routes to the glassy state. In the examples above we described cooling experiments but one can also use crunches in which the system is set under increasing pressure or other.

The **structure and dynamics** of liquids and glasses can be studied by investigating the **two-time dependent density-density correlation**:

$$\begin{aligned} g(r; t, t_w) &\equiv \langle \delta\rho(\vec{x}, t) \delta\rho(\vec{y}, t_w) \rangle \quad \text{with} \quad r = |\vec{x} - \vec{y}| \\ &= N^{-2} \sum_{i=1}^N \sum_{j=1}^N \langle \delta(\vec{x} - \vec{r}_i(t)) \delta(\vec{y} - \vec{r}_j(t_w)) \rangle \end{aligned}$$

where we ignored linear and constant terms.  $\delta\rho$  is the density variation with respect to the mean  $N/V$ . The average over different dynamical histories (simulation/experiment)  $\langle \dots \rangle$  implies isotropy (all directions are equivalent) and invariance under translations of the reference point  $\vec{y}$ . Its Fourier transform is

$$F(q; t, t_w) = N^{-1} \sum_{i,j=1}^N \langle e^{i\vec{q}(\vec{r}_i(t) - \vec{r}_j(t_w))} \rangle \quad (1.5)$$

The **incoherent intermediate or self** correlation:

$$F_s(q; t, t_w) = N^{-1} \sum_{i=1}^N \langle e^{i\vec{q}(\vec{r}_i(t) - \vec{r}_i(t_w))} \rangle \quad (1.6)$$

can be accessed with (neutron or other) diffraction experiments.

In the main panel of Fig. 10-left the equal-time two-point correlation function of a Lennard-Jones mixture at different times after an infinite rapid quench below the glassy crossover temperature  $T_g$  is shown. The data vary very little although a wide range of time-scales is explored. In the inset a zoom over the first peak taken at the same time for different final temperatures, three of them below  $T_g$  the reference one at the numerically determined  $T_g$ . Again, there is little variation in these curves. One concludes that the structure of the sample in all these cases is roughly the same.

The change is much more pronounced when one studies the dynamics of the sample, that is to say, when one compares the configuration of the system at different times. The curves on the right panel display the relaxation of the correlation function at different temperatures, all above  $T_g$ . The relaxation is stationary in all cases, i.e.

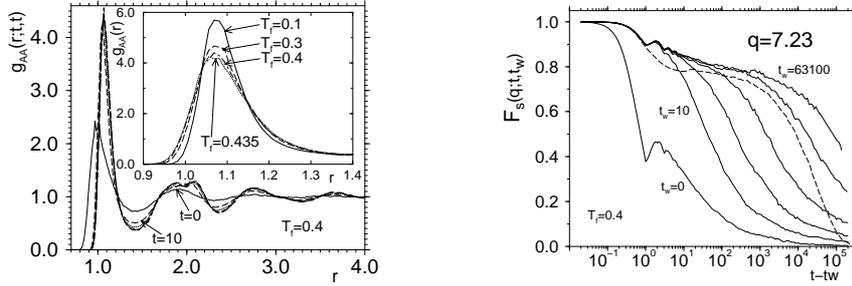


Figure 10: Structure and dynamics of a binary Lennard-Jones mixture. Left: the two-point correlation function of the A atoms at different times (main panel) and at different temperatures (inset). Right: the decay of the Fourier transform of the correlation function at the wave-vector associated to the first peak in  $g_{AA}(r)$ . Data from Kob & J-L Barrat.

a function of  $t - t_w$  only, but it becomes much slower when the working temperature approaches  $T_g$ .

In a family of glass formers called **fragile**, in double logarithmic scale used in the plot, a clear plateau develops for decreasing  $T$  and may seem to diverge in the  $T \rightarrow T_g$  limit. In another family of glass formers called **strong** no plateau is seen.

From the analysis of the temperature dependence of the relaxation time, say the time needed for the correlation to decay to half its value at zero time delay<sup>4</sup> one finds two kinds of fitting laws:

$$\tau_\alpha = \begin{cases} \tau_0 e^{A/(T-T_0)} & \text{Vogel-Fulcher-Tamann} \\ \tau_0 e^{A/T} & \text{Arrhenius} \end{cases} \quad (1.7)$$

In fits  $T_0$  is usually very close to  $T_K$ . The former class of systems are the fragile ones while the latter are the strong ones. Note that the first form yields a divergence at a finite  $T_K$  while the second one yields a divergence at  $T = 0$ . Silica belongs to the second class while most polymer glasses belong to the first one. This relaxation time is usually called the **alpha or structural relaxation time**. Recall that in a usual second order phase transition (as realized in an Ising model, for instance) the divergence of the relaxation time close to the critical point is of power law type.

A **real space analysis** of the motion of the particles in atomic, molecules in molecular, or strings in polymeric glasses (and granular matter as well) demonstrates that the elements move, over short time scales, in cages formed by their neighbors. During this short time span the correlation function decays to the plateau and the mean-square displacement reaches a plateau (in a double logarithmic scale). Note, however, that the particle's displacement is much smaller than the particle radius meaning that the displacement is indeed tiny during this time regime. the second structural relaxation is the one that take the correlation (displacement) below (above)

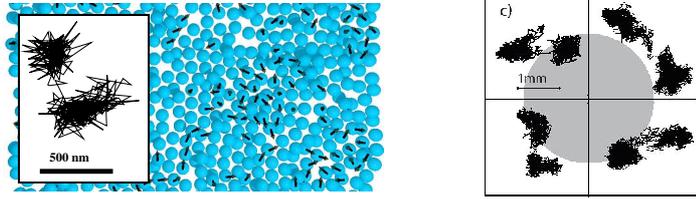


Figure 11: Colloidal suspension (data from E. Weeks group) and granular matter (data from O. Pouliquen's group).

the plateau.

Very recently stress has been put on the analysis of the motion of the elements over longer time-scales. Dynamic heterogeneities [12] were thus uncovered. Dynamic regions with high mobility immersed in larger regions with little mobility were identified. Sometimes stringly motion of particles following each other in a periodic path were also observed in confocal microscopy measurements or in molecular dynamics simulations. The length of these strings seems to increase when approaching the crossover temperature  $T_g$ . Moreover, dynamic heterogeneities, and a growing length associated to it, were quantified from the analysis of a four-point correlation function. This function takes different forms depending on the problem at hand but basically searches for spatial correlations in the displacement of particles between on time intervals. Calling  $\delta\rho(\vec{r}, t) = \rho(\vec{r}, t) - \rho_0$  with  $\rho_0 = N/V$ ,

$$C_4(r; t, t_w) = \langle \delta\rho(\vec{x}, t_w)\delta\rho(\vec{x}, t)\delta\rho(\vec{y}, t_w)\delta\rho(\vec{y}, t) \rangle - \langle \delta\rho(\vec{x}, t_w)\delta\rho(\vec{x}, t) \rangle \langle \delta\rho(\vec{y}, t_w)\delta\rho(\vec{y}, t) \rangle. \quad (1.8)$$

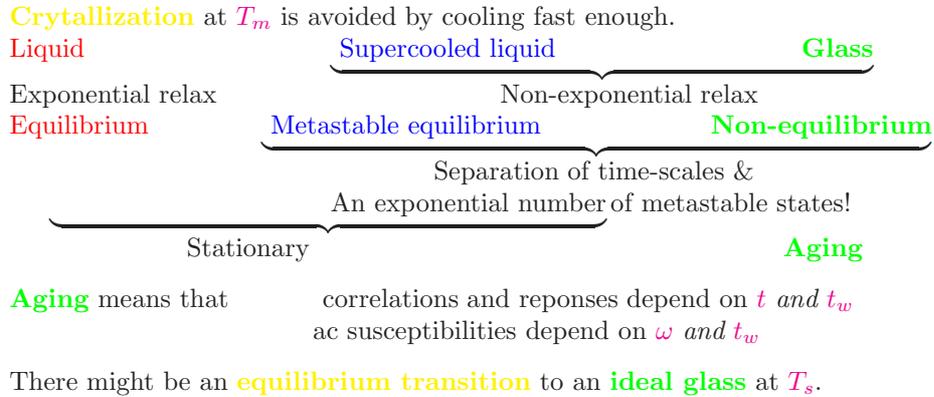
Terms involving one position only can be extracted from the average since they do not contain information about the spatial correlation. The idea is, roughly, to consider that  $\delta\rho(\vec{x}, t)\delta\rho(\vec{x}, t_w)$  is the **order parameter**. The double spatial integral of this quantity defines a **generalized susceptibility**  $\chi_4(t, t_w)$  that has been studied in many numerical and laboratory experiments. It shows a peak at the time-delay  $t - t_w$  that coincides with the relaxation time  $\tau_\alpha$ . Assuming a usual kind of scaling with a typical growing length for the four point correlation the characteristics of the appearance of the peak should yield the length of these dynamic heterogeneities. The data can be interpreted as leading to a divergence of the growing length at some temperature but the actual values found are very small, of the order of a few inter-particle distances in the sample.

The defining features of glasses, i.e., the characterization of their **out of equilibrium relaxation** and **aging phenomena** [13], will be discussed below.

A **summary** of the liquid-super-cooled liquid-glass behavior is given in the table below.

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<sup>4</sup>This is a very naive definition of  $\tau_\alpha$ , others much more precise are used in the literature.



## 1.6 Quenched disorder: still glassiness

In the paragraphs above we characterized the low temperature regime of certain particle models and claimed that their structure is disordered (at least at first sight). Another sense in which the word **disorder** is used is to characterize the **interactions**. Quenched interactions are due to a very sharp separation of time-scales. The traditional example is the one of **spin-glasses** in which the characteristic time for diffusion of magnetic impurities in an inert host is much longer than the characteristic time for magnetic moment change:

$$\tau_d \gg \tau_{exp} \gg \tau_0 . \quad (1.9)$$

The position of the magnetic moments are decided at the preparation of the sample. These position are then random and they do not change during experimental times. The interactions between pairs of spins depend on the distance between the magnetic moments via the RKKY formula

$$V_{\text{RKKY}}(r_{ij}) = -J \frac{\cos(2k_F r_{ij})}{r_{ij}^3} s_i s_j . \quad (1.10)$$

Therefore quenched competing interactions are fixed in the observational time-scale and they transmit ‘contradictory’ messages. Typical examples are systems with ferromagnetic and/or antiferromagnetic exchanges that are not organized in a simple way with respect to the geometry and connectivity of the lattice such as spin-glasses [7] (see Fig. 7-right).

Theoretically, this is modeled by random interactions drawn from a probability distribution. For simplicity the spins (magnetic moments) are placed on the vertices of a finite dimensional lattice, typically a cubic one. The Edwards-Anderson

Hamiltonian then reads

$$H_J[\{s_i\}] = \sum_{\langle ij \rangle} J_{ij} s_i s_j \quad \text{with} \quad J_{ij} \quad \text{taken from} \quad P(J_{ij}) \quad (1.11)$$

**Annealed interactions** may have a slow time-dependence. Both lead to **disorder**. These can be realized by coupling strengths as in the magnetic example in Fig. 7, but also by magnetic fields, pinning centers, potential energies, *etc.* Disordered interactions usually lead to low-temperature behavior that is similar to the one observed in systems with dynamic competing interactions.

Data showing the cusp in the susceptibility of a spin-glass sample are shown in Fig. 12.

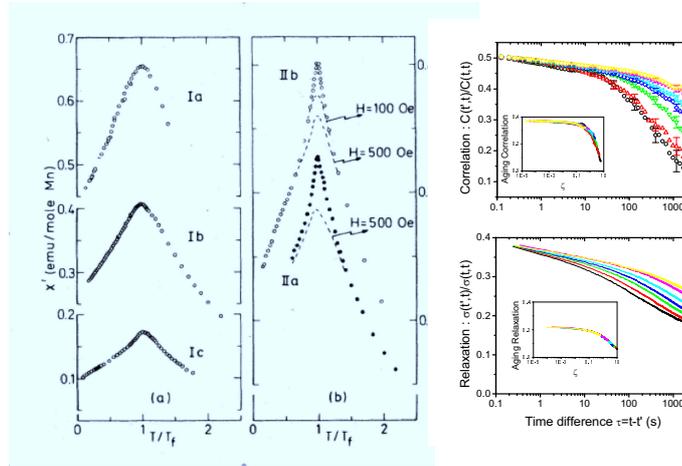


Figure 12: Spin-glasses: Susceptibility data (Mydosh). Aging phenomena (Hérisson and Ocio).

## 1.7 Static questions

In these lectures we shall only deal with a canonical setting, the microcanonical one being more relevant to quantum systems. Disordered systems (in both senses) are usually in contact with external reservoirs at fixed temperature; their description is done in the canonical (or grand-canonical in particle systems with the possibility of particle exchange with the environment) ensemble.

Many questions arise for the **static properties** of systems with competing interactions. Some of them, that we shall discuss in the rest of the course are:

- Are there equilibrium phase transitions between low-temperature and high temperature phases?

- Is there any kind of order at low temperatures?
- At the phase transition, if there is one, does all the machinery developed for clean systems (scaling, RG) apply?
- Are these phases, and critical phenomena or dynamic crossovers, the same or very different when disorder is quenched or annealed?
- What is the mechanism leading to glassiness?

## 1.8 Random manifolds

A problem that finds applications in many areas of physics is the dynamics of elastic manifolds under the effect (or not) of quenched random potentials, with (Kardar-Parisi-Zhang) or without (Edwards-Wilkinson, Mullins-Herring) non-linear interactions, with short-range or long-range elastic terms [8, 14].

Under certain circumstances the interfaces **roughen**, that is to say, their asymptotic averaged width depends on their linear size. Take for instance, the local height  $h(\vec{r}, t)$  of a  $d$  dimensional surface (with no overhangs). Its time-dependent width is defined as

$$W_L(t) = L^{-d} \int d^d r [h(\vec{r}, t) - \langle h(\vec{r}, t) \rangle]^2 \quad (1.12)$$

where  $\langle \dots \rangle = L^{-d} \int d^d r \dots$ . This quantity verifies the so-called **Family-Vicsek scaling**. In its simplest form, in which all dependences are power laws, it first increases as a function of time,  $W_L(t) \sim t^{2\alpha}$  and independently of  $L$ . At a crossover time  $t_x \sim L^z$  it crosses over to saturation at a level that grows as  $L^{2\zeta}$ .  $\alpha$  is the growth exponent,  $z$  is the dynamic exponent and  $\zeta$  is the roughness exponent. Consistency implies that they are related by  $z\alpha = \zeta$ . The values of the exponents are known in a number of cases. For the Edwards-Wilkinson surface one has  $\alpha = (2-d)/4$ ,  $z = 2$  and  $\zeta = (2-d)/2$  for  $d \leq 2$ . For the non-linear KPZ line  $\alpha = 1/3$ ,  $z = 3/2$  and  $\zeta = 1/2$ .

In the presence of quenched disorder the dependence of the asymptotic roughness with the length of the line undergoes a crossover. For lines that are shorter than a temperature and disorder strength dependent value  $L_T$  the behavior is controlled by thermal fluctuations and relation as the one above holds with  $\zeta = \zeta_T$ , the thermal roughness exponent. This exponent is the one corresponding to the EW equation. In this thermally dominated scale, the dynamics is expected to be normal in the sense that lengths and times should be thus related by power laws of types with the exponents discussed above. For surfaces such that  $L > L_T$  one finds that the same kind of scaling holds but with a roughness exponent that takes a different value. The time dependence and cross-over time are expected, though, not to be power laws and we shall discuss them later.

The relaxation dynamics of such elastic manifolds in the very large limit presents many other interesting phenomena that resemble features observed in more complex glassy systems. Moreover, such elastic surfaces appear in the nucleation and growth

kinetics problems discussed above as the interfaces between equilibrium (sometimes metastable) states.

## 1.9 Aging

In practice a further complication appears [13]. Usually, disordered phases are prepared with a relatively rapid quench from the high temperature phase. When approaching a characteristic temperature the systems cannot follow the pace of evolution dictated by the environment and **fall out of equilibrium** [2]. Indeed, their key feature is that below some characteristic temperature  $T_g$ , or above a critical density  $\rho_g$ , the relaxation time goes beyond the experimentally accessible time-scales and the system is next bound to evolve out of equilibrium. Although the mechanism leading to such a slow relaxation is unknown – and might be different in different cases – the out of equilibrium relaxation presents very similar properties. The left panel in Fig. 13 shows one aspect of glassy dynamics, aging, as shown by the two-time relaxation of the self-correlation of a colloidal suspension, that is remarkably similar to the decay of the magnetic correlation in the Ising model shown in the right panel and in Fig. ??.

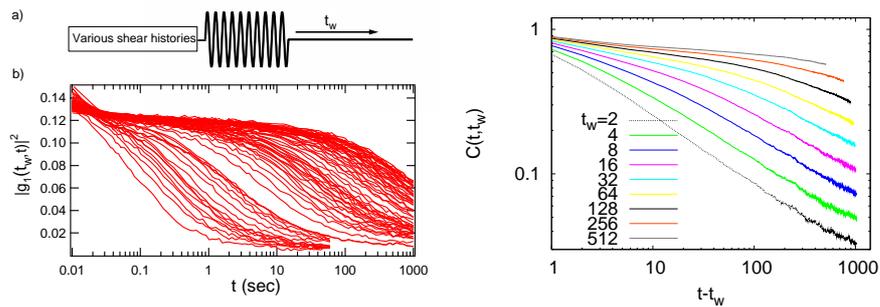


Figure 13: Left: two-time evolution of the self-correlation in a colloidal suspension initialized by applying a shearing rate (data from Viasnoff and Lequeux) The longer the waiting time the slower the decay. Right: two-time evolution in the bi-dimensional Ising model quenched below its phase transition at  $T_c$ . A two-scale relaxation with a clear plateau at a special value of the correlation is seen in the double logarithmic scale. Data from Sicilia *et al.* We shall discuss this feature at length in the lectures.

A purely static description, based on the use of the canonical (or grand-canonical) partition function is then not sufficient. One is forced to include the time evolution of the individual agents (spins, particles, molecules) and from it derive the macroscopic *time-dependent* properties of the full system. The microscopic time-evolution is given by a stochastic process. The macroscopic evolution is usually very slow and, in probability terms, it is not a small perturbation around the Gibbs-Boltzmann distri-

bution function but rather something quite different. This gives rise to new interesting phenomena.

The questions that arise in the **non-equilibrium** context are

- How to characterize the non-equilibrium dynamics of glassy systems phenomenologically.
- Which are the minimal models that reproduce the phenomenology.
- Which is the relation between the behavior of these and other non-equilibrium systems, in particular, those kept away from equilibrium by external forces, currents, *etc.*
- Which features are generic to all systems with slow dynamics.
- Whether one could extend the equilibrium statistical mechanics ideas; *e.g.* can one use temperature, entropy and other thermodynamic concepts out of equilibrium?
- Related to the previous item, whether one can construct a non-equilibrium measure that would substitute the Gibbs-Boltzmann one in certain cases.

## 1.10 Driven systems

An out of equilibrium situation can be externally maintained by applying forces and thus injecting energy into the system and driving it. There are several ways to do this and we explain below two quite typical ones that serve also as theoretical traditional examples.

**Rheological measurements** are common in soft condensed matter; they consist in driving the systems out of equilibrium by applying an external force that does not derive from a potential (e.g. shear, shaking, *etc.*). The dynamics of the system under the effect of such a strong perturbation is then monitored.

The effect of shear on domain growth is one of great technological and theoretical importance. The growth of domains is anisotropic and there might be different growing lengths in different directions. Moreover, it is not clear whether shear might interrupt growth altogether giving rise to a non-equilibrium stationary state or whether coarsening might continue for ever. Shear is also commonly used to study the mechanical properties of diverse glasses.

Another setting is to couple the system to **different external reservoirs** all in equilibrium but at different temperature or chemical potential thus inducing a heat or a particle current through the system. This set-up is relevant to quantum situations in which one can couple a system to, say, a number of leads at different chemical potential. The heat transport problem in classical physics also belongs to this class.

A pinned interface at zero temperature can be depinned by pulling it with an external force. The depinning problem that is to say the analysis of the dynamics close to the critical force needed to depin the manifold, and the creep dynamics at non-vanishing temperature have also been the subject of much analysis.

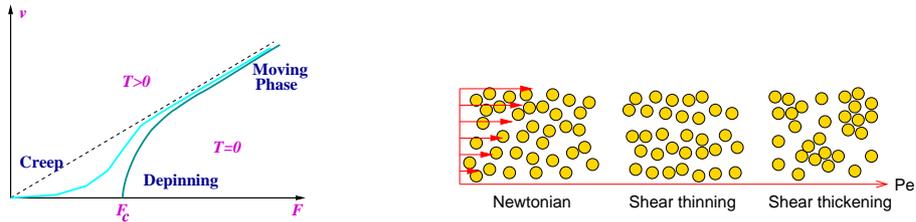


Figure 14: Left: Creep and depinning of elastic objects under quenched randomness. Right: Rheology of complex fluids. Shear thinning:  $\tau$  decreases or thickening  $\tau$  increases.

## 1.11 Interdisciplinary aspects

The theory of disordered systems has become quite interdisciplinary in the sense that problems in computer science, biology or even sociology and finance have disorder aspects and can be mimicked with similar models and solved with similar methods to the ones we shall discuss here.

### 1.11.1 Optimization problems

The most convenient area of application is, most probably, the one of **combinatorial optimization** in computer science [9]. These problems can usually be stated in a form that corresponds to minimizing a cost (energy) function over a large set of variables. Typically these cost functions have a very large number of local minima – an exponential function of the number of variables – separated by barriers that scale with  $N$  and finding the truly absolute minimum is hardly non-trivial. Many interesting optimization problems have the great advantage of being defined on random graphs and are then mean-field in nature. The mean-field machinery that we shall discuss at length is then applicable to these problems with minor (or not so minor) modifications due to the finite connectivity of the networks.

Let us illustrate this kind of problems with two examples. The **graph partitioning** problem consists in, given a graph  $G(N, E)$  with  $N$  vertices and  $E$  edges, to partition it into smaller components with given properties. In its simplest realization the uniform graph partitioning problem is how to partition, in the optimal way, a graph with  $N$  vertices and  $E$  links between them in two (or  $k$ ) groups of equal size  $N/2$  (or  $N/k$ ) and the minimal the number of edges between them. Many other variations are possible. This problem is encountered, for example, in computer design where one wishes to partition the circuits of a computer between two chips. More recent applications include the identification of clustering and detection of cliques in social, pathological and biological networks.

Another example is **k satisfiability (k-SAT)**. This is the computer science problem of determining whether the variables of a given Boolean formula can be assigned in such a way as to make the formula evaluate to ‘true’. Equally important is to

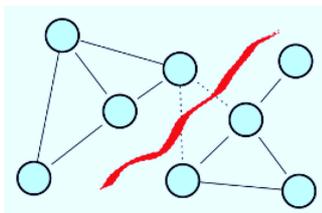


Figure 15: Graph partitioning.

determine whether no such assignments exist, which would imply that the function expressed by the formula is identically ‘false’ for all possible variable assignments. In this latter case, we would say that the function is unsatisfiable; otherwise it is satisfiable. For example, the formula  $C_1 : x_1 \text{ OR } x_2$  made by a single clause  $C_1$  is satisfiable because one can find the values  $x_1 = \text{true}$  (and  $x_2$  free) or  $x_2 = \text{true}$  (and  $x_1$  free), which make  $C_1 : x_1 \text{ OR } x_2$  true. This example belongs to the  $k = 2$  class of satisfiability problems since the clause is made by two literals (involving different variables) only. Harder to decide formulæ are made of  $M$  clauses involving  $k$  literals required to take the true value ( $x$ ) or the false value ( $\bar{x}$ ) each, these taken from a pool of  $N$  variables. An example in 3-SAT is

$$F = \begin{cases} C_1 : x_1 \text{ OR } \bar{x}_2 \text{ OR } x_3 \\ C_2 : \bar{x}_5 \text{ OR } \bar{x}_7 \text{ OR } x_9 \\ C_3 : x_1 \text{ OR } \bar{x}_4 \text{ OR } x_7 \\ C_4 : x_2 \text{ OR } \bar{x}_5 \text{ OR } x_8 \end{cases} \quad (1.13)$$

All clauses have to be satisfied simultaneously so the formula has to be read  $F : C_1 \text{ AND } C_2 \text{ AND } C_3 \text{ AND } C_4$ . It is not hard to believe that when  $\alpha \equiv M/N > \alpha_c$  the problems typically become unsolvable while one or more solutions exist on the other side of the phase transition. In **random k-SAT** an instance of the problem, i.e. a formula, is chosen at random with the following procedure: first one takes  $k$  variables out of the  $N$  available ones. Second one decides to require  $x_i$  or  $\bar{x}_i$  for each of them with probability one half. Third one creates a clause taking the OR of these  $k$  literals. Fourth one returns the variables to the pool and the outlined three steps are repeated  $M$  times. The  $M$  resulting clauses form the final formula.

The Boolean character of the variables in the  $k$ -SAT problem suggests to transform them into Ising spins, i.e.  $x_i$  evaluated to true (false) will correspond to  $s_i = 1$  ( $-1$ ). The requirement that a formula be evaluated true by an assignment of variables (i.e. a configuration of spins) will correspond to the ground state of an adequately

chosen energy function. In the simplest setting, each clause will contribute zero (when satisfied) or one (when unsatisfied) to this cost function. There are several equivalent ways to reach this goal. For instance  $C_1$  above can be represented by a term  $(1-s_1)(1+s_2)(1-s_3)/8$ . The fact that the variables are linked together through the clauses suggests to define  $k$ -uplet interactions between them. We then choose the interaction matrix to be

$$J_{ai} = \begin{cases} 0 & \text{if neither } x_i \text{ nor } \bar{x}_i \in C_a \\ 1 & \text{if } x_i \in C_a \\ -1 & \text{if } \bar{x}_i \in C_a \end{cases} \quad (1.14)$$

and the energy function as

$$H_J[\{s_i\}] = \sum_{a=1}^M \delta\left(\sum_{i=1}^N J_{aj}s_i, -k\right) \quad (1.15)$$

where  $\delta(x, y)$  is a Kronecker-delta. This cost function is easy to understand. The Kronecker delta contributes one to the sum only if all terms in the sum  $\sum_{i=1}^N J_{ai}s_i$  are equal  $-1$ . This can happen when  $J_{ai} = 1$  and  $s_i = -1$  or when  $J_{ai} = -1$  and  $s_i = 1$ . In both cases the condition on the variable  $x_i$  is not satisfied. Since this is required from all the variables in the clause, the clause itself and hence the formula are not satisfied.

These problems are ‘solved’ numerically, with algorithms that do not necessarily respect physical rules. Thus, one can use non-local moves in which several variables are updated at once – as in cluster algorithms of the Swendsen-Wang type used to beat critical slowing down close to phase transitions or one can introduce a temperature to go beyond cost-function barriers and use dynamic local moves that do not, however, satisfy a detail balance. The problem is that with hard instances of the optimization problem none of these strategies is successful. Indeed, one can expect that glassy aspects, as the proliferation of metastable states separated by barriers that grow very fast with the number of variables, can hinder the resolutions of these problems in polynomial time for *any* algorithm.

**Complexity theory** in computer science, and the classification of optimization problems in classes of complexity – P for problems solved with algorithms that use a number of operations that grows as a polynomial of the number of variables, *e.g.* as  $N^2$  or even  $N^{100}$ , NP for problems for which no polynomial algorithm is known and one needs a number of operations that grow exponentially with  $N$ , *etc.* – applies to the worst instance of a problem. Worst instance, in the graph-partitioning example, means the **worst** possible realization of the connections between the nodes. Knowing which one this is is already a very hard problem!

But one can try to study optimization problems on average, meaning that the question is to characterize the **typical** – and not the worst – realization of a problem. The use of techniques developed in the field of disordered physical systems, notably spin-glasses, have proven extremely useful to tackle typical single randomly generated instances of hard optimization problems.

Note that in statistical mechanics information about averaged macroscopic quantities is most often sufficiently satisfactory to consider a problem solved. In the optimization context one seeks for exact microscopic configurations that correspond to the exact ground state and averaged information is not enough. Nevertheless, knowledge about the averaged behavior can give us qualitative information about the problem that might be helpful to design powerful algorithms to attack single instances.

### 1.11.2 Biological applications

In the biological context disordered models have been used to describe **neural networks**, *i.e.* an ensemble of many neurons (typically  $N \sim 10^9$  in the human brain) with a very elevated connectivity. Indeed, each neuron is connected to  $\sim 10^4$  other neurons and receiving and sending messages *via* their axons. Moreover, there is no clear-cut notion of distance in the sense that axons can be very long and connections between neurons that are far away have been detected. Hebb proposed that the memory lies in the connections and the peculiarity of neural networks is that the connectivity must then change in time to incorporate the process of learning.

The simplest neural network models [10] represent neurons with Boolean variables or spins, that either fire or are quiescent. The interactions link pairs of neurons and they are assumed to be symmetric (which is definitely not true). The state of a neuron is decided by an activity function  $f$ ,

$$\phi_i = f\left(\sum_{j(\neq i)} J_{ij}\phi_j\right), \quad (1.16)$$

that in its simplest form is just a theta-function leading to simply two-valued neurons.

Memory of an object, action, *etc.* is associated to a certain pattern of neuronal activity. It is then represented by an  $N$ -component vector in which each component corresponds to the activity of each neuron. Finally, sums over products of these patterns constitute the interactions. As in optimization problems, one can study the particular case associated to a number of chosen specific patterns to be stored and later recalled by the network, or one can try to answer questions on average, as how many typical patterns can a network of  $N$  neurons store. The models then become fully-connected or dilute models of spins with quenched disorder. The microscopic dynamics cannot be chosen at will in this problem and, in general, will not be as simple as the single spin flip ones used in more conventional physical problems. Still, if the disordered modeling is correct, glassy aspects can render recall very slow due to the presence of metastable states for certain values of the parameters.

Another field of application of disordered system techniques is the description of **hetero-polymers** and, most importantly, protein folding. The question is how to describe the folding of a linear primary structure (just the sequence of different amino-acids along the main backbone chain) into an (almost) unique compact native structure whose shape is intimately related to the biological function of the protein. In modeling these very complex systems one proposes that the non-random, selected

through evolution, macromolecules may be mimicked by random polymers. This assumption is based on the fact that amino-acids along the chain are indeed very different. One then uses monomer-monomer and/or monomer-solvent interactions that are drawn from some probability distribution and are fixed in time (quenched disorder). Still, a long bridge between the theoretical physicists' and the biologists' approaches remain to be crossed. Some of the important missing links are: proteins are mesoscopic objects with of the order of 100 monomers thus far from the thermodynamic limit; interest is in the particular, and not averaged, case in biology, in other words, one would really like to know what is the secondary structure of a particular primary sequence; *etc.* In the protein folding problem it is clear that the time needed to reach the secondary structure from an initially stretched configuration depends strongly on the existence of metastable states that could trap the (hetero) polymer. Glassy aspects have been conjectured to appear in this context too.

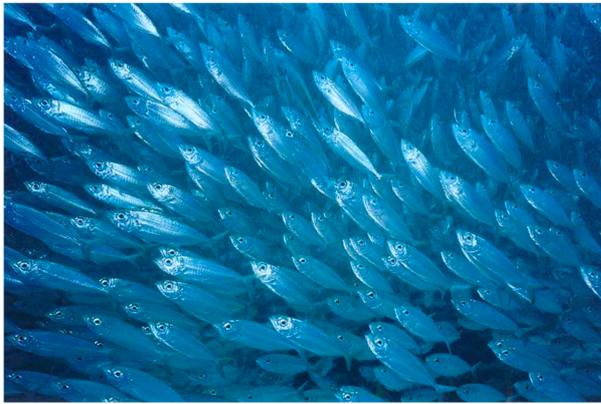


Figure 16: Active matter.

The constituents of **active matter**, be them particles, lines or other, absorb energy from their environment or internal fuel tanks and use it to carry out motion. In this new type of soft condensed matter energy is partially transformed into mechanical work and partially dissipated in the form of heat [11]. The units interact directly or through disturbances propagated in the medium. In systems of biological interest, conservative forces (and thermal fluctuations) are complemented by non-conservative forces. Realizations of active matter in biology are thus manifold and exist at different scales. Some of them are: bacterial suspensions, the cytoskeleton in living cells, or even swarms of different animals. Clearly enough, active matter is far from equilibrium and typically kept in a non-equilibrium steady state. The difference between active matter and other driven systems, such as sheared fluids, vibrated granular matter and driven vortex lattices is that the energy input is located on internal units (e.g.

motors) and therefore homogeneously distributed in the sample. In the other driven systems mentioned above, the energy input occurs on the boundaries of the sample. Moreover, the effect of the motors can be dictated by the state of the particle and/or its immediate neighborhood and it is not necessarily fixed by an external field.

The dynamics of active matter presents a number of interesting features that are worth mentioning here. Active matter displays out of equilibrium phase transitions that may be absent in their passive counterparts. The dynamic states display large scale spatio-temporal dynamical patterns and depend upon the energy flux and the interactions between their constituents. Active matter often exhibits unusual mechanical properties, very large responses to small perturbations, and very large fluctuations – not consistent with the central limit theorem. Much theoretical effort has been recently devoted to the description of different aspects of these systems, such as self-organization of living microorganisms, the identification and analysis of states with spatial structure, such as bundles, vortices and asters, the study of the rheological properties of active particle suspensions with the aim of grasping which are the mechanical consequences of biological activity. A rather surprisingly result was obtained with a variational solution to the many-body master equation of the motorized version of the standard hard sphere fluid often used to model colloids: instead of stirring and thus destabilize ordered structures, the motors do, in some circumstances enlarge the range of stability of crystalline and amorphous structures relative to the ones with purely thermal motion.



Figure 17: Left: random graph with finite connectivity.

## 1.12 Summary

The main steps in the development and application of Statistical Mechanics ideas to macroscopic cooperative systems have been

- The development of the basic ideas (Boltzmann-Gibbs).
- The recognition of collective phenomena and the identification and mean-field description of phase transitions (Curie-Weiss).
- The correct description of critical phenomena with scaling theories and the renormalization group (Kadanoff, Widom, M. Fisher, Wilson) and more recently the development of conformal field theories for two-dimensional systems.

- The study of stochastic processes and time-dependent properties (Langevin, Fokker-Planck, Glauber, *etc.*).

To describe the problems introduced above the same route has been followed. There is no doubt that Equilibrium Statistical Mechanics yields the static properties of these systems. In the case of coarsening problems one understands very well the static phases and phase transitions. In the case of glassy systems this is not so clear. In the case of active matter or other driven systems there are equilibrium phases in the vanishing drive limit only but one can also study the **dynamic phase transitions** with a critical phenomena perspective.

Although the study of equilibrium phases might be a little irrelevant from the practical point of view since, most glassy systems are out of equilibrium in laboratory time-scales, it is certainly a necessary step on which one can try to build a truly dynamic theory. The mean-field study – the second step in the list above – of the equilibrium properties of disordered systems, in particular those with quenched disorder, has revealed an incredibly rich theoretical structure. We still do not know whether it carries through to finite dimensional cases. Even though, it is definitely interesting *per se* and it finds a very promising field of application in combinatorial optimization problems that are defined on random networks, see Fig. 17, with mean-field character. Scaling arguments have been applied to describe finite dimensional disordered systems but they remain – as their parent ones for clean systems – quite phenomenological and difficult to put to sufficiently restrictive numerical or experimental test. The extension of renormalisation group methods to systems with quenched disorder is also under development and still needs quite a lot of work – the third step. As for the out of equilibrium dynamics of these systems, again, it has been solved at the mean-field level but little is known in finite dimensions – apart from numerical simulations or the solution to toy models. As in its static counterpart, the results from the study of dynamic mean-field models have been very rich and they have suggested a number of new phenomena later searched for in numerical simulations and experiments of finite dimensional systems. In this sense, these solutions have been a very important source of inspiration.

## 2 Formalism

In this section I will revisit certain aspects of statistical physics that are not commonly discussed and that become important for our purposes.

### 2.1 Fluctuations

There are several possible sources of fluctuations:

- **Classical thermal**: the system is coupled to an environment that ensures fluctuations (noise) and dissipation (the fact that the total energy is not conserved). E.g. coarsening, classical glasses, spin-glasses.
- **Quantum**: the system is coupled to a quantum environment that ensures fluctuations (noise) and dissipation. The temperature of the bath can be zero or not. E.g. quantum coarsening and glasses, quantum spin-glasses.
- **Stochastic motors**: forces that act on the system's particles stochastically. The energy injected in the sample is partially dissipated to the bath and partially used as work. As the system is also coupled to a bath there are also thermal fluctuations in it. E.g. active matter.

Classical and quantum environments are usually modeled as large ensembles of non-interacting variables (oscillators [16], spins [17], fermions) with chosen distributions of coupling constants and energies.

### 2.2 The classical reduced partition function

We analyze the statistical **static** properties of a **classical canonical system** in equilibrium at inverse temperature  $\beta$  and itself formed by two sub-parts, one that will be treated as an environment (not necessarily of infinite size) and another one that will be the (sub-)system of interest. We study the **partition function** or Gibbs functional,  $Z_{\text{TOT}}$ :

$$Z_{\text{TOT}}[\eta] = \sum_{\substack{\text{CONF ENV} \\ \text{CONF SYST}}} \exp(-\beta H_{\text{TOT}} - \beta \eta x) \quad (2.1)$$

where the sum represents an integration over the phase space of the full system, i.e. the system's and the environmental ones.  $\eta$  is a source. We take

$$H_{\text{TOT}} = H_{\text{SYST}} + H_{\text{ENV}} + H_{\text{INT}} + H_{\text{COUNTER}} = H_{\text{SYST}} + \tilde{H}_{\text{ENV}} . \quad (2.2)$$

For simplicity we use a single particle moving in  $d = 1$ :  $H_{\text{SYST}}$  is the Hamiltonian of the isolated particle,

$$H_{\text{SYST}} = \frac{p^2}{2M} + V(x) , \quad (2.3)$$

with  $p$  and  $x$  its momentum and position.  $H_{\text{ENV}}$  is the Hamiltonian of a ‘thermal bath’ that, for simplicity, we take to be an ensemble of  $N$  independent harmonic oscillators [15, 16] with masses  $m_a$  and frequencies  $\omega_a$ ,  $a = 1, \dots, N$

$$H_{\text{ENV}} = \sum_{a=1}^N \frac{\pi_a^2}{2m_a} + \frac{m_a \omega_a^2}{2} q_a^2 \quad (2.4)$$

with  $\pi_a$  and  $q_a$  their momenta and positions. This is indeed a very usual choice since it may represent phonons.  $H_{\text{INT}}$  is the coupling between system and environment. We shall restrict the following discussion to a linear interaction in the oscillator coordinates,  $q_a$ , and in the particle coordinate,

$$H_{\text{INT}} = x \sum_{a=1}^N c_a q_a, \quad (2.5)$$

with  $c_a$  the coupling constants. The counter-term  $H_{\text{COUNTER}}$  is added to avoid the generation of a negative harmonic potential on the particle due to the coupling to the oscillators (that may render the dynamics unstable). We choose it to be

$$H_{\text{COUNTER}} = \frac{1}{2} \sum_{a=1}^N \frac{c_a^2}{m_a \omega_a^2} x^2. \quad (2.6)$$

The generalization to more complex systems and/or to more complicated baths and higher dimensions is straightforward. The calculations can also be easily generalized to an interaction of the oscillator coordinate with a more complicated dependence on the system’s coordinate,  $\mathcal{V}(x)$ , that may be dictated by the symmetries of the system. Non-linear functions of the oscillator coordinates cannot be used since they render the problem unsolvable analytically.

Having chosen a quadratic bath and a linear coupling, the integration over the oscillators’ coordinates and momenta can be easily performed. This yields the **reduced** Gibbs functional

$$Z_{\text{RED}}[\eta] \propto \sum_{\text{CONF SYST}} \exp \left[ -\beta \left( H_{\text{SYST}} + H_{\text{COUNTER}} + \eta x - \frac{1}{2} \sum_{a=1}^N \frac{c_a^2}{m_a \omega_a^2} x^2 \right) \right]. \quad (2.7)$$

The ‘counter-term’  $H_{\text{COUNTER}}$  is chosen to cancel the last term in the exponential and it avoids the renormalization of the particle’s mass (the coefficient of the quadratic term in the potential) due to the coupling to the environment that could have even destabilized the potential by taking negative values. An alternative way of curing this problem would be to take a vanishingly small coupling to the bath in such a way that the last term must vanish by itself (say, all  $c_a \rightarrow 0$ ). However, this might be problematic when dealing with the stochastic dynamics since a very weak coupling to the bath implies also a very slow relaxation. It is then conventional to include the counter-term to cancel the mass renormalization. One then finds

$$\boxed{Z_{\text{RED}}[\eta] \propto \sum_{\text{CONF SYST}} \exp [-\beta (H_{\text{SYST}} + \eta x)] = Z_{\text{SYST}}[\eta]}. \quad (2.8)$$

For a non-linear coupling  $H_{\text{INT}} = \sum_{a=1}^N c_a q_a \mathcal{V}(x)$  the counter-term is  $H_{\text{COUNTER}} = \frac{1}{2} \sum_{a=1}^N \frac{c_a^2}{m_a \omega_a^2} [\mathcal{V}(x)]^2$ .

The interaction with the reservoir does not modify the statistical properties of the particle since  $Z_{\text{RED}} \propto Z_{\text{SYS}}$ , independently of the choices of  $c_a$ ,  $m_a$ ,  $\omega_a$  and  $N$ .

If one is interested in the **dynamics** of a coupled problem, the characteristics of the sub-system that will be considered to be the bath have an influence on the reduced dynamic equations found for the system, that are of generic Langevin kind, as explained in Sect. 2.3.

**Quantum mechanically** the reduced partition function depends explicitly on the properties of the bath. The interaction with quantum harmonic oscillators introduces non-local interactions (along the Matsubara time direction) and there is no physical way to introduce a counter-term to correct for this feature.

The **dynamics of quantum systems** has all these difficulties.

## 2.3 The Langevin equation

Examples of experimental and theoretical interest in condensed matter and biophysics in which quantum fluctuation can be totally neglected are manifold. In this context one usually concentrates on systems in contact with an environment: one selects some relevant degrees of freedom and treats the rest as a bath. It is a canonical view. Among these instances are colloidal suspensions which are particles suspended in a liquid, typically salted water, a ‘soft condensed matter’ example; spins in ferromagnets coupled to lattice phonons, a ‘hard condensed matter’ case; and proteins in the cell a ‘biophysics’ instance. These problems are modeled as stochastic processes with Langevin equations [23], the Kramers-Fokker-Planck formalism or master equations depending on the continuous or discrete character of the relevant variables and analytic convenience.

The Langevin equation is a stochastic differential equation that describes phenomenologically a large variety of problems. It models the time evolution of a set of slow variables coupled to a much larger set of fast variables that are usually (but not necessarily) assumed to be in thermal equilibrium at a given temperature. We first introduce it in the context of Brownian motion and we derive it in more generality in Sect. 2.3.2.

### 2.3.1 Langevin’s Langevin equation

The Langevin equation<sup>5</sup> for a particle moving in one dimension in contact with a **white-noise** bath reads

$$\boxed{m\dot{v} + \gamma_0 v = F + \xi, \quad v = \dot{x},} \quad (2.9)$$

with  $x$  and  $v$  the particle’s position and velocity.  $\xi$  is a Gaussian white noise with zero mean and correlation  $\langle \xi(t)\xi(t') \rangle = 2\gamma_0 k_B T \delta(t-t')$  that mimics thermal agitation.

<sup>5</sup>P. Langevin, *Sur la théorie du mouvement brownien*, Comptes-Rendus de l’Académie des Sciences **146**, 530-532 (1908).

$\gamma_0 v$  is a friction force that opposes the motion of the particle. The force  $F$  designates all external deterministic forces and depends, in the most common cases, on the position of the particle  $x$  only. In cases in which the force derives from a potential,  $F = -dV/dx$ . The generalization to higher dimensions is straightforward. Note that  $\gamma_0$  is the parameter that controls the strength of the coupling to the bath (it appears in the friction term as well as in the noise term). In the case  $\gamma_0 = 0$  one recovers Newton equation of motion. The relation between the friction term and thermal correlation is non-trivial. Langevin fixed it by requiring  $\langle v^2(t) \rangle \rightarrow \langle v^2 \rangle_{eq}$ . We shall give a different argument for it in the next section.

### 2.3.2 Derivation of the Langevin equation

Let us take a system in contact with an environment. The interacting system+environment ensemble is ‘closed’ while the system is ‘open’. The nature of the environment, *e.g.* whether it can be modeled by a classical or a quantum formalism, depends on the problem under study. We focus here on the classical problem. A derivation of a generalized Langevin equation with memory is very simple starting from Newton dynamics of the full system [15, 18].

We shall then study the coupled system introduced in Sect. .

The generalization to more complex systems and/or to more complicated baths and higher dimensions is straightforward. The calculations can also be easily generalized to an interaction of the oscillator coordinate with a more complicated dependence on the system’s coordinate,  $\mathcal{V}(x)$ , that may be dictated by the symmetries of the system, see Ex. 1.

Hamilton’s equations for the particle are

$$\dot{x}(t) = \frac{p(t)}{m}, \quad \dot{p}(t) = -V'[x(t)] - \sum_{a=1}^N c_a q_a(t) - \sum_{a=1}^N \frac{c_a^2}{m_a \omega_a^2} x(t) \quad (2.10)$$

(the counter-term yields the last term) while the dynamic equations for each member of the environment read

$$\dot{q}_a(t) = \frac{\pi_a(t)}{m_a}, \quad \dot{\pi}_a(t) = -m_a \omega_a^2 q_a(t) - c_a x(t), \quad (2.11)$$

showing that they are all massive harmonic oscillators **forced by the chosen particle**. These equations are readily solved by

$$q_a(t) = q_a(0) \cos(\omega_a t) + \frac{\pi_a(0)}{m_a \omega_a} \sin(\omega_a t) - \frac{c_a}{m_a \omega_a} \int_0^t dt' \sin[\omega_a(t-t')] x(t') \quad (2.12)$$

with  $q_a(0)$  and  $\pi_a(0)$  the initial coordinate and position at time  $t = 0$  when the particle is set in contact with the bath. It is convenient to integrate by parts the last term. The replacement of the resulting expression in the last term in the RHS of eq. (2.10) yields

$$\boxed{\dot{p}(t) = -V'[x(t)] + \xi(t) - \int_0^t dt' \Gamma(t-t') \dot{x}(t')}, \quad (2.13)$$

with the **symmetric and stationary kernel**  $\Gamma$  given by

$$\Gamma(t-t') = \sum_{a=1}^N \frac{c_a^2}{m_a \omega_a^2} \cos[\omega_a(t-t')], \quad (2.14)$$

$\Gamma(t-t') = \Gamma(t'-t)$ , and the **time-dependent force**  $\xi$  given by

$$\xi(t) = - \sum_{a=1}^N c_a \left[ \frac{\pi_a(0)}{m_a \omega_a} \sin(\omega_a t) + \left( q_a(0) + \frac{c_a x(0)}{m_a \omega_a^2} \right) \cos(\omega_a t) \right]. \quad (2.15)$$

This is the equation of motion of the **reduced** system. It is still **deterministic**.

The third term on the RHS of eq. (2.13) represents a rather complicated **friction force**. Its value at time  $t$  depends explicitly on the history of the particle at times  $0 \leq t' \leq t$  and makes the equation **non-Markovian**. One can rewrite it as an integral running up to a total time  $\mathcal{T} > \max(t, t')$  introducing the **retarded friction**:

$$\gamma(t-t') = \Gamma(t-t') \theta(t-t'). \quad (2.16)$$

Until this point the dynamics of the system remain deterministic and are completely determined by its initial conditions as well as those of the reservoir variables. The **statistical element** comes into play when one realizes that it is impossible to know the initial configuration of the large number of oscillators with great precision and one proposes that the initial coordinates and momenta of the oscillators have a canonical distribution at an **inverse temperature**  $\beta$ . Then, one chooses  $\{\pi_a(0), q_a(0)\}$  to be initially distributed according to a canonical phase space distribution:

$$P(\{\pi_a(0), q_a(0)\}, x(0)) = 1/\tilde{\mathcal{Z}}_{\text{ENV}}[x(0)] e^{-\beta \tilde{H}_{\text{ENV}}[\{\pi_a(0), q_a(0)\}, x(0)]} \quad (2.17)$$

with  $\tilde{H}_{\text{ENV}} = H_{\text{ENV}} + H_{\text{INT}} + H_{\text{COUNTER}}$ , that can be rewritten as

$$\tilde{H}_{\text{ENV}} = \sum_{a=1}^N \left[ \frac{m_a \omega_a^2}{2} \left( q_a(0) + \frac{c_a}{m_a \omega_a^2} x(0) \right)^2 + \frac{\pi_a^2(0)}{2m_a} \right]. \quad (2.18)$$

The randomness in the initial conditions gives rise to a random force acting on the reduced system. Indeed,  $\xi$  is now a **Gaussian random variable**, that is to say a noise, with

$$\langle \xi(t) \rangle = 0, \quad \langle \xi(t) \xi(t') \rangle = k_B T \Gamma(t-t') \equiv \tilde{\Gamma}(t-t'). \quad (2.19)$$

One can easily check that higher-order correlations vanish for an odd number of  $\xi$  factors and factorize as products of two time correlations for an even number of  $\xi$  factors. In consequence  $\xi$  has Gaussian statistics. Defining the inverse of  $\Gamma$  over the interval  $[0, t]$ ,  $\int_0^t dt'' \Gamma(t-t'') \Gamma^{-1}(t''-t') = \delta(t-t')$ , one has the Gaussian pdf:

$$P[\xi] = \mathcal{Z}^{-1} e^{-\frac{1}{2k_B T} \int_0^t dt \int_0^t dt' \xi(t) \Gamma^{-1}(t-t') \xi(t')}. \quad (2.20)$$

$\mathcal{Z}$  is the normalization. A random force with non-vanishing correlations on a finite support is usually called a **coloured noise**. Equation (2.13) is now a genuine Langevin equation. A multiplicative retarded noise arises from a model in which one couples the coordinates of the oscillators to a generic function of the coordinates of the system, see Ex. 1 and eq. (2.27).

The use of an **equilibrium measure** for the oscillators implies the relation between the friction kernel and the noise-noise correlation, which are proportional, with a constant of proportionality of value  $k_B T$ . This is a generalized form of the **fluctuation-dissipation relation**, and it applies to the environment.

Different choices of the environment are possible by selecting different ensembles of harmonic oscillators. The simplest one, that leads to an approximate Markovian equation, is to consider that the oscillators are coupled to the particle via coupling constants  $c_a = \tilde{c}_a/\sqrt{N}$  with  $\tilde{c}_a$  of order one. One defines

$$S(\omega) \equiv \frac{1}{N} \sum_{a=1}^N \frac{\tilde{c}_a^2}{m_a \omega_a} \delta(\omega - \omega_a) \quad (2.21)$$

a function of  $\omega$ , of order one with respect to  $N$ , and rewrites the kernel  $\Gamma$  as

$$\Gamma(t - t') = \int_0^\infty d\omega \frac{S(\omega)}{\omega} \cos[\omega(t - t')] . \quad (2.22)$$

A common choice is

$$\frac{S(\omega)}{\omega} = 2\gamma_0 \left(\frac{|\omega|}{\tilde{\omega}}\right)^{\alpha-1} f_c\left(\frac{|\omega|}{\Lambda}\right) . \quad (2.23)$$

The function  $f_c(x)$  is a high-frequency cut-off of typical width  $\Lambda$  and is usually chosen to be an exponential. The frequency  $\tilde{\omega} \ll \Lambda$  is a reference frequency that allows one to have a coupling strength  $\gamma_0$  with the dimensions of viscosity. If  $\alpha = 1$ , the friction is said to be **Ohmic**,  $S(\omega)/\omega$  is constant when  $|\omega| \ll \Lambda$  as for a white noise. This name is motivated by the electric circuit analog exposed by the end of this Section. When  $\alpha > 1$  ( $\alpha < 1$ ) the bath is **superOhmic** (**subOhmic**). The exponent  $\alpha$  is taken to be  $> 0$  to avoid divergencies at low frequency. For the exponential cut-off the integral over  $\omega$  yields

$$\Gamma(t) = 2\gamma_0 \tilde{\omega}^{-\alpha+1} \frac{\cos[\alpha \arctan(\Lambda t)]}{[1 + (\Lambda t)^2]^{\alpha/2}} \Gamma\alpha(\alpha) \Lambda^\alpha \quad (2.24)$$

with  $\Gamma\alpha(x)$  the Gamma-function, that in the Ohmic case  $\alpha = 1$  reads

$$\Gamma(t) = 2\gamma_0 \frac{\Lambda}{[1 + (\Lambda t)^2]} , \quad (2.25)$$

and in the  $\Lambda \rightarrow \infty$  limit becomes a delta-function,  $\Gamma(t) \rightarrow 2\gamma_0 \delta(t)$ . At long times, for any  $\alpha > 0$  and different from 1, one has

$$\lim_{\Lambda t \rightarrow \infty} \Gamma(t) = 2\gamma_0 \tilde{\omega}^{-\alpha+1} \cos(\alpha\pi/2) \Gamma\alpha(\alpha) \Lambda^{-1} t^{-\alpha-1} , \quad (2.26)$$

a **power law decay**.

Time-dependent,  $f(t)$ , and constant non-potential forces,  $f^{\text{NP}}$ , as the ones applied to granular matter and in rheological measurements, respectively, are simply included in the right-hand-side (RHS) as part of the deterministic force. When the force derives from a potential,  $F(x, t) = -dV/dx$ .

In so far we have discussed systems with position and momentum degrees of freedom. Other variables might be of interest to describe the dynamics of different kind of systems. In particular, a continuous Langevin equation for classical spins can also be used if one replaces the hard Ising constraint,  $s_i = \pm 1$ , by a soft one implemented with a potential term of the form  $V(s_i) = u(s_i^2 - 1)^2$  with  $u$  a coupling strength (that one eventually takes to infinity to recover a hard constraint). The soft spins are continuous unbounded variables,  $s_i \in (-\infty, \infty)$ , but the potential energy favors the configurations with  $s_i$  close to  $\pm 1$ . Even simpler models are constructed with spherical spins, that are also continuous unbounded variables globally constrained to satisfy  $\sum_{i=1}^N s_i^2 = N$ . The extension to fields is straightforward and we shall discuss one when dealing with the  $O(N)$  model.

**Exercise 1.** Prove that for a non-linear coupling  $H_{\text{INT}} = \mathcal{V}[x] \sum_{a=1}^N c_a q_a$  there is a choice of counter-term for which the Langevin equation reads

$$\dot{p}(t) = -V'[x(t)] + \xi(t)\mathcal{V}'[x(t)] - \mathcal{V}'[x(t)] \int_0^t dt' \Gamma(t-t')\mathcal{V}'[x(t')]\dot{x}(t') \quad (2.27)$$

with the same  $\Gamma$  as in eq. (2.14) and  $\xi(t)$  given by eq. (2.15) with  $x(0) \rightarrow \mathcal{V}[x(0)]$ . The noise appears now **multiplying** a function of the particles' coordinate.

Another derivation of the Langevin equation uses collision theory and admits a generalization to relativistic cases [19].

**The electric analog:** take an LRC circuit. The resistance is of the usual Ohmic type, that is to say, the potential drop,  $V_R$ , across it is given by  $V_R = IR$  with  $I$  the current and  $R$  the resistance. The potential drop,  $V_L$ , across the inductor  $L$  is given by  $V_L = LdI/dt$ . Finally, the potential drop across the capacitor is  $V_C = -C^{-1} \int Idt$ . The balance between these potentials implies a Langevin type equation for the current circulating across the circuit:

$$L \frac{d^2 I}{dt^2} + R \frac{dI}{dt} + C^{-1} I = 0. \quad (2.28)$$

This analogy justifies the Ohmic name given to a dissipative term proportional to the velocity in the general presentation.

### 2.3.3 Irreversibility and dissipation.

The friction force  $-\gamma_0 v$  in eq. (2.9) – or its retarded extension in the non-Markovian case – explicitly breaks time-reversal ( $t \rightarrow -t$ ) invariance, a property that has to be

respected by any set of microscopic dynamic equations. Newton equations describing the whole system, the particle and all the molecules of the fluid, are time reversal invariant. However, time-reversal can be broken in the **reduced** equation in which the fluid is treated in an effective statistical form and the fact that it is in equilibrium is assumed from the start.

Even in the case in which all forces derive from a potential,  $F = -dV/dx$ , the energy of the particle,  $mv^2/2 + V$ , is not conserved and, in general, flows to the bath leading to **dissipation**. At very long times, however, the particle may reach a stationary regime in which the particle gives and receives energy from the bath at equal rate, on average.

**Exercise 2.** Prove the time-irreversibility of the Langevin equation and the fact that the symmetry is restored if  $\gamma_0 = 0$ . Show that  $d\langle H_{\text{SYST}} \rangle / dt \neq 0$  when  $\gamma_0 \neq 0$ .

### 2.3.4 Smoluchowski (overdamped) limit

In many situations in which friction is very large, the characteristic time for the relaxation of the velocity degrees of freedom to their Maxwellian distribution,  $t_r^v$ , is very short (see the examples in Sect. 2.3). In consequence, observation times are very soon longer than this time-scale, the inertia term  $m\dot{v}$  can be dropped, and the Langevin equation becomes

$$\gamma_0 \dot{x} = F + \xi \quad (2.29)$$

(for simplicity we wrote the white-noise case). Indeed, this **overdamped** limit is acceptable whenever the observation times are much longer than the characteristic time for the velocity relaxation. Inversely, the cases in which the friction coefficient  $\gamma_0$  is small are called **underdamped**.

In the overdamped limit with white-noise the friction coefficient  $\gamma_0$  can be absorbed in a rescaling of time. One defines the new time  $\tau$

$$t = \gamma_0 \tau \quad (2.30)$$

the new position,  $\tilde{x}(\tau) = x(\gamma_0 \tau)$ , and the new noise  $\eta(\tau) = \xi(\gamma_0 \tau)$ . In the new variables the Langevin equation reads  $\dot{\tilde{x}}(\tau) = F(\tilde{x}, \tau) + \eta(\tau)$  with  $\langle \eta(\tau) \eta(\tau') \rangle = 2k_B T \delta(\tau - \tau')$ .

### 2.3.5 Discretization of stochastic differential equations

The way in which the stochastic differential equation (2.29) [with no inertia and with white noise] is to be discretized is a subtle matter that we shall not discuss in these lectures, unless where it will be absolutely necessary. There are basically two schemes, called the Itô and Stratonovich calculus, that are well documented in the literature <sup>6</sup>.

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<sup>6</sup>A clear and non-technical discussion of the two schemes is given in N. G. van Kampen, *Itô versus Stratonovich*, J. Stat. Phys. **24**, 175 (1981).

In short, we shall use a prescription in which the pair velocity-position of the particle at time  $t + \delta$ , with  $\delta$  an infinitesimal time-step, depends on the pair velocity-position at time  $t$  and the value of the noise at time  $t$ .

### 2.3.6 Markov character

In the case of a white noise (delta correlated) the full set of equations defines a **Markov process**, that is a stochastic process that depends on its history only through its very last step.

### 2.3.7 Generation of memory

The Langevin equation (2.9) is actually a set of two first order differential equations. Notice, however, that the pair of first-order differential equations could also be described by a single second-order differential equation:

$$m\ddot{x} + \gamma_0\dot{x} = F + \xi . \tag{2.31}$$

Having replaced the velocity by its definition in terms of the position  $x(t)$  depends now on  $x(t - \delta)$  and  $x(t - 2\delta)$ . This is a very general feature: by integrating away some degrees of freedom (the velocity in this case) one generates memory in the evolution. Generalizations of the Langevin equation, such as the one that we have just presented with colored noise, and the ones that will be generated to describe the slow evolution of super-cooled liquids and glasses in terms of correlations and linear responses, do have memory.

## 2.4 Classical dynamics: generating functional

In Sect. 2.3 we showed a proof of the (generally non-Markov) Langevin equation based on the integration over a large ensemble of harmonic oscillators that act as a bath with which the system is set in contact.

Observables which are functions of the solution to the Langevin equation can also be computed using a dynamic generating functional that reads [30, 31, 35]

$$Z_D[\eta] \equiv \int \mathcal{D}\xi \, dP(t_0) \, e^{-\frac{1}{2k_B T} \int_{t_0}^{\mathcal{T}} dt' \int_{t_0}^{\mathcal{T}} dt'' \xi(t') \Gamma^{-1}(t'-t'') \xi(t'') + \int_{t_0}^{\mathcal{T}} dt' \eta(t') x_\xi(t')}$$

$x_\xi(t)$  is the solution to the Langevin equation with initial condition  $x_0 = x(t_0)$ ,  $\dot{x}_0 = \dot{x}(t_0)$  at the initial time  $t_0$ . The factor  $dP(t_0)$  is the measure of the initial condition,  $dP(t_0) \equiv dx_0 d\dot{x}_0 P_1[x_0, \dot{x}_0]$ . The Gaussian factor is proportional to  $P[\xi]$  the functional probability measure of the noise. The measure is  $\mathcal{D}\xi \equiv \prod_{k=0}^{\mathcal{N}} d\xi(t_k)$  with  $k = 0, \dots, \mathcal{N}$ ,  $t_k = t_0 + k(\mathcal{T} - t_0)/\mathcal{N}$  and  $\mathcal{N} \rightarrow \infty$  while  $(\mathcal{T} - t_0)$  remains finite. The inverse kernel  $\Gamma^{-1}$  is defined within the interval  $[t_0, \mathcal{T}]$ :  $\int_{t_0}^{\mathcal{T}} dt'' \Gamma(t-t'') \Gamma^{-1}(t''-t') = \delta(t-t')$ .

A very useful expression for  $Z_D[\eta]$ , usually called the Martin-Siggia-Rose generating functional (actually derived by Janssen [31]), is obtained by introducing the identity

$$\text{Eq}[x(t)] \equiv m\ddot{x}(t) + \int_{t_0}^{\mathcal{T}} dt' \gamma(t-t') \dot{x}(t') + V'[x(t)] = \xi(t) \quad (2.32)$$

valid at each time  $t$ , with the delta function

$$1 = \int \mathcal{D}x \, \delta[\text{Eq}[x(t)] - \xi(t)] \left| \det \frac{\delta \text{Eq}[x(t)]}{\delta x(t')} \right|, \quad (2.33)$$

with  $\mathcal{D}x \equiv \prod_{k=1}^{\mathcal{N}} dx(t_k)$ . The factor  $|\det \dots|$  is the determinant of the operator  $\delta(t-t')\{m\partial_t^2 + V''[x(t)]\} + \gamma(t-t')\partial_t$  and ensures that the integral equals one.<sup>7</sup> The delta function can be exponentiated with an auxiliary field  $i\hat{x}$  (using the Fourier representation of the  $\delta$ -function).  $\mathcal{D}i\hat{x} = \prod_{k=1}^{\mathcal{N}-1} di\hat{x}(t_k)$ . The determinant can be exponentiated with time-dependent anticommuting variables – opening the way to the use of super-symmetry, a subject that we shall not touch in these notes. However, since it does not yield a relevant contribution to the kind of dynamics we are interested in, we forget it (one can show that the determinant is a constant for Langevin processes with coloured noise and/or inertia and that the discretization of an over-damped

<sup>7</sup>Its origin is in the change of variables. In the same way as in the one dimensional integral,  $\int dx \delta[g(x)] = \int dz 1/|g'[g^{-1}(z)]| \delta(z) = 1/|g'[g^{-1}(0)]|$ , to get 1 as a result one includes the inverse of the Jacobian within the integral:  $\int dx \delta[g(x)] |g'(x)| = 1$ .

Langevin equation with white-noise can also be chosen to set it to one – Itô convention.  $Z_D$  reads

$$\begin{aligned} Z_D[\eta, \hat{\eta}] &\equiv \int \mathcal{D}\xi \mathcal{D}x \mathcal{D}i\hat{x} dP(t_0) \\ &\times e^{-\int_{t_0}^T dt' i\hat{x}(t') \left[ m\ddot{x}(t') + \int_{t_0}^T dt'' \gamma(t' - t'')\dot{x}(t'') + V'[x(t')] - \xi(t') \right]} \\ &\times e^{-\frac{1}{2k_B T} \int_{t_0}^T dt' \int_{t_0}^T dt'' \xi(t') \Gamma^{-1}(t' - t'') \xi(t'') + \int_{t_0}^T dt' [\eta(t')x(t') + \hat{\eta}(t')i\hat{x}(t')]} \end{aligned}$$

where we have introduced a new source  $\hat{\eta}(t)$ , coupled to the auxiliary field  $i\hat{x}(t)$ . The integration over the noise  $\xi(t)$  is Gaussian and it can be readily done; it yields

$$+ \frac{k_B T}{2} \int_{t_0}^T dt' \int_{t_0}^T dt'' i\hat{x}(t') \Gamma(t' - t'') i\hat{x}(t'') \quad (2.34)$$

and, for a **coloured bath**, the environment generates a **retarded interaction** in the effective action. In the usual white noise case, this term reduces to,  $k_B T \gamma_0 \int_{t_0}^T dt' [i\hat{x}(t')]^2$ , a local expression. In the end, the generating function and resulting **Martin-Siggia-Rose-Jaensen-deDominicis** (MSRJD) action reads

$$\begin{aligned} \mathcal{Z}_D[\eta, \hat{\eta}] &\equiv \int \mathcal{D}x \mathcal{D}i\hat{x} dP(t_0) e^{S[x, i\hat{x}, \eta, \hat{\eta}]} \\ S[x, i\hat{x}, \eta, \hat{\eta}] &= - \int dt' i\hat{x}(t') \left\{ m\ddot{x}(t') + \int dt'' \gamma(t' - t'')\dot{x}(t'') + V'[x(t')] \right\} \\ &+ \frac{k_B T}{2} \int dt' \int dt'' i\hat{x}(t') \Gamma(t' - t'') i\hat{x}(t'') + \text{sources} . \end{aligned} \quad (2.35)$$

All integrals runs over  $[t_0, T]$ . Causality in the integral over  $t'$  is ensured by the fact that  $\gamma$  is proportional to  $\theta$ . A totally equivalent form that we will see appearing in the quantum case is

$$\begin{aligned} \mathcal{Z}_D[\eta, \hat{\eta}] &\equiv \int \mathcal{D}x \mathcal{D}i\hat{x} dP(t_0) e^{S[x, i\hat{x}, \eta, \hat{\eta}]} \\ S[x, i\hat{x}, \eta, \hat{\eta}] &= - \int dt' i\hat{x}(t') \left\{ m\ddot{x}(t') + \int dt'' \gamma(t' - t'')\dot{x}(t'') + V'[x(t')] \right\} \\ &+ \frac{1}{2} \int dt' \int dt'' i\hat{x}(t') \tilde{\Gamma}(t' - t'') i\hat{x}(t'') + \text{sources} . \end{aligned} \quad (2.36)$$

The MSRJD action has two kinds of contributions: the ones that depend on the characteristics of the bath (through  $\Gamma$ ) and the ones that do not. The latter also exist in a functional representation of Newton dynamics and we call them  $S^{\text{DET}}$  (for deterministic) while the former contain all information about thermal fluctuations and dissipation and we call it  $S^{\text{DISS}}$  (for dissipation):

$$S[x, i\hat{x}, \eta, i\hat{\eta}] = S^{\text{DISS}}[x, i\hat{x}; \Gamma] + S^{\text{DET}}[x, i\hat{x}, \eta, i\hat{\eta}] . \quad (2.37)$$

If the distribution of the initial condition were to be included in the action as an additional term,  $\ln P_1[x_0, i\hat{x}_0]$ ,  $\phi t$  would be part of  $S^{\text{DET}}$ .

Interestingly enough, the **dynamic generating functional at zero sources is identical to one** for any model:

$$\mathcal{Z}_{\text{D}}[\eta = 0, \hat{\eta} = 0] = 1 \quad (2.38)$$

as can be concluded from its very first definition. In particular, it does not depend on the coupling constants of the chosen model. This property will be utilized in disordered systems to render the dynamic calculations relatively easier than the static ones.

#### 2.4.1 Generic correlation and response.

The mean value at time  $t$  of a generic observable  $A$  is

$$\langle A(t) \rangle = \int \mathcal{D}x \mathcal{D}i\hat{x} dP(t_0) A[x(t)] e^{S[x, i\hat{x}]}, \quad (2.39)$$

where  $S[x, i\hat{x}]$  is shorthand notation for  $S[x, i\hat{x}, \eta = 0, \hat{\eta} = 0]$ . The self-correlation and linear response of  $x$  are given by

$$C(t, t') = \langle x(t)x(t') \rangle = \frac{1}{Z_{\text{D}}[\eta, \hat{\eta}]} \left. \frac{\delta^2 Z_{\text{D}}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\eta(t')} \right|_{\eta=\hat{\eta}=0} = \frac{\delta^2 Z_{\text{D}}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\eta(t')} \Big|_{\eta=\hat{\eta}=0} \quad (2.40)$$

$$\begin{aligned} R(t, t') &= \left. \frac{\delta\langle x(t) \rangle}{\delta h(t')} \right|_{h=0} = \langle x(t) \frac{\delta S[x, i\hat{x}; h]}{\delta h(t')} \rangle \Big|_{h=0} = \langle x(t) i\hat{x}(t') \rangle \\ &= \frac{1}{Z_{\text{D}}[\eta, \hat{\eta}]} \left. \frac{\delta^2 Z_{\text{D}}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\hat{\eta}(t')} \right|_{\eta=\hat{\eta}=0} = \frac{\delta^2 Z_{\text{D}}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\hat{\eta}(t')} \Big|_{\eta=\hat{\eta}=0} \end{aligned} \quad (2.41)$$

with  $h(t')$  a small field applied at time  $t'$  that modifies the potential energy according to  $V \rightarrow V - h(t')x(t')$ . The  $i\hat{x}$  auxiliary function is sometimes called the **response field** since it allows one to compute the linear response by taking its correlations with  $x$ . Similarly, we define the two-time correlation between two generic observables  $A$  and  $B$ ,

$$C_{AB}(t, t') \equiv \int \mathcal{D}x \mathcal{D}i\hat{x} dP(t_0) A[x(t)] B[x(t')] e^{S[x, i\hat{x}]} = \langle A[x(t)] B[x(t')] \rangle \quad (2.42)$$

and the linear response of  $A$  at time  $t$  to an infinitesimal perturbation linearly applied to  $B$  at time  $t' < t$ ,

$$R_{AB}(t, t') \equiv \left. \frac{\delta\langle A[x(t)] \rangle_{f_B}}{\delta f_B(t')} \right|_{f_B=0}, \quad (2.43)$$

with  $V(x) \mapsto V(x) - f_B B(x)$ . The function  $B(x)$  depends only on  $x$  (or on an even number of time derivatives, that is to say, it is even with respect to  $t \rightarrow -t$ ). By

plugging eq. (2.39) in this definition we get the **classical Kubo formula** for generic observables:

$$R_{AB}(t, t') = \left\langle A[x(t)] \frac{\delta S[x, i\hat{x}; f_B]}{\delta f_B(t')} \right\rangle_{f_B=0} = \langle A[x(t)] i\hat{x}(t') B'[x(t')] \rangle \quad (2.44)$$

with  $B'[x(t')] = \partial_x B[x(t')]$ . This relation is also causal and hence proportional to  $\theta(t-t')$ ; it is valid in and out of equilibrium. For  $B[x] = x$  it reduces to the correlation between  $x$  and  $i\hat{x}$ .

If the system has **quenched random exchanges** or any kind of **disorder**, one may be interested in calculating the averaged correlations and responses over different realizations of disorder. Surprisingly, this average is very easy to perform in a dynamic calculation [32]. The normalization factors  $1/Z_D[\eta, \hat{\eta}]$  in (2.40) and (2.41) have to be evaluated at zero external sources in which they are trivially independent of the random interactions. Hence, it is sufficient to average  $Z_D[\eta, \hat{\eta}]$  over disorder and then take variations with respect to the sources to derive the thermal and disorder averaged two-point functions. This property contrasts with an equilibrium calculation where the expectation values are given by  $[\langle A \rangle] = [1/Z \sum_{\text{CONF}} A \exp(-\beta H)]$ , with  $[\cdot]$  denoting the disorder average. In this case, the partition function  $Z$  depends explicitly on the random exchanges and one has to introduce **replicas** [7] to deal with the normalization factor and do the averaging.

Having assumed the initial equilibration of the environment ensures that a normal system will eventually equilibrate with it. The interaction with the bath allows the system to dissipate its energy and to relax until thermalization is reached. However, in some interesting cases, as the dynamics across phase transitions and glassy models, the time needed to equilibrate is a fast growing function of  $N$ , the number of dynamic degrees of freedom. Thus, the evolution of the system in the thermodynamic limit occurs out of equilibrium. In real systems, a similar situation occurs when the equilibration time crosses over the observation time and falls out of the experimental time-window.

A final interesting remark on the relevance of quenched disorder is the following. When a system with quenched disorder evolves out of equilibrium at finite temperature, the correlation function and the response function do not depend on the realization of disorder if the size of the system is large enough (the realization of disorder has to be a typical one). These quantities are **self-averaging**. This statement is easily checked in a simulation. When times get sufficiently long as to start seeing the approach to equilibrium, dependencies on the realizations of disorder appear.

#### 2.4.2 The linear response as a variable-noise correlation

The correlation between coordinate and a generic colored noise can be obtained from the variation with respect to  $\lambda(t, t')$  of the generating functional once the source

$$\int dt'' dt''' \lambda(t'', t''') x(t'') \xi(t''') \quad (2.45)$$

has been added. Integrating over the noise and keeping only the linear terms in  $\lambda$  in the effective action since all others will vanish when setting  $\lambda = 0$

$$\begin{aligned} \text{Linear terms} &= \frac{k_B T}{2} \int dt_1 dt_2 dt_3 dt_4 [\lambda(t_1, t_2)x(t_1)\gamma(t_2, t_3)i\hat{x}(t_4)\delta(t_4 - t_3) \\ &\quad + i\hat{x}(t_1)\delta(t_1 - t_2)\gamma(t_2, t_3)\lambda(t_4, t_3)x(t_4)] . \end{aligned} \quad (2.46)$$

The variation with respect to  $\lambda(t, t')$  yields  $(k_B T)/2 \int dt'' [\gamma(t', t'') + \gamma(t'', t')]$   
 $\langle x(t)i\hat{x}(t'') \rangle = \langle x(t)\xi(t') \rangle$ .

### 2.4.3 Time-reversal

Since it will be used in the rest of this chapter, we introduce the time-reversed variable  $\bar{x}$  by  $\bar{x}(t) \equiv x(-t)$  for all  $t$ . The time-reversed observable is defined as

$$A_r([x], t) \equiv A([\bar{x}], -t). \quad (2.47)$$

It has the effect of changing the sign of all odd time-derivatives in the expression of local observables, *e.g.* if  $A[x(t)] = \partial_t x(t)$  then  $A_r[x(t)] = -\partial_t x(-t)$ . As an example for non-local observables, the time-reversed Langevin equation reads

$$\text{EQ}_r([x], t) = m\ddot{x}(t) - F_r([x], t) - \int_{-\mathcal{T}}^{\mathcal{T}} du \gamma(u - t)\dot{x}(u). \quad (2.48)$$

Notice the change of sign in front of the friction term that is no longer dissipative in this new equation.

## 2.5 Quantum formalism

We now consider a quantum system

$$[\hat{p}, \hat{x}] = -i\hbar. \quad (2.49)$$

The density operator evolves according to the equation

$$\frac{\partial \hat{\rho}(t)}{\partial t} = -\frac{i}{\hbar} [\hat{H}(t), \hat{\rho}(t)] \quad (2.50)$$

that is solved by

$$\hat{\rho}(t) = \hat{U}(t, t_0)\hat{\rho}(t_0)[\hat{U}(t, t_0)]^\dagger = \hat{U}(t, t_0)\hat{\rho}(t_0)\hat{U}(t_0, t) \quad (2.51)$$

with

$$\hat{U}(t, t_0) = T e^{-\frac{i}{\hbar} \int_{t_0}^t dt' \hat{H}(t')} \quad t > t_0. \quad (2.52)$$

Averaged observables read

$$\begin{aligned} \langle \hat{A}(t) \rangle &= \frac{\text{Tr} \left\{ \hat{A} \hat{\rho}(t) \right\}}{\text{Tr} \hat{\rho}(t)} = \frac{\text{Tr} \left\{ \hat{A} T e^{-\frac{i}{\hbar} \hat{H} t} \hat{\rho}_0 [T e^{-\frac{i}{\hbar} \hat{H} t}]^\dagger \right\}}{\text{Tr} \left\{ T e^{-\frac{i}{\hbar} \hat{H} t} \hat{\rho}_0 [T e^{-\frac{i}{\hbar} \hat{H} t}]^\dagger \right\}} \\ &= \frac{\text{Tr} \left\{ T [e^{-\frac{i}{\hbar} \hat{H} t}]^\dagger \hat{A} T e^{-\frac{i}{\hbar} \hat{H} t} \hat{\rho}_0 \right\}}{\text{Tr} \hat{\rho}_0}. \end{aligned} \quad (2.53)$$

(To ease the notation we do not write the possible time-dependence in the Hamiltonian and the integral over  $t$  in the exponential.) We then use the Heisenberg operators

$$\hat{A}_H(t) \equiv [T e^{-\frac{i}{\hbar} \hat{H} t}]^\dagger \hat{A} T e^{-\frac{i}{\hbar} \hat{H} t} \quad (2.54)$$

The underscript  $H$  recalls that these are operators in the Heisenberg representation but we shall drop it in the following.

### 2.5.1 Feynman path integral for quantum time-ordered averages

Feynman's path-integral represents the (forward) propagator  $\mathcal{K}(x, t; x', t') = \langle x | e^{-iH(t-t')/\hbar} | x' \rangle$  as a sum over all paths leading from, in the Lagrangian representation,  $x' = x(t')$  to  $x = x(t)$  **with  $t > t'$**  weighted with the exponential of the action (times  $i/\hbar$ ):

$$\mathcal{K}(x, t; x', t') = \int_{x(t')=x'}^{x(t)=x} \mathcal{D}x e^{\frac{i}{\hbar} S[x, \dot{x}]} \quad (2.55)$$

$$S[x, \dot{x}] = \int_{t'}^t dt'' \left\{ \frac{m}{2} \dot{x}^2(t'') - V[x(t'')] \right\}. \quad (2.56)$$

The formalism is well-suited to compute any type of **time-ordered correlation** since the evolution is done towards the future. A concise review article on the construction of path-integrals with some applications is [27]; several books on the subject are [28].

### 2.5.2 The Matsubara imaginary-time formalism

The statistical properties of a canonical quantum system and, in particular, its equilibrium partition function, can also be obtained with the path-integral method,

$$Z = \text{Tr} e^{-\beta H} = \text{Tr} e^{-iH(t=-i\beta\hbar)/\hbar} = \int dx \mathcal{K}(x, -i\beta\hbar; x, 0). \quad (2.57)$$

Having used an imaginary-time  $t = -i\beta\hbar$  corresponds to a **Wick-rotation**. The propagator  $\mathcal{K}$  is now represented as a path-integral with periodic boundary conditions to ensure the fact that one sums over the same initial and finite state. Introducing  $\tau = it$ ,  $\tau : 0 \rightarrow \beta\hbar$  (since  $t : 0 \rightarrow -i\beta\hbar$ ), defining functions of  $\tau$ ,  $\tilde{x}(\tau) = x(t = -i\tau)$

and dropping the tilde one has

$$\mathcal{K}(x, -i\beta\hbar; x, 0) = \int_{x(0)=x(\beta\hbar)} \mathcal{D}x e^{-\frac{1}{\hbar}S^E[x, \dot{x}]} \quad (2.58)$$

with the **Euclidean action**

$$S^E[x, \dot{x}] = \int_0^{\beta\hbar} d\tau \left[ \frac{m}{2} \dot{x}^2(\tau) + V[x(\tau)] \right]. \quad (2.59)$$

### 2.5.3 The equilibrium reduced density matrix

We now follow the same route as in the derivation of the classical Langevin equation by coupling the system to an ensemble of quantum harmonic oscillators,

$$[\hat{\pi}_a, \hat{q}_b] = -i\hbar\delta_{ab}. \quad (2.60)$$

The equilibrium density matrix reads

$$\rho_{\text{TOT}}(x'', q''_a; x', q'_a) = \frac{1}{Z_{\text{TOT}}} \langle x'', q''_a | e^{-\beta\hat{H}_{\text{TOT}}} | x', q'_a \rangle, \quad (2.61)$$

with the partition function given by  $Z_{\text{TOT}} = \text{Tr} e^{-\beta\hat{H}_{\text{TOT}}}$  and the trace taken over all the states of the full system. As usual the density matrix can be represented by a functional integral in imaginary time,

$$\rho_{\text{TOT}}(x'', q''_a; x', q'_a; \eta) = \frac{1}{Z_{\text{TOT}}} \int_{x(0)=x'}^{x(\hbar\beta)=x''} \mathcal{D}x \int_{q_a(0)=q'_a}^{q_a(\hbar\beta)=q''_a} \mathcal{D}q_a e^{-\frac{1}{\hbar}S_{\text{TOT}}^E[\eta]}. \quad (2.62)$$

The Euclidean action  $S^E$  has contributions from the system, the reservoir, the interaction and the counterterm:  $S_{\text{TOT}}^E[\eta] = S_{\text{SYST}}^E + S_{\text{ENV}}^E + S_{\text{INT}}^E + S_{\text{COUNTER}}^E + \int_0^{\beta\hbar} d\tau \eta(\tau)x(\tau)$  and we have included a source  $\eta$  coupled to the particle's coordinate in order to use it to compute expectation values of the kind defined in (2.53). The environment action is

$$S_{\text{ENV}}^E = \sum_{\alpha=1}^N \int_0^{\beta\hbar} d\tau \left\{ \frac{m_\alpha}{2} [\dot{q}_\alpha(\tau)]^2 + \frac{m_\alpha\omega_\alpha^2}{2} [q_\alpha(\tau)]^2 \right\}, \quad (2.63)$$

that is to say, we choose an ensemble of independent oscillators. For simplicity we take a linear coupling

$$S_{\text{INT}}^E = \int_0^{\hbar\beta} d\tau x(\tau) \sum_{a=1}^N c_a q_a(\tau) \quad (2.64)$$

but others, as used in the derivation of the Langevin equation, are also possible. As in the classical case, the path integral over the oscillators' coordinates and positions is quadratic. The calculation of expectation values involves a trace over states of the full system. For operators that depend only on the particle, as  $A(\hat{x})$  above, the

trace over the oscillators can be done explicitly. Hence, if one constructs the **reduced equilibrium density operator**  $\hat{\rho}_{\text{RED}} = \text{Tr}_{\text{ENV}} \hat{\rho}_{\text{TOT}}$  that acts on the system's Hilbert space, the expectation value of the observables of the system is given by

$$\langle A(x) \rangle = \frac{\text{Tr}_{\text{SYST}} A(\hat{x}) \hat{\rho}_{\text{RED}}}{\text{Tr} \hat{\rho}_{\text{TOT}}}. \quad (2.65)$$

In the path-integral formalism this amounts to performing the functional integral over periodic functions  $q_\alpha(\tau)$ . From the point of view of the oscillators the system's coordinate is an external  $\tau$ -dependent force. Using a Fourier representation,  $q_\alpha(\tau) = \sum_{n=-\infty}^{\infty} q_\alpha^n e^{i\nu_n \tau}$  with  $\nu_n = \frac{2\pi n}{\beta\hbar}$  the **Matsubara frequencies**, the integration over the  $q_\alpha(\tau)$  can be readily done. A long series of steps, very carefully explained in [26] allow one to obtain the reduced density matrix:

$$\begin{aligned} \rho_{\text{RED}}(x'', x'; \eta) &= \text{Tr}_{\text{ENV}} \rho_{\text{TOT}}(x'', q''_a; x', q'_a; \eta) \\ &= \frac{1}{Z_{\text{RED}}} \int_{x(0)=x'}^{x(\hbar\beta)=x''} \mathcal{D}x \, e^{-\frac{1}{\hbar} S_{\text{SYST}}^E - \frac{1}{\hbar} \int_0^{\hbar\beta} d\tau \int_0^\tau d\tau' x(\tau) K(\tau-\tau') x(\tau')} \end{aligned} \quad (2.66)$$

where  $Z_{\text{RED}}$  is the partition function of the reduced system,  $Z_{\text{RED}} = Z_{\text{TOT}}/Z_{\text{ENV}}$  and  $Z_{\text{ENV}}$  the partition function of the isolated ensemble of oscillators. The interaction with the reservoir generated a renormalization of the mass – cancelled by the counterterm – but also a retarded interaction in the effective action controlled by the kernel

$$K(\tau) = \frac{2}{\pi\hbar\beta} \sum_{n=-\infty}^{\infty} \int_0^\infty d\omega \frac{S(\omega)}{\omega} \frac{\nu_n^2}{\nu_n^2 + \omega^2} e^{i\nu_n \tau}, \quad (2.67)$$

with  $S(\omega)$  the spectral density of the bath, see eq. (2.23) for its definition. The last retarded interaction in (2.66) remains. The imaginary time dependence of  $K$  varies according to  $S(\omega)$ . Power laws in  $S$  lead to power-law decays in  $K$  and thus to a long-range interaction in the imaginary-time direction.

The effect of the quantum bath is more cumbersome than in the classical case and it can lead to rather spectacular effects. A well-known example is the localization transition, as function of the coupling strength to an Ohmic bath in the behaviour of a quantum particle in a double well potential [29]. This means that quantum tunneling from the well in which the particle is initially located to the other one is completely suppressed by sufficiently strong couplings to the bath. In the context of interacting macroscopic systems, *e.g.* ferromagnets or spin-glasses, the locus of the transition between the ordered and the disordered phase depends strongly on the coupling to the bath and on the type of bath considered [29], as discussed in Section ??.

## 2.6 Quantum dynamics: generating functional

We shall see that the distinction between the effect of a reservoir on the statistical properties of a classical and quantum system is absent from a fully dynamic treatment.

In both classical and quantum problems, the coupling to an environment leads to a *retarded* interaction. In classical problems one generally argues that the retarded interaction can be simply replaced by a local one due to the very short correlation times involved in cases of interest, *i.e.* one uses white baths, but in the quantum problems one cannot do the same.

### 2.6.1 Schwinger-Keldysh path integral

The Schwinger-Keldysh formalism [33, 34] allows one to analyse the real-time dynamics of a quantum system. The starting point is the time dependent density operator

$$\hat{\rho}(t) = T e^{-\frac{i}{\hbar}\hat{H}t} \hat{\rho}(0) \bar{T} e^{\frac{i}{\hbar}\hat{H}t}. \quad (2.68)$$

We have set the initial time to be  $t_o = 0$ . Introducing identities, an element of the time-dependent density matrix reads

$$\begin{aligned} \rho(x'', x'; t) = & \int_{-\infty}^{\infty} dX dX' \langle x'' | T e^{-\frac{i}{\hbar}\hat{H}t} | X \rangle \langle X | \hat{\rho}(0) | X' \rangle \\ & \times \langle X' | \bar{T} e^{\frac{i}{\hbar}\hat{H}t} | x' \rangle. \end{aligned} \quad (2.69)$$

The first and third factors are the coordinate representation of the evolution operators  $e^{-i\hat{H}t/\hbar}$  and  $e^{i\hat{H}t/\hbar}$ , respectively, and they can be represented as functional integrals:

$$\langle x'' | T e^{-\frac{i}{\hbar}\hat{H}t} | X \rangle = \int_X^{x''} \mathcal{D}x^+ e^{\frac{i}{\hbar}S^+} \quad (2.70)$$

$$\langle X' | \bar{T} e^{\frac{i}{\hbar}\hat{H}t} | x' \rangle = \int_{x'}^{X'} \mathcal{D}x^- e^{-\frac{i}{\hbar}S^-}. \quad (2.71)$$

Interestingly enough, the evolution operator in eq. (2.71) gives rise to a path integral going backwards in time, from  $x^-(t) = x'$  to  $x^-(0) = X'$ . The full time-integration can then be interpreted as being closed, going forwards from  $t_0 = 0$  to  $t$  and then backwards from  $t$  to  $t_0 = 0$ . This motivates the name **closed time-path formalism**. A doubling of degrees of freedom ( $x^+, x^-$ ) appeared and it is intimately linked to the introduction of Lagrange multipliers in the functional representation of the Langevin dynamics in the classical limit, see Sect. 2.4. The action of the system has two terms as in (2.56) one evaluated in  $x^+$  and the other in  $x^-$ .

$$S_{\text{SVST}}^{\pm}[\eta^{\pm}] = \pm \int_0^t dt' \left[ \frac{m}{2} (\dot{x}^{\pm}(t'))^2 - V(x^{\pm}(t')) + \eta^{\pm}(t') x^{\pm}(t') \right] \quad (2.72)$$

where we have introduced two time-dependent sources  $\eta^{\pm}(t)$ , that appear in the exponential with the sign indicated.

### 2.6.2 Green functions

We define the **position and fermionic** Green functions

$$G_{ab}^B(t, t') \equiv -i \langle T_C x_a(t) x_b(t') \rangle \quad (2.73)$$

$$G_{ab}^F(t, t') \equiv -i \langle T_C \psi_a(t) \psi_b^\dagger(t') \rangle \quad (2.74)$$

where  $a, b = \pm$  and  $T_C$  is time ordering on the close contour (see App. ).

The definitions (2.73) and (2.74) and the fact that the insertion evaluated at the later time can be put on the upper (+) or lower (-) branch with no distinction yield the following relations between different Green functions

$$G_{++}(t, t') = G_{-+}(t, t')\theta(t - t') + G_{+-}(t, t')\theta(t' - t), \quad (2.75)$$

$$G_{--}(t, t') = G_{+-}(t, t')\theta(t - t') + G_{-+}(t, t')\theta(t' - t), \quad (2.76)$$

that hold for the bosonic and fermionic cases as well. We thus erase the superscripts  $B, F$  that become superfluous. Adding the last two identities one finds

$$G_{++} + G_{--} - G_{+-} - G_{-+} = 0 \quad \text{for all } t \text{ and } t'. \quad (2.77)$$

In both cases one defines **MSRDJ-like fields**. For bosons these are

$$\sqrt{2} x(t) = x_+(t) + x_-(t), \quad \sqrt{2\hbar} \hat{x}(t) = x_+(t) - x_-(t), \quad (2.78)$$

while for fermions they are

$$\begin{aligned} \sqrt{2} \psi(t) &\equiv \psi^+(t) + \psi^-(t) & \sqrt{2\hbar} \hat{\psi}(t) &\equiv \psi^+(t) - \psi^-(t) \\ \sqrt{2} \psi^\dagger(t) &\equiv \psi^{+\dagger}(t) + \psi^{-\dagger}(t) & \sqrt{2\hbar} \hat{\psi}^\dagger(t) &\equiv \psi^{+\dagger}(t) - \psi^{-\dagger}(t). \end{aligned}$$

One then constructs the Green functions

$$\begin{aligned} G_{xx}^B(t, t') &\equiv -i \langle T_C x(t) x(t') \rangle = \frac{1}{2} (G_{++}^B + G_{--}^B + G_{-+}^B + G_{+-}^B) \\ &\equiv -2i G_K^B(t, t') \\ G_{x\hat{x}}^B(t, t') &\equiv -i \langle T_C x(t) \hat{x}(t') \rangle = \frac{1}{2\hbar} (G_{++}^B - G_{--}^B + G_{-+}^B - G_{+-}^B) \\ &\equiv -G_R^B(t, t') \\ G_{\hat{x}x}^B(t, t') &\equiv -i \langle T_C \hat{x}(t) x(t') \rangle = \frac{1}{2\hbar} (G_{++}^B - G_{--}^B - G_{-+}^B + G_{+-}^B) \\ &\equiv -G_A^B(t, t') \\ G_{\hat{x}\hat{x}}^B(t, t') &\equiv -i \langle T_C \hat{x}(t) \hat{x}(t') \rangle = \frac{1}{2\hbar^2} (G_{++}^B + G_{--}^B - G_{-+}^B - G_{+-}^B) \\ &\equiv -G_4^B(t, t') = 0, \end{aligned} \quad (2.79)$$

and the fermionic ones

$$\begin{aligned}
G_{\psi\psi}^F(t, t') &\equiv -i\langle T_C \psi(t)\psi^\dagger(t') \rangle = \frac{1}{2} (G_{++}^F + G_{--}^F + G_{-+}^F + G_{+-}^F) \\
&\equiv -2iG_K^F(t, t') , \\
G_{\psi\hat{\psi}}^F(t, t') &\equiv -i\langle T_C \psi(t)\hat{\psi}^\dagger(t') \rangle = \frac{1}{2\hbar} (G_{++}^F - G_{--}^F + G_{-+}^F - G_{+-}^F) \\
&\equiv -G_R^F(t, t') , \\
G_{\hat{\psi}\psi}(t, t') &\equiv -i\langle T_C \hat{\psi}(t)\psi^\dagger(t') \rangle = \frac{1}{2\hbar} (G_{++}^F - G_{--}^F - G_{-+}^F + G_{+-}^F) \\
&\equiv -G_A^F(t, t') , \\
G_{\hat{\psi}\hat{\psi}}^F(t, t') &\equiv -i\langle T_C \hat{\psi}(t)\hat{\psi}^\dagger(t') \rangle = \frac{1}{2\hbar^2} (G_{++}^F + G_{--}^F - G_{-+}^F - G_{+-}^F) \\
&\equiv -G_4^F(t, t') = 0 , 
\end{aligned} \tag{2.80}$$

From the definition of  $G_K^B$  it is obvious that

$$G_K^B(t, t') = G_K^B(t', t) \in \text{Re} . \tag{2.81}$$

Using eq. (2.77) the ‘rotated’ Green functions are rewritten as

$$G_K = \frac{i}{2}(G_{++} + G_{--}) = \frac{i}{2}(G_{+-} + G_{-+}) , \tag{2.82}$$

$$G_R = -\frac{1}{\hbar}(G_{++} - G_{+-}) = \frac{1}{\hbar}(G_{--} - G_{-+}) , \tag{2.83}$$

$$G_A = -\frac{1}{\hbar}(G_{++} - G_{-+}) = \frac{1}{\hbar}(G_{--} - G_{+-}) . \tag{2.84}$$

Using eqs. (2.75)-(2.76) one also finds

$$G_R(t, t') = -\frac{1}{\hbar}[G_{+-}(t, t') - G_{-+}(t, t')] \theta(t - t') , \tag{2.85}$$

$$G_A(t, t') = \frac{1}{\hbar}[G_{+-}(t, t') - G_{-+}(t, t')] \theta(t' - t) . \tag{2.86}$$

which show explicitly the **retarded** and **advanced** character of  $G_R$  and  $G_A$ , respectively. Moreover,

$$G_R^B(t, t') = G_A^B(t't) \in \text{Re} , \tag{2.87}$$

$$G_R^F(t, t') = [G_A^F(t', t)]^* , \tag{2.88}$$

$$G_K^F(t, t') = [G_K^F(t', t)]^* . . \tag{2.89}$$

Inverting the above relations one has

$$\begin{aligned}
iG_{++} &= G_K - i\hbar(G_R + G_A)/2 , & iG_{+-} &= G_K + i\hbar(G_R - G_A)/2 , \\
iG_{-+} &= G_K - i\hbar(G_R - G_A)/2 , & iG_{--} &= G_K + i\hbar(G_R + G_A)/2 .
\end{aligned} \tag{2.90}$$

Going back to an operational formalism

$$G_R^B(t, t') \equiv \frac{2i}{\hbar} \theta(t - t') \langle [\hat{x}(t), \hat{x}(t')] \rangle , \quad (2.91)$$

$$G_K^B(t, t') \equiv \langle \{\hat{x}(t), \hat{x}(t')\} \rangle , \quad (2.92)$$

for bosons (see App. ), where one recognizes the **Kubo formulæ** in the first two lines, and

$$G_R^F(t, t') \equiv \frac{2i}{\hbar} \theta(t - t') \langle \{\hat{\psi}(t), \hat{\psi}^\dagger(t')\} \rangle , \quad (2.93)$$

$$G_K^F(t, t') \equiv \langle [\hat{\psi}(t), \hat{\psi}^\dagger(t')] \rangle , \quad (2.94)$$

for fermions.

### 2.6.3 Generic correlations

A generic two time correlation that depends only on the system is given by

$$\langle \hat{A}(t) \hat{B}(t') \rangle = Z_{\text{RED}}^{-1}(0) \text{Tr} \hat{A}(t) \hat{B}(t') \hat{\rho}_{\text{RED}}(0) . \quad (2.95)$$

Clearly  $\langle \hat{A}(t) \hat{B}(t') \rangle \neq \langle \hat{B}(t') \hat{A}(t) \rangle$  and one can define symmetrized and anti-symmetrized correlations:

$$C_{\{A,B\}}(t, t') = \langle \hat{A}(t) \hat{B}(t') + \hat{B}(t') \hat{A}(t) \rangle / 2 , \quad (2.96)$$

$$C_{[A,B]}(t, t') = \langle \hat{A}(t) \hat{B}(t') - \hat{B}(t') \hat{A}(t) \rangle / 2 , \quad (2.97)$$

respectively.

Within the Keldysh path-integral representation these correlations can be written as

$$\begin{aligned} C_{\{A,B\}}(t, t') &= \langle A[x^+](t) \{B[x^+](t') + B[x^-](t')\} \rangle / 2 , \\ C_{[A,B]}(t, t') &= \langle A[x^+](t) \{B[x^+](t') - B[x^-](t')\} \rangle / 2 , \end{aligned} \quad (2.98)$$

### 2.6.4 Linear response and Kubo relation

The linear response is defined as the variation of the averaged observable  $A$  at time  $t$  due to a change in the Hamiltonian operated at time  $t'$  in such a way that  $\hat{H} \rightarrow \hat{H} - f_B \hat{B}$ . In linear-response theory, it can be expressed in terms of the averaged commutator:

$$R_{AB}(t, t') \equiv \left. \frac{\delta \langle \hat{A}(t) \rangle}{\delta f_B(t')} \right|_{f_B=0} = \frac{2i}{\hbar} \theta(t - t') \langle [\hat{A}(t), \hat{B}(t')] \rangle . \quad (2.99)$$

In the case  $\hat{A} = \hat{x}$  and  $\hat{B} = \hat{x}$  this implies  $R_{xx}(t, t') = G_R^B(t, t')$ . The path-integral representation is in terms of the Keldysh fields  $x^+$ ,  $x^-$ :

$$R_{AB}(t, t') = i \langle A[x^+](t) \{ B[x^+](t') - B[x^-](t') \} \rangle / \hbar . \quad (2.100)$$

### 2.6.5 The influence functional

As in the derivation of the Langevin equation we model the environment as an ensemble of many non-interaction variables that couple to the relevant system's degrees of freedom in some convenient linear way. The choice of the environment variables depends on the type of bath one intends to consider. Phonons are typically modeled by independent quantum harmonic oscillators that can be dealt with exactly. We then consider a system  $(\hat{x}, \hat{p})$  coupled to an environment made of independent harmonic oscillators  $(\hat{q}_a, \hat{\pi}_a)$ . An element of the total density function reads

$$\begin{aligned} \rho(x'', q''; x', q'_a; t) = & \int_{-\infty}^{\infty} dX dX' dQ_a dQ'_a \langle x'', q'' | T e^{-\frac{i}{\hbar} \hat{H}_{\text{TOT}} t} | X, Q_a \rangle \langle X, Q_a | \hat{\rho}_{\text{TOT}}(0) | X', Q'_a \rangle \\ & \times \langle X', Q'_a | \bar{T} e^{\frac{i}{\hbar} \hat{H}_{\text{TOT}} t} | x', q'_a \rangle . \end{aligned} \quad (2.101)$$

The first and third factors are the coordinate representation of the evolution operators  $e^{-i\hat{H}_{\text{TOT}}t/\hbar}$  and  $e^{i\hat{H}_{\text{TOT}}t/\hbar}$ , respectively, and they can be represented as functional integrals:

$$\langle x'', q'' | T e^{-\frac{i}{\hbar} \hat{H}_{\text{TOT}} t} | X, Q_a \rangle = \int_X^{x''} \mathcal{D}x^+ \int_{Q_a}^{q''} \mathcal{D}q_a^+ e^{\frac{i}{\hbar} S_{\text{TOT}}^+} \quad (2.102)$$

$$\langle X', Q'_a | \bar{T} e^{\frac{i}{\hbar} \hat{H}_{\text{TOT}} t} | x', q'_a \rangle = \int_{x'}^{X'} \mathcal{D}x^- \int_{q'_a}^{Q'_a} \mathcal{D}q_a^- e^{-\frac{i}{\hbar} S_{\text{TOT}}^-} . \quad (2.103)$$

The action  $S_{\text{TOT}}$  has the usual four contributions, from the system, the reservoir, the interaction and the counterterm.

As usual we are interested in the dynamics of the system under the effect of the reservoir. Hence, we compute the reduced density matrix

$$\rho_{\text{RED}}(x'', x'; t) = \int_{-\infty}^{\infty} dq_a \langle x'', q_a | \hat{\rho}_{\text{TOT}}(t) | x', q_a \rangle . \quad (2.104)$$

### 2.6.6 Initial conditions

#### *Factorization*

The initial density operator  $\hat{\rho}_{\text{TOT}}(0)$  has the information about the initial state of the whole system. If one assumes that the system and the bath are set in contact at the initial time, the operator **factorizes**

$$\hat{\rho}(0) = \hat{\rho}_{\text{SYST}}(0) \hat{\rho}_{\text{ENV}}(0) . \quad (2.105)$$

(Other initial preparations, where the factorization does not hold, can also be considered and may be more realistic in certain cases [26] and see below.) If the environment is initially in equilibrium at an inverse temperature  $\beta$ ,

$$\hat{\rho}_{\text{ENV}}(0) = Z_{\text{ENV}}^{-1} e^{-\beta \hat{H}_{\text{ENV}}}, \quad (2.106)$$

the dependence on the bath variables is quadratic; they can be traced away to yield the reduced density matrix:

$$\begin{aligned} \rho_{\text{RED}}(x'', x'; t) &= \int_{-\infty}^{\infty} dX \int_{-\infty}^{\infty} dX' \int_{x^+(0)=X}^{x^+(t)=x''} \mathcal{D}x^+ \int_{x^-(0)=X'}^{x^-(t)=x'} \mathcal{D}x^- \\ &\quad \times e^{\frac{i}{\hbar} S_{\text{EFF}}} \langle X | \hat{\rho}_{\text{SYST}}(0) | X' \rangle \end{aligned} \quad (2.107)$$

with the effective action  $S_{\text{EFF}} = S_{\text{SYST}}^+ - S_{\text{SYST}}^- + S_{\text{ENV EFF}}$ . The last term has been generated by the interaction with the environment and it reads

$$\begin{aligned} \frac{i}{\hbar} S_{\text{ENV}} &= -i \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' \frac{[x^+(t') - x^-(t')]}{\hbar} \eta(t' - t'') \frac{[x^+(t'') + x^-(t'')]}{2} \\ &\quad - \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' \frac{[x^+(t') - x^-(t')]}{\hbar} \frac{\hbar}{4} \tilde{\Gamma}(t' - t'') \frac{[x^+(t'') - x^-(t'')]}{\hbar}. \end{aligned} \quad (2.108)$$

The noise and dissipative kernels  $\tilde{\Gamma}$  and  $\eta$  are given by

$$\tilde{\Gamma}(t) = \int_0^{\infty} d\omega S(\omega) \coth\left(\frac{1}{2}\beta\hbar\omega\right) \cos(\omega t), \quad (2.109)$$

$$\eta(t) = \theta(t) \frac{d\tilde{\Gamma}(t)}{dt} = -\theta(t) \int_0^{\infty} d\omega S(\omega) \sin(\omega t). \quad (2.110)$$

One can easily check that  $\tilde{\Gamma}(t) = \tilde{\Gamma}(-t)$  and  $\eta(t)$  is causal; moreover they verify the bosonic FDT, as they should since the bath was assumed to be in equilibrium.  $\eta$  is like a response and  $\tilde{\Gamma}$  is a correlation. One can also write the bath-generated action in the form

$$S_{\text{K,eff}} \equiv - \sum_{a,b=\pm} \frac{1}{2} \int \int dt dt' x^a(t) \Sigma_{ab}(t, t') x^b(t'), \quad (2.111)$$

with

$$4\Sigma_{++} = 2\eta - i\tilde{\Gamma} \quad 4\Sigma_{+-} = 2\eta + i\tilde{\Gamma}, \quad (2.112)$$

$$4\Sigma_{-+} = -2\eta + i\tilde{\Gamma} \quad 4\Sigma_{--} = -2\eta - i\tilde{\Gamma} \quad (2.113)$$

and  $\Sigma_{++} + \Sigma_{--} + \Sigma_{+-} + \Sigma_{-+} = 0$ . Although these relations resemble the ones satisfied by the  $G_{ab}$ s a more careful analysis shows that the matrix  $\Sigma$  is more like  $G^{-1}$  than  $G$  (see the discussion on the classical dynamics of the random manifold and the dependence on  $k$ ; the relation between  $G$  and  $\Sigma$  is the same here).

In these equations, as in the classical case,  $S(\omega)$  is the spectral density of the bath:

$$S(\omega) = \frac{\pi}{2} \sum_{a=1}^{N_b} \frac{c_a^2}{m_a \omega_a} \delta(\omega - \omega_a), \quad (2.114)$$

that can also be taken of the form in (2.23),

$$S(\omega) = 2\gamma_0 \tilde{\omega} \left( \frac{\omega}{\tilde{\omega}} \right)^\alpha e^{-\omega/\Lambda}. \quad (2.115)$$

As usual, a counter-term cancels the mass renormalization. The  $\eta$  and  $\Gamma$  kernels are independent of  $T$  and  $\hbar$  and are thus identical to the classical ones, see eq. (2.24). The kernel  $\tilde{\Gamma}$  does depend on  $T$  and  $\hbar$ . After a change of variables in the integral, in the cases in which  $S(\omega) \propto \omega^\alpha$ ,

$$\tilde{\Gamma}(t) = t^{-(1+\alpha)} g \left( \frac{\beta \hbar}{t}, \Lambda t \right) \quad (2.116)$$

and

$$\lim_{\beta \hbar/t \rightarrow 0} \beta \hbar \tilde{\Gamma}(t) = 2\Gamma(t). \quad (2.117)$$

The **classical limit** is realized at **high temperature** and/or **long times**.

Figure 19-left shows the time-dependence of the kernels  $\tilde{\Gamma}$  in the quantum Ohmic case for different values of  $T$ . In the right panel of the same figure we show the dependence on  $\alpha$  of the kernel  $\tilde{\Gamma}$ .

*Upper critical initial conditions for the system*

Next, we have to choose an initial density matrix for the system. One natural choice, having in mind the quenching experiments usually performed in classical system, is the **diagonal density matrix**

$$\langle X | \hat{\rho}_{\text{SYST}}(0) | X' \rangle = \delta(X - X') \quad (2.118)$$

that corresponds to a random ‘high-temperature’ situation and that simplifies considerably the expression in (2.107). As in the classical stochastic problem,  $\text{Tr} \hat{\rho}_{\text{RED}}(0) = 1$  and it is trivially independent of disorder. Hence, there is no need to introduce replicas in such a quantum dynamic calculation.

*Equilibrium initial conditions for the system*

One might also be interested in using equilibrium initial conditions for the isolated system

$$\langle X | \hat{\rho}_{\text{SYST}}(0) | X' \rangle = Z_{\text{SYS}}^{-1} \langle X | e^{-\beta H_{\text{SYST}}} | X' \rangle. \quad (2.119)$$

This factor introduces interesting real-time – imaginary-time correlations.

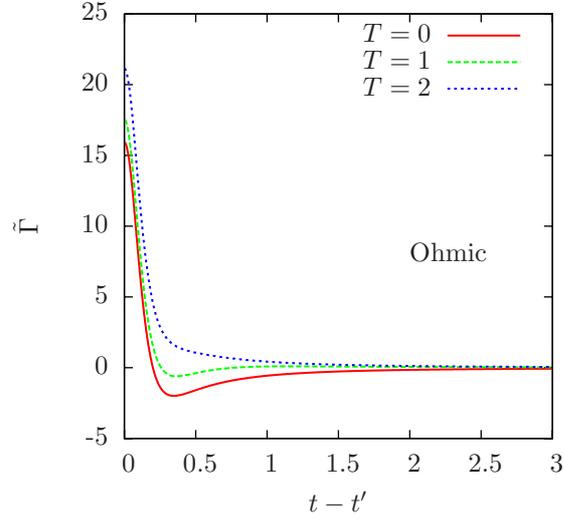


Figure 18: The kernel  $\tilde{\Gamma}$  in the Ohmic  $\alpha = 1$  case for different values of  $T$  ( $\Lambda = 5$ ).

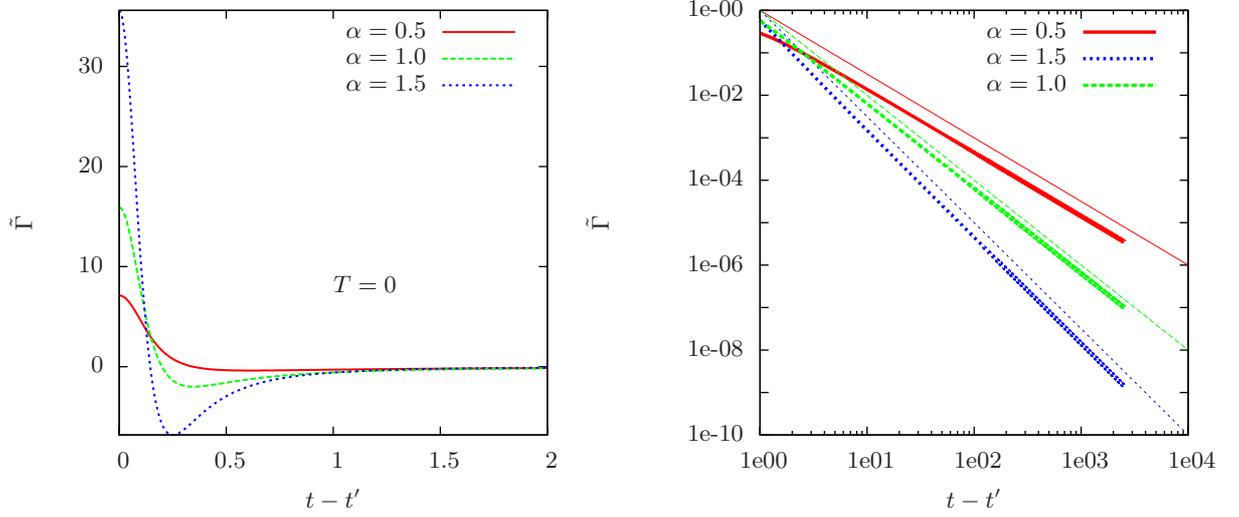


Figure 19: The kernel  $\tilde{\Gamma}$  at  $T = 0$  for different values of  $\alpha$  ( $\hbar = 1 = \gamma_0 = \tilde{\omega} = 1$  and  $\Lambda = 5$ ) in linear (left) and logarithmic (right) scales.

### 2.6.7 Transformation to ‘MSR-like fields’

*Newton dynamics*

We use  $x_{\pm} = x \pm (\hbar/2) \hat{x}$ . We first study the kinetic terms:

$$\frac{i}{\hbar} \int dt \frac{m}{2} (\dot{x}_+^2 - \dot{x}_-^2) = \frac{i}{\hbar} \int dt \frac{m}{2} \left[ \left( \dot{x} + \frac{\hbar}{2} \dot{\hat{x}} \right)^2 - \left( \dot{x} - \frac{\hbar}{2} \dot{\hat{x}} \right)^2 \right] \quad (2.120)$$

expanding the squares the integrand equals  $-2\hbar \dot{\hat{x}} \dot{x}$  and integrating by parts

$$- \int dt i \hat{x} m \ddot{x} . \quad (2.121)$$

*The potential term*

The potential term is treated similarly

$$-\frac{i}{\hbar} [V(x_+) - V(x_-)] = -\frac{i}{\hbar} \left[ V \left( x + \frac{\hbar}{2} \hat{x} \right) - V \left( x - \frac{\hbar}{2} \hat{x} \right) \right] \quad (2.122)$$

Note that this expression is specially simple for quadratic and quartic potentials:

$$= \begin{cases} -xi\hat{x} & \text{quadratic} & V(y) = y^2 \\ -4xi\hat{x} \left[ x^2 - \phi_0^2 + \left(\frac{\hbar}{2}\right)^2 (i\hat{x})^2 \right] & \text{quartic} & V(y) = (y^2 - y_0^2)^2 \end{cases}$$

*The noise terms*

We introduce the variables  $x$  and  $i\hat{x}$  in the action terms generated by the coupling to the environment and the classical limit of the kernel  $\tilde{\Gamma}$ :

$$\begin{aligned} \frac{i}{\hbar} S_{\text{ENV}} &= - \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' i\hat{x}(t') \theta(t' - t'') \frac{d\Gamma(t' - t'')}{dt'} x(t'') \\ &\quad + \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' i\hat{x}(t') \frac{\hbar}{4} \tilde{\Gamma}(t' - t'') i\hat{x}(t'') \\ &= \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' i\hat{x}(t') \gamma(t' - t'') \dot{x}(t'') \\ &\quad + \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' i\hat{x}(t') \frac{\hbar}{4} \tilde{\Gamma}(t' - t'') i\hat{x}(t'') . \end{aligned} \quad (2.123)$$

(Apart from a border term that can be treated more carefully and check that it disappears.)

### 2.6.8 Classical limit

In the classical limit,  $\hbar \rightarrow 0$ , the Schwinger-Keldysh effective action reduces to the one in the functional representation of a Newton classical mechanics (no bath) or a Langevin process with coloured noise (bath). The kinetic term eq. (2.121) is already in the expected form with no need to take  $\hbar \rightarrow 0$ . The potential term

$$-\frac{i}{\hbar} [V(x_+) - V(x_-)] = -V'(x)i\hat{x} + O(\hbar^2) \simeq -V'(x)i\hat{x} \quad (2.124)$$

up to first order in  $\hbar$ . In the noise terms we just have to take the classical limit of the kernel  $\tilde{\Gamma}$ :

$$\begin{aligned} \frac{i}{\hbar} S_{\text{ENV}} &\simeq \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' i\hat{x}(t') \gamma(t' - t'') \dot{x}(t'') \\ &\quad + \frac{k_B T}{2} \int_0^{\mathcal{T}} dt' \int_0^{\mathcal{T}} dt'' i\hat{x}(t') \Gamma(t' - t'') i\hat{x}(t'') \end{aligned} \quad (2.125)$$

with  $O(\hbar)$  corrections (apart from a border term that can be treated more carefully and check that it disappears.)

### 3 Classical dissipative coarsening

Take a piece of material in contact with an external reservoir. The material will be characterized by certain observables, energy density, magnetization density, *etc.* The external environment will be characterized by some parameters, like the temperature, magnetic field, pressure, *etc.* In principle, one is able to tune the latter and study the variation of the former. Note that we are using a **canonical setting** in the sense that the system under study is not isolated but open.

Sharp changes in the behavior of macroscopic systems at critical points (or lines) in parameter space have been observed experimentally. These correspond to **equilibrium phase transitions**, a non-trivial collective phenomenon appearing in the thermodynamic limit. We shall assume that the main features of, and analytic approaches used to study, phase transitions are known.

Imagine now that one changes an external parameter instantaneously or with a finite rate going from one phase to another in the (equilibrium) phase diagram. The kind of internal system interactions are not changed. In the statistical physics language the first kind of procedure is called a **quench** and the second one an **annealing** and these terms belong to the metalurgy terminology. We shall investigate how the system evolves by trying to accomodate to the new conditions and equilibrate with its environment. We shall first focus on the dynamics at the critical point or going through phase transitions between well-known phases (in the sense that one knows the order parameter, the structure, and all thermodynamic properties on both sides of the transition). Later we shall comment on cases in which one does not know all characteristics of one of the phases and sometimes one does not even know whether there is a phase transition.

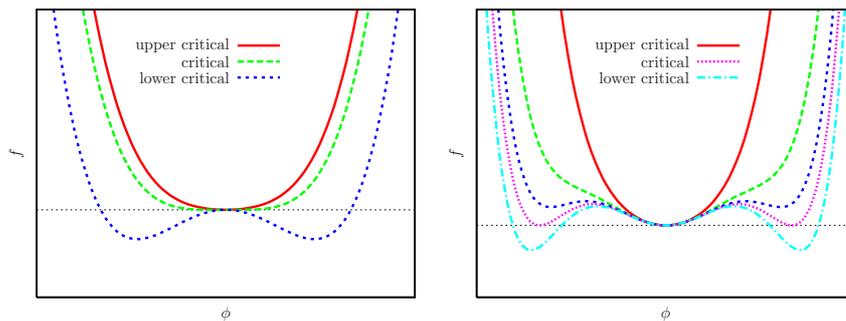


Figure 20: Left: second-order phase transition. Right: first order phase transition.

The evolution of the **free-energy landscape** (as a function of an order parameter) with the control parameter driving a phase transition is a guideline to grasp the dynamics following a quench or annealing from, typically, a disordered phase to the phase transition or into the ordered phase. See Fig. 20 for a sketch. We shall discuss quenches to the phase transition and below it. In the former case, the system can get to a critical point (Fig. 20-left) in which the free-energy is metastable in the sense that its second derivative vanishes (second order phase transition cases) or to a first-order phase transition (Fig. 20-right) in which various minima are degenerate. In the latter case the initial state becomes **unstable**, that is to say a maximum, and the phase transition is of second-order (see Fig. 20-left) or **metastable**, that is to say a local minimum, and the phase transition is of first order (see Fig. 20-right) in the final externally imposed conditions.<sup>8</sup> In the former case the **ordering process** occurs **throughout the material**, and not just at **nucleation sites**. Two typical examples are spinodal decomposition, *i.e.* the method whereby a mixture of two or more materials can separate into distinct regions with different material concentrations, or magnetic domain growth in ferromagnetic materials. Instead, in the latter case, the stable phase conquers the system through the **nucleation of a critical localized bubble** via thermal activation and its further growth.

Having described the dependence of the free-energy landscape on the external parameters we now need to choose the microscopic dynamics of the order parameter. Typically, one distinguishes two classes: one in which the order parameter is locally conserved and another one in which it is not. **Conserved** order parameter dynamics are found for example in phase separation in magnetic alloys or immiscible liquids. Ferromagnetic domain growth is an example of the **non-conserved** case.

The kinetics of systems undergoing critical dynamics or an ordering process is an important problem for material science but also for our generic understanding of pattern formation in non-equilibrium systems. The late stage dynamics is believed to be governed by a few properties of the systems whereas material details should be irrelevant. Among these relevant properties one may expect to find the number of degenerate ground states, the nature of the conservation laws and the hardness or softness of the domain walls that is intimately related to the dimension of the order parameter. Thus, classes akin to the universality ones of critical phenomena have been identified. These systems constitute a first example of a problem with **slow dynamics**. Whether all systems with slow dynamics, in particular structural and spin glasses, undergo some kind of simple though slow domain growth is an open question.

### 3.1 Time-dependent Ginzburg-Landau description

In order to treat phase-transitions and the coarsening process analytically it is preferable to introduce a coarse-grained description in terms of a continuous coarse-

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<sup>8</sup>Strictly speaking metastable states with infinite life-time exist only in the mean-field limit.

grained field,

$$\phi(\vec{x}, t) \equiv \frac{1}{V} \sum_{i \in V_{\vec{x}}} s_i(t), \quad (3.126)$$

the fluctuating magnetization density. In a first approximation a Landau-Ginzburg free-energy functional is introduced

$$F[\phi] = \int d^d x \left\{ \frac{c}{2} [\nabla \phi(\vec{x}, t)]^2 + V[\phi(\vec{x}, t)] \right\}. \quad (3.127)$$

With the choice of the potential one distinguishes between a second order and a first order phase transition. In the former case, the typical form is the  $\phi^4$  form:

$$V(\phi) = a\phi^4 + b(g)\phi^2. \quad (3.128)$$

The first term in eq. (3.127) represents the energy cost to create a domain wall or the elasticity of an interface. The second term depends on a parameter,  $g$ , and changes sign from positive at  $g > g_c$  to negative at  $g < g_c$ . Above the critical point determined by  $b(g_c) = 0$  it has a single minimum at  $\phi = 0$ , at  $g_c$  it is flat at  $\phi = 0$  and below  $g_c$  it has a double well structure with two minima,  $\phi = \pm[-b(g)/(2a)]^{1/2} = \langle \phi \rangle_{eq}(g)$ , that correspond to the equilibrium states in the ordered phase. Equation (3.127) is exact for a fully connected Ising model where  $V(\phi)$  arises from the multiplicity of spin configurations that contribute to the same  $\phi(\vec{x}) = m$ . The order-parameter dependent free-energy density reads  $f(m) = -Jm^2 - hm + k_B T \{ (1+m)/2 \ln[(1+m)/2] + (1-m)/2 \ln[(1-m)/2] \}$  that close to the critical point where  $m \simeq 0$  becomes  $f(m) \simeq (k_B T - 2J)/2 m^2 - hm + k_B T/12 m^4$  demonstrating the passage from a harmonic form at  $k_B T > k_B T_c = 2J$ , to a quartic well at  $T = T_c$ , and finally to a double-well structure at  $T < T_c$ .

**Exercise.** Prove the above.

When discussing dynamics one should write down the stochastic evolution of the individual spins and compute time-dependent averaged quantities. This is the procedure used in numerical simulations. Analytically it is more convenient to work with a field-theory and an evolution equation of Langevin-type. This is the motivation for the introduction of continuous field equations that regulate the time-evolution of the coarse-grained order parameter. Ideally these equations should be derived from the spin stochastic dynamics but in practice they are introduced phenomenologically. In the magnetic case as well as in many cases of interest, the domain wall and interface dynamics can be argued to be **overdamped** (i.e.  $t \gg t_r^\phi$ ).

Two very similar approaches are used. Assuming  $T$  is only relevant to determine the equilibrium coarse-grained field one uses the phenomenological **zero-temperature time-dependent Ginzburg-Landau** equation or **model A** in the classification of Hohenberg-Halperin deterministic equation

$$\frac{\partial \phi(\vec{x}, t)}{\partial t} = - \frac{\delta F[\phi]}{\delta \phi(\vec{x}, t)} \quad (3.129)$$

(the friction coefficient has been absorbed in a redefinition of time). Initial conditions are usually chosen to be random with short-range correlations

$$[\phi(\vec{x}, 0)\phi(\vec{x}', 0)]_{ic} = \Delta\delta(\vec{x} - \vec{x}') \quad (3.130)$$

thus mimicking the high-temperature configuration ( $[\dots]_{ic}$  represent the average over its probability distribution). The numeric solution to this equation with the quartic potential and  $b < 0$  shows that such a random initial condition evolves into a field configuration with patches of ordered region in which the field takes one of the two values  $[-b/(2a)]^{1/2}$  separated by sharp walls. It ignores temperature fluctuations within the domains meaning that the field is fully saturated within the domains and, consequently, one has access to the aging part of the correlations only. The phase transition is controlled by the parameter  $b$  in the potential.

Another, similar approach, is to add a thermal noise to the former

$$\frac{\partial\phi(\vec{x}, t)}{\partial t} = -\frac{\delta F[\phi]}{\delta\phi(\vec{x}, t)} + \xi(\vec{x}, t). \quad (3.131)$$

This is the field-theoretical extension of the Langevin equation in which the potential is replaced by the order-parameter-dependent functional free-energy in eq. (3.127) with a potential form with fixed parameters (independent of  $T$ ).  $\xi$  is a noise taken to be Gaussian distributed with zero mean and correlations

$$\langle\xi(\vec{x}, t)\xi(\vec{x}', t')\rangle = 2k_B T\delta^d(\vec{x} - \vec{x}')\delta(t - t'). \quad (3.132)$$

The friction coefficient has been absorbed in a redefinition of time. For a quartic potential a dynamic phase transition arises at a critical  $T_c$ ; above  $T_c$  the system freely moves above the two minima and basically ignores the double well structure while below  $T_c$  this is important. Within the growing domains the field  $\phi$  fluctuates about its mean also given by  $[-b/(2a)]^{1/2}$  and the fluctuations are determined by  $T$ . One can describe the rapid relaxation at ties such that the domain walls do not move with this approach. This formulation is better suited to treat critical and sub-critical dynamics in the same field-theoretical framework.

These equations do not conserve the order parameter neither locally nor globally. Extensions for cases in which it is conserved exist (model B). Cases with vectorial or even tensorial order parameters can be treated similarly and are also of experimental relevance, notably for vectorial magnets or liquid crystals.

### 3.1.1 Short-time dynamics

Take an initial configuration  $\phi(\vec{x}, 0) = 0$  on average with small fluctuations, as in equilibrium at very high temperature, and quench the system. At very short time one can expand the non-linear potential and the Ginzburg-Landau equation (3.129), for the Fourier components,  $\phi(\vec{k}, t) = L^{-d/2} \int d^d x \phi(\vec{x}, t)e^{-i\vec{k}\vec{x}}$  with  $\vec{k} = 2\pi/L (n_1, \dots, n_d)$  and  $n_k$  integer, reads

$$\frac{\partial\phi(\vec{k}, t)}{\partial t} = [-k^2 - V''(0)]\phi(\vec{k}, t) + \xi(\vec{k}, t). \quad (3.133)$$

If  $V''(0) > 0$  all modes decay exponentially and no order develops. If  $V''(0) < 0$  instead modes with  $-k^2 - V''(0) > 0$  are unstable and grow exponentially until a time  $t^* \simeq -1/V''(0)$  when the small  $\phi$  expansion ceases to be justified. The instability of the small wave-vector modes indicates that the system tends to order. To go beyond this analysis one needs to consider the full non-linear equation.

### 3.2 An instructive case: the large $N$ approximation

A very useful approximation is to upgrade the scalar field to a vectorial one with  $N$  components

$$\phi(\vec{x}, t) \rightarrow \vec{\phi}(\vec{x}, t) = (\phi_1(\vec{x}, t), \dots, \phi_N(\vec{x}, t)), \quad (3.134)$$

and modify the free-energy

$$F = \int d^d x \left[ \frac{1}{2} (\nabla \vec{\phi})^2 + \frac{N}{4} (\phi_0^2 - N^{-1} \phi^2)^2 \right], \quad (3.135)$$

with  $\phi^2 = \sum_{\alpha=1}^N \phi_\alpha^2$  and  $\phi_0$  finite. The  $T = 0$  dynamic equation then becomes

$$\partial_t \phi_\alpha(\vec{x}, t) = \nabla^2 \phi_\alpha(\vec{x}, t) - 4\phi_\alpha(\vec{x}, t) [\phi_0^2 - N^{-1} \phi^2(\vec{x}, t)] \quad (3.136)$$

and it is clearly **isotropic** in the  $N$  dimensional space implying

$$C_{\alpha\beta}(\vec{x}, t; \vec{x}', t') = \delta_{\alpha\beta} C(\vec{x}, t; \vec{x}', t') \quad (3.137)$$

In the limit  $N \rightarrow \infty$  while keeping the dimension of real space fixed to  $d$ , the cubic term in the right-hand-side can be replaced by

$$-\phi_\alpha(\vec{x}, t) N^{-1} \phi^2(\vec{x}, t) \rightarrow -\phi_\alpha(\vec{x}, t) N^{-1} [\phi^2(\vec{x}, t)]_{ic} \equiv -\phi_\alpha(\vec{x}, t) a(t) \quad (3.138)$$

since  $N^{-1} \phi^2(\vec{x}, t)$  does not fluctuate, it is equal to its average over the initial conditions and it is therefore not expected to depend on the spatial position if the initial conditions are chosen from a distribution that is statistically translational invariant. For the scalar field theory the replacement (3.138) is just the **Hartree approximation**. The dynamic equation is now **linear** in the field  $\phi_\alpha(\vec{x}, t)$  that we rename  $\phi(\vec{x}, t)$  (and it is now order 1):

$$\partial_t \phi(\vec{x}, t) = [\nabla^2 + a(t)] \phi(\vec{x}, t), \quad (3.139)$$

where the time-dependent harmonic constant  $a(t) = \phi_0^2 - [\phi^2(\vec{x}, t)]_{ic} = \phi_0^2 - [\phi^2(\vec{0}, t)]_{ic}$  has to be determined self-consistently. Equation (3.139) can be Fourier transformed

$$\partial_t \phi(\vec{k}, t) = [-k^2 + a(t)] \phi(\vec{k}, t), \quad (3.140)$$

and it takes now the form of almost independent oscillators under different time-dependent harmonic potentials coupled only through the self-consistent condition on

$a(t)$ . The stability properties of the oscillators depend on the sign of the prefactor in the RHS. The solution is

$$\phi(\vec{k}, t) = \phi(\vec{k}, 0) e^{-k^2 t + \int_0^t dt' a(t')} \quad (3.141)$$

and the equation on  $a(t)$  reads:

$$a(t) = \phi_0^2 - \Delta e^2 \int_0^t dt' a(t') \left( \frac{2\pi}{4t} \right)^{d/2}, \quad (3.142)$$

where one used  $[\phi^2(\vec{x}, t)]_{ic} = [\phi^2(\vec{0}, t)]_{ic}$  and a delta-correlated Gaussian distribution of initial conditions with strength  $\Delta$ . The self-consistency equation is not singular at  $t = 0$  since there is an underlying cut-off in the integration over  $k$  corresponding to the inverse of the lattice spacing, this implies that times should be translated as  $t \rightarrow t + 1/\Lambda^2$  with  $\Lambda = 1/a$  the lattice spacing.

Without giving all the details of the calculation, eq. (3.142), generalized to the finite  $T$  case, can be solved at all temperatures [36]. One finds that there exists a finite  $T_c(d)$  and

*Upper-critical quench*

$$a(t) \rightarrow -\xi^{-2} \quad (3.143)$$

with  $\xi$  the equilibrium correlation length, and the ‘mass’ (in field theoretical terms) or the harmonic constant saturates to a finite value:  $-k^2 + a(t) \rightarrow -k^2 - \xi^{-2}$ .

*Critical quench*

$$a(t) \rightarrow -w/(2t) \quad \text{with } w = 0 \text{ for } d > 4 \text{ and } w = (d-4)/2 \text{ for } d < 4. \quad (3.144)$$

The dynamics is trivial for  $d > 4$  but there is critical coarsening in  $d < 4$ .  $z_{eq}$  equals 2 in agreement with the result from the  $\epsilon$  expansion once evaluated at  $N \rightarrow \infty$ .

*Sub-critical coarsening*

In the long times limit in which the system tends to decrease its elastic and potential energies  $[\phi^2(\vec{x}, t)]_{ic}$  must converge to  $\phi_0^2 \neq 0$  **below criticality** and this imposes  $2 \int_0^t dt' a(t') \simeq \frac{d}{2} \ln(t/t_0)$  with  $t_0 = \pi/2 (\Delta/\phi_0^2)^{2/d}$  at large times, *i.e.*

$$a(t) \simeq \frac{d}{4t} \quad \text{for } t \gg t_0 \quad (3.145)$$

and the time-dependent contribution to the spring constant vanishes asymptotically. Knowing the long-time behavior of  $a(t)$  implies that each mode  $[\phi(\vec{k}, t)]_{ic}$  with  $\vec{k} \neq 0$  vanishes asymptotically but the  $\vec{k} = 0$  mode grows as  $t^{d/4}$ . The growth of the  $\vec{k} = 0$  reflects the domain growth process whereby all modulations tend to disappear and the configuration gets more and more uniform as time passes.

We focus now on two interesting cases: quenches to  $T_c$  and  $T < T_c$ . The asymptotic behavior of the space-time correlation function in the aging regime is

$$[\phi(\vec{x}, t)\phi(\vec{x}', t')]_{ic} = \phi_0^2 \left[ \frac{4tt'}{(t+t')^2} \right]^{d/4} \exp \left[ -\frac{(\vec{x} - \vec{x}')^2}{4(t+t')} \right], \quad (3.146)$$

for  $t \geq t'$  for a quench to  $T < T_c$  and

$$[\phi(\vec{x}, t)\phi(\vec{x}', t')]_{ic} = \phi_0^2 t'^{1-d/2} f(t/t') \exp \left[ -\frac{(\vec{x} - \vec{x}')^2}{4(t+t')} \right], \quad (3.147)$$

for a quench to  $T_c$ . We focus on  $d < 4$ . These expressions capture the main features of the domain growth process:

- In Fourier space all  $k \neq 0$  modes have an exponential decay while the  $k = 0$  one is fully massless asymptotically and diffuses.
- In sub-critical quenches, for any finite and fixed  $(\vec{x} - \vec{x}')$ , in the long times limit the exponential factor approaches one and one obtains a function of  $t'/t$  only.
- In critical quenches the two-time dependent prefactor is of the form expected from dynamic scaling.
- Due to the exponential factor, for fixed but very large time  $t$  and  $t'$  the correlation falls off to zero over a distance  $|\vec{x} - \vec{x}'| \propto \sqrt{t+t'}$ . This means that, at time  $t$ , the typical size of the regions in the states  $\pm\phi_0$  is  $R(t) \propto t^{1/2}$ . This holds for critical and sub-critical quenches as well and it is a peculiar property of the large  $N$   $O(N)$  model that has  $z_{eq} = z_d$ .
- For fixed  $|\vec{x} - \vec{x}'|$ , the correlation always falls to zero over a time separation  $t - t'$  which is larger than  $t'$ . This means that the time it takes to the system to decorrelate from its configuration at time  $t'$  is of the order of  $t'$  itself,  $t_d \simeq t'$ . The age of the system is the characteristic time-scale for the dynamical evolution: the older is the system, the slower is its dynamics. After a time of the order of the age of the system any point  $\vec{x}$  will be swept by different domain walls and the correlation will be lost.
- In a critical quench the correlation always decays to zero due to the prefactor that goes as  $t^{(2-d)/2}$  and vanishes in all  $d > 2$ . The aging curves have an envelope that approaches zero as a power law.
- In a sub-critical quench, for any finite and fixed  $(\vec{x} - \vec{x}')$ , in the long  $t'$  and  $t$  limit such that  $t'/t \rightarrow 1$  the time dependence disappears and the correlation between two points converges to  $\phi_0^2$ . This means that, typically, if one looks at a finite spatial region on a finite time-scale this region will be in one of the two states  $\pm\phi_0$ , i.e. within a domain.

Note that we have obtained the field and then computed correlations from the time-dependent configuration. We have not needed to compute the linear response. We shall see later that in other more complex glassy systems one cannot follow this simple route and one needs to know how the linear response behave.

## 4 A single harmonic oscillator

The idea here is to investigate thermalization issues in a very simple problem: a single isolated classical harmonic oscillator. This simple calculation is work in progress but it is also intimately linked to what we have presented [37].

The Hamiltonian of a one-dimensional harmonic oscillator of mass  $m$  and spring constant  $k = m\omega^2$  is

$$H = \frac{m\dot{x}^2}{2} + \frac{m\omega^2 x^2}{2}. \quad (4.148)$$

We will study the conservative (Newton) and dissipative (Langevin) dynamics of the oscillator.

The initial condition,  $x(0) = x_0$  and  $\dot{x}(0) = \dot{x}_0 = v_0$  can be chosen to be fixed by, *i.e.*, attributing values to  $x_0$  and  $\dot{x}_0$ . Otherwise, they can be drawn from a probability distribution  $P(x_0, \dot{x}_0)$  and the dynamics be examined on average over this pdf. A natural choice is a thermal distribution,

$$P(x_0, \dot{x}_0) = \mathcal{Z}^{-1}(\beta) e^{-\beta H(x_0, \dot{x}_0)} \quad (4.149)$$

with  $H$  given in eq. (4.148) evaluated at  $x_0$  and  $\dot{x}_0$ ,  $\beta$  an inverse temperature introduced in this way even in the deterministic case, and  $\mathcal{Z}^{-1}(\beta)$  the normalization.

The initial energy of the oscillator is

$$E_0 = E(t=0) = \frac{m\dot{x}_0^2}{2} + \frac{m\omega^2 x_0^2}{2}. \quad (4.150)$$

The Langevin equation of motion reads

$$m\ddot{x}(t) = -\gamma\dot{x}(t) - kx(t) + h(t) + \xi(t). \quad (4.151)$$

with  $h(t)$  a time-dependent deterministic force.  $\xi$  is the white noise with zero mean and correlations  $\langle \xi(t)\xi(t') \rangle = 2k_B T \gamma \delta(t-t')$ . The coupling to the bath can be switched off by simply setting  $\gamma = 0$ . In the absence of a bath the energy of the oscillator is constant and determined by the initial condition, see eq. (4.150). By setting  $k = 0$  (or  $\omega^2 = 0$ ) one recovers the motion of a Brownian particle.

The full differential equation (4.151) can be easily solved by first evaluating the Green function  $G(t)$  from

$$\ddot{G}(t) + \gamma/m \dot{G}(t) + k/m G(t) = \delta(t) \quad (4.152)$$

Two other important properties of  $G(t) = g(t)\theta(t)$  are  $g(0) = 0$  and  $\dot{g}(0) = 1$  that follow from integrating (4.152) between  $t = -\delta$  and  $t = \delta$  and taking  $\delta \rightarrow 0$ . In Fourier transform<sup>9</sup>

$$\tilde{G}(\omega) = 1/(-\omega^2 - i\gamma/m \omega + k/m). \quad (4.153)$$

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<sup>9</sup>The convention used is  $G(t) = \int d\omega/(2\pi)e^{-i\omega t}\tilde{G}(\omega)$  and  $\tilde{G}(\omega) = \int dt e^{i\omega t}G(t)$ .

The right-hand-side has two poles:

$$\omega_{\pm} = -\frac{i\gamma}{2m} \left[ 1 \pm \sqrt{1 - \frac{4km}{\gamma^2}} \right], \quad (4.154)$$

that are complex or imaginary depending on the relative values of the parameters:

$$4km - \gamma^2 > 0 \quad \omega_{\pm} \text{ complex (underdamped)}, \quad (4.155)$$

$$4km - \gamma^2 \leq 0 \quad \omega_{\pm} \text{ imaginary (overdamped)}. \quad (4.156)$$

In both cases the poles are located in the lower half complex plane ensuring the causal property of the Green function,  $G(t) = g(t)\theta(t)$ . In the case  $k = 0$  the pole  $\omega_-$  vanishes and  $\omega_+$  is purely imaginary. This case is special in many respects that we will discuss below.

Using Cauchy's formula to transform back in time one finds that, for  $t > 0$ ,  $G(t) = g(t)\theta(t)$  reads

$$G(t) = \frac{i}{\omega_+ - \omega_-} (e^{-i\omega_+t} - e^{-i\omega_-t}) \theta(t) \quad (4.157)$$

that satisfies  $g(0) = 0$ ,  $\dot{g}(0) = 1$  and  $\ddot{g}(0) = \omega_+ + \omega_- = -i\gamma/m$ . In the two special cases signaled above this expression implies

$$g(t) = \begin{cases} \frac{1}{\omega_R} \sin \omega_R t e^{-|\omega_I|t} & \text{if } \omega_{\pm} = \pm\omega_R - i|\omega_I| \\ \frac{-1}{(|\omega_I^{(+)}| - |\omega_I^{(-)}|)} \left( e^{-|\omega_I^{(+)}|t} - e^{-|\omega_I^{(-)}|t} \right) & \text{if } \omega_{\pm} = -i|\omega_I^{(+,-)}| \end{cases}$$

and it vanishes identically for  $t < 0$ . Note that since  $|\omega_I^{(+)}| > |\omega_I^{(-)}|$ , as long as  $k \neq 0$ , asymptotically

$$g(t) \rightarrow \frac{-i}{(\omega_+ - \omega_-)} e^{-|\omega_I^{(-)}|t} \quad \text{in the overdamped case, for } k \neq 0. \quad (4.158)$$

Instead,

$$g(t) \rightarrow \frac{1}{|\omega_I^{(-)}|} = \frac{m}{\gamma} \quad \text{in the overdamped case, for } k = 0. \quad (4.159)$$

The time-dependent position of the particle is given by

$$x(t) = [\dot{g}(t) - (\omega_+ + \omega_-)g(t)]x_0 + g(t)\dot{x}_0 + \int_0^{\infty} dt'' G(t-t'') [\xi(t'') + h(t'')]/m. \quad (4.160)$$

The first two terms on the RHS represent the effect of the initial conditions. Note that  $G(t)$  is proportional to a Heaviside theta function and hence the integration over time has an effective upper limit at  $t'' = t$ .

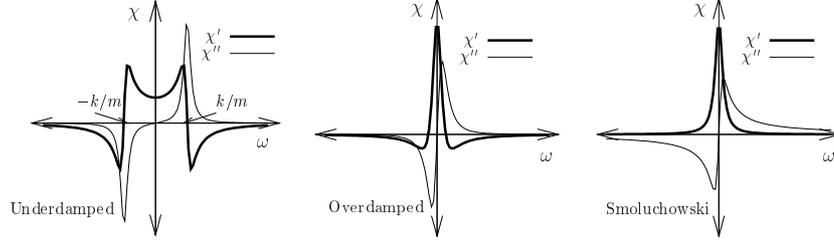


Figure 21: The Fourier transform of the linear response to an instantaneous perturbation of the type  $H \rightarrow H - hx$ . Displayed are the underdamped (left), overdamped (centre) and Smoluchowski (right) cases. Note that  $\chi(\omega)$  equals the Green function  $\tilde{G}(\omega)$  in the frequency domain.

## 4.1 Newton dynamics

The time-dependent position of the particle is given by

$$\begin{aligned}
 x_h(t) &= x_0 \dot{g}(t) + v_0 g(t) + \int_0^\infty dt'' G(t-t'') h(t'')/m \\
 &= x_0 \cos \omega t + v_0 \frac{\sin \omega t}{\omega} + \int_0^t dt'' \frac{\sin \omega(t-t'')}{m\omega} h(t'') \quad (4.161)
 \end{aligned}$$

### 4.1.1 The total energy

The initial total energy is conserved by the dynamics. If we take an initial condition from the pdf with frequency  $\omega_0$  and we evolve with the Hamiltonian with frequency  $\omega$ , the initial condition for the dynamics has energy:

$$E_0 = \frac{1}{2} m v_0^2 + \frac{1}{2} m \omega^2 x_0^2. \quad (4.162)$$

Note that the initial energy is a fluctuating quantity,  $P(E_0)$ . This energy is conserved, i.e.  $E(t) = E_0$ . The average over the initial conditions is

$$[E_0]_{ic} = [E_0]_{ic} = \left(1 + \frac{\omega^2}{\omega_0^2}\right) \frac{k_B T_0}{2} \equiv k_B T_{\text{eff}}^E(\omega_0, \omega, T_0) \quad (4.163)$$

If  $\omega = \omega_0$  one recovers the expected result  $T_{\text{eff}}^E = T_0$ . Note that if one naively takes the limit  $\omega \rightarrow 0$  in this expression one finds  $T_0/2$ . But, as we will see below, this limit is non-trivial.

### 4.1.2 One-time quantities

It is quite evident that any one-time observable, such as the position or the velocity of the particle, is not a constant of motion and depend periodically on time. One can take the average over initial conditions drawn from the Gibbs-Boltzmann pdf and find

$$[x(t)]_{ic} = [v(t)]_{ic} = 0 , \quad (4.164)$$

that is to say that the zero-averaged is conserved by the averaged dynamics. One could have considered the time average over at least one  $\omega\mathcal{T} = 2\pi$  period to find that such time-averaged position and velocity vanish identically independently of the initial conditions:

$$[x(t)]_{\mathcal{T}} = [v(t)]_{\mathcal{T}} = 0 . \quad (4.165)$$

Let us consider now the time-dependent kinetic and potential energy separately:

$$\begin{aligned} \frac{1}{2}m\omega^2 x^2(t) &= \frac{1}{2}m\omega^2 ([\dot{g}(t)]^2 x_0^2 + [g(t)]^2 v_0^2 + \dot{g}(t)g(t)x_0 v_0) , \\ \frac{1}{2}mv^2(t) &= \frac{1}{2}m ([\ddot{g}(t)]^2 x_0^2 + [\dot{g}(t)]^2 v_0^2 + \ddot{g}(t)\dot{g}(t)x_0 v_0) . \end{aligned} \quad (4.166)$$

Say that one evolves the system with a frequency  $\omega$  while the initial condition was prepared with another frequency  $\omega_0$ . If one takes the average over the initial conditions using the Gibbs-Boltzmann measure one finds

$$\frac{1}{2}m\omega^2 [x^2(t)]_{ic} = \frac{k_B T}{2} \left( \cos^2 \omega t \frac{\omega^2}{\omega_0^2} + \sin^2 \omega t \right) \quad (4.167)$$

(similarly for the kinetic energy with  $\cos^2 \omega t$  replaced by  $\sin^2 \omega t$  and viceversa). If one further averages over a period,

$$\frac{1}{2}m\omega^2 [x^2(t)]_{ic, \mathcal{T}} = \frac{k_B T}{2} \frac{1}{2} \left( \frac{\omega^2}{\omega_0^2} + 1 \right) \quad (4.168)$$

and similarly for the kinetic energy. Therefore, one has equipartition for each degree of freedom with the effective temperature deduced from the analysis of the total energy. If  $\omega_0 = \omega$  the time-average is not needed and one finds

$$\frac{1}{2}m\omega^2 [x^2(t)]_{ic} = \frac{1}{2}m [v^2(t)]_{ic} = \frac{1}{2}k_B T_0 . \quad (4.169)$$

and similarly for the kinetic energy. Equipartition is also conserved by the dynamics, though only averaged over the initial condition.

### 4.1.3 Effective temperature from FDT

From here we compute the linear response:

$$R(t, t') = \frac{\delta x_h(t)}{\delta h(t')} = \frac{1}{m} G(t - t') = \frac{\sin \omega(t - t')}{m\omega} \theta(t - t') \quad (4.170)$$

that is independent of the initial conditions and is invariant under translations of time  $t \rightarrow t + \Delta$  and  $t' \rightarrow t' + \Delta$ .

We can also compute the two-time composite function

$$\begin{aligned} C(t, t') &= x(t)x(t') \\ &= x_0^2 \dot{g}(t)\dot{g}(t') + v_0^2 g(t)\dot{g}(t') \\ &\quad + x_0 v_0 \dot{g}(t)g(t') + x_0 v_0 g(t)\dot{g}(t') \end{aligned} \quad (4.171)$$

and its derivative with respect to  $t'$ :

$$\begin{aligned} \partial_{t'} C(t, t') &= x(t)\dot{x}(t') \\ &= x_0^2 \dot{g}(t)\ddot{g}(t') + v_0^2 g(t)\ddot{g}(t') \\ &\quad + x_0 v_0 \dot{g}(t)\dot{g}(t') + x_0 v_0 g(t)\ddot{g}(t') \\ &= \left( \frac{v_0^2}{2\omega} + \frac{\omega x_0^2}{2} \right) \sin \omega(t - t') \\ &\quad + \sin \omega(t + t') \left( \frac{v_0^2}{2\omega} - \frac{\omega x_0^2}{2} \right) + \cos \omega(t + t') x_0 v_0 . \end{aligned} \quad (4.172)$$

This object strongly depends on the initial condition and it is not just a function of  $t - t'$  as it also depends on  $t + t'$  explicitly. So does the effective temperature:

$$\begin{aligned} k_B T_{\text{eff}}(t, t'; \omega, x_0, v_0) &\equiv \frac{\partial_{t'} C(t, t')}{R(t, t')} \\ &= \left( \frac{mv_0^2}{2} + \frac{m\omega^2 x_0^2}{2} \right) \\ &\quad + \frac{\sin \omega(t + t')}{\sin \omega(t - t')} \left( \frac{mv_0^2}{2} - \frac{m\omega^2 x_0^2}{2} \right) + \frac{\cos \omega(t + t')}{\sin \omega(t - t')} m\omega x_0 v_0 . \end{aligned} \quad (4.173)$$

If the parameters of the oscillator Hamiltonian are held fixed after the initial time, the first line is just the initial energy of the oscillator. The second line contains all the non-trivial time dependencies.

$\omega > 0$

Three particular cases are clearly read from this expression

- If the initial condition is drawn from the Gibbs-Boltzmann pdf at temperature  $T_0$ , with Hamiltonian  $H$  with the same parameters used in the evolution,  $m\omega^2[x_0^2]_{ic} = k_B T_0$ ,  $m[v_0^2]_{ic} = k_B T_0$  and  $[x_0 v_0]_{ic} = 0$ . Therefore,

$$k_B [T_{\text{eff}}(t, t'; \omega, x_0, v_0)]_{ic} = k_B T_0 . \quad (4.174)$$

- Let us now take fixed initial conditions,  $x_0, v_0$ , with initial energy  $E_0$ . Let us use a kind of ‘ergodic hypothesis’ in the sense that if we take the average of eq. (4.173) over the reference time  $t'$  over a period by keeping  $t - t'$  fixed (note that the sum of the two times can be re-written as  $t + t' = (t - t') + 2t'$ ), the second and third lines in eq. (4.173) average out to zero and one is again left with

$$k_B[T_{\text{eff}}(t, t'; \omega, x_0, v_0)]_{\mathcal{T}} = E_0 . \quad (4.175)$$

Note that longer and longer time-averages are needed for decreasing values of the oscillator’s internal frequency for this average to yield the searched result.

- The system starts from equilibrium at  $T_0$  with a Hamiltonian with frequency  $\omega_0$  such that  $m[v_0^2]_{ic} = k_B T_0$ ,  $m\omega_0^2[x_0^2]_{ic} = k_B T_0$  and  $[x_0 v_0]_{ic} = 0$  but it evolves with a different Hamiltonian, one with a frequency  $\omega$ . This is the classical equivalent of a quantum quench. Then, after averaging over the initial conditions one still has a time dependence,

$$\begin{aligned} k_B[T_{\text{eff}}(t, t'; \omega, x_0, v_0)]_{ic} &= \frac{1}{2} \left( 1 + \frac{\omega^2}{\omega_0^2} \right) k_B T_0 \\ &+ \frac{1}{2} \frac{\sin \omega(t + t')}{\sin \omega(t - t')} \left( 1 - \frac{\omega^2}{\omega_0^2} \right) k_B T_0 , \end{aligned} \quad (4.176)$$

that disappears only if a further average over  $t'$  (as the one described in the previous item) is performed. One finds

$$k_B[T_{\text{eff}}(t, t'; \omega, x_0, v_0)]_{ic, \mathcal{T}} = \frac{1}{2} \left( 1 + \frac{\omega^2}{\omega_0^2} \right) k_B T_0 \quad (4.177)$$

that coincides with eq. (4.174) for  $\omega = \omega_0$ . We will come back to this result later, when discussing the dissipative problem. Note that one cannot take the limit  $\omega \rightarrow 0$  here since the time average does not make sense in this limit.

The total energy is conserved by the dynamics. Then, its average over the thermal initial conditions at frequency  $\omega_0$  is conserved as well and it can be evaluated at time  $t = 0$ . One finds

$$\begin{aligned} [E(t; \omega, \omega_0)]_{ic} &= [E(0; \omega, \omega_0)]_{ic} = \frac{1}{2} \left( 1 + \frac{\omega^2}{\omega_0^2} \right) k_B T \\ &= k_B [T_{\text{eff}}(t, t'; \omega, x_0, v_0)]_{ic, \mathcal{T}} \end{aligned} \quad (4.178)$$

where we recovered the effective temperature calculated with the fluctuation-dissipation relation.

The same conclusions can be reached by working with the Green-Kubo formula, that relates the velocity-velocity correlation to the linear response of the velocity *via* the temperature (in other words, it is the derivative with respect to  $t$  of the fluctuation-dissipation relation that we used above):  $T_{\text{eff}} = v(t)v(t')/[\delta v_h(t)/\delta h(t')]$ .

$\omega = 0$

Quenching to a flat potential is quite different. One finds

$$k_B T_{\text{eff}}(t, t'; \omega, x_0, v_0) = \frac{1}{2} m v_0^2 \left( \frac{2t}{t-t'} \right) + m x_0 v_0 \frac{1}{t-t'} \quad (4.179)$$

that after averaging over initial conditions becomes

$$k_B T_{\text{eff}}(t, t'; \omega, x_0, v_0) = \frac{k_B T_0}{2} \left( \frac{2t}{t-t'} \right) \quad (4.180)$$

a non-trivial function of times. The zero mode is bizarre, as expected.

## A Conventions

### A.1 Fourier transform

The convention for the Fourier transform is

$$f(\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega\tau} f(\omega), \quad (A.181)$$

$$f(\omega) = \int_{-\infty}^{\infty} d\tau e^{+i\omega\tau} f(\tau). \quad (A.182)$$

The Fourier transform of the theta function reads

$$\theta(\omega) = i \text{vp} \frac{1}{\omega} + \pi \delta(\omega). \quad (A.183)$$

The convolution is

$$[f \cdot g](\omega) = f \otimes g(\omega) \equiv \int \frac{d\omega'}{2\pi} f(\omega') g(\omega - \omega'). \quad (A.184)$$

### A.2 Commutation relations

We defined the commutator and anticommutator:  $\{A, B\} = (AB + BA)/2$  and  $[A, B] = (AB - BA)/2$ .

### A.3 Time ordering

We define the time ordering operator acting on bosons as

$$T \hat{q}(t) \hat{q}(t') \equiv \theta(t, t') \hat{q}(t) \hat{q}(t') + \theta(t', t) \hat{q}(t') \hat{q}(t). \quad (A.185)$$

For fermions, we define the time ordering operator as

$$T\hat{\psi}(t)\hat{\psi}(t') \equiv \theta(t, t')\hat{\psi}(t)\hat{\psi}(t') - \theta(t', t)\hat{\psi}(t')\hat{\psi}(t) , \quad (\text{A.186})$$

$$T\hat{\psi}(t)\hat{\psi}^\dagger(t') \equiv \theta(t, t')\hat{\psi}(t)\hat{\psi}^\dagger(t') - \theta(t', t)\hat{\psi}^\dagger(t')\hat{\psi}(t) , \quad (\text{A.187})$$

In both cases  $\theta(t, t')$  is the Heaviside-function.

We define the time-ordering operator  $T_C$  on the Keldysh contour in such a way that times are ordered along it:

$$\begin{aligned} T_C x_+(t)x_-(t') &= x_-(t')x_+(t) & T_C x_-(t)x_+(t') &= x_-(t)x_+(t') \\ T_C \psi_+(t)\psi_-(t') &= -\psi_-(t')\psi_+(t) & T_C \psi_-(t)\psi_+(t') &= \psi_-(t)\psi_+(t') \end{aligned} \quad (\text{A.188})$$

for all  $t$  and  $t'$ .

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