Out of equilibrium dynamics of complex systems

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1 Introduction

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.

However, the vast majority of physical systems are out of equilibrium. At the largest scale, the Universe itself is still evolving out of equilibrium from its initial state. Jumping over many scales one singles out the Sun, among other similar stars, which is a complex out of equilibrium system in which plasma and magnetic fields produce many interesting patters such as convection cells, solar flares and sunspots. Climate modelling is a celebrated hard out of equilibrium problem due to the complex interaction between the earth, the ocean and the atmosphere. Living bodies are obviously very complex objects; at a molecular scale one can think of them as made of complex organic molecules embedded mostly in water, and continuously moving, transforming and interacting. Out of equilibrium phenomena at nanoscales are also common with many examples including sliding carbon nanotubes, evaporating nanoclusters, fluids in nanohydrodynamics, and biological molecular motors. Out of equilibrium aspects of particle physics are expected in the relativistic heavy ion collision processes used to create quark-gluon plasma. Quite naturally, theoretical, experimental and observational attention has therefore turned to the study of the evolution of many-body systems in **far from equilibrium** conditions.

1.1 Falling out of equilibrium

Take a system in conventional equilibrium or in any state. Out of equilibrium conditions can then be achieved in the lab 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. Isolated cases and, in particular, 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 would otherwise reach equilibrium in observable time-scales, with an external perturbation. In the context of macroscopic systems a traditional far from equilibrium example is Rayleigh-Bénard convection induced in a layer of fluid by two parallel plates maintained at different temperature. Another possibility is to create shear in a flow by inducing relative motion in it, as done, for instance, using Couette-Taylor cells. 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. In this case, and other instances, the out of equilibrium situation is created by a time-dependent external force. An electric current across an electric circuit also generates non-equilibrium dynamics. Transport in nano-structures is also of special interest at present.

Some of the problems discussed above pertain to the **classical** World. In other cases of practical interest, **quantum** fluctuations play an important rôle. Relativistic effects may or may not be relevant. Still, even with these microscopic differences, general questions arise for all cases in parallel. We will discuss these and the approach adopted to treat them in the following.

1.2 Focus

Our interest will be set on **macroscopic complex**[1] **systems:**

- Under out of equilibrium initial condition, i.e. a quench. These include
  - open dissipative systems;
  - closed systems with energy conserving dynamics.
- Under the effect of 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.)?

[1] Complex simply means 'not easy to understand' here.

- 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 the steady state depends?
- What **microscopic/mesoscopic relaxation mechanism** takes place after a quench?
- 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.

1.3 Presentation

In these notes we start by exposing some examples of out of equilibrium dynamics **phenomenology** we are interested in. We focus on classical problems and their precise setting. We introduce nucleation [3], phase ordering kinetics [4], critical dynamics [6] structural glasses [8] and disordered systems [9, 10]. We also discuss some interdisciplinary problems that have many points in common with glassy physics including optimization problems [11], neural networks [12] and active matter [13].

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 will 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.

1.4 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 as soon as multiple nucleation and competition between different states intervenes the problem becomes rapidly hard to describe quantitatively and very relevant to the mean-field theory of fragile structural glasses that we will discuss.

1.5 Phase ordering kinetics

Figure 1.1: 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. 1.1. 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 will see later on.

Another example of phase ordering kinetics is given by the **crystal grain growth** sketched in the left-most panel in Fig. 1.2. 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

$$H_J[\{s_i\}] = -J \sum_{\langle ij \rangle} \delta_{s_i s_j} \qquad\qquad J > 0 \ , \tag{1.1}$$

with $s_i = 1, \ \ldots, \ q = 8$ 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.

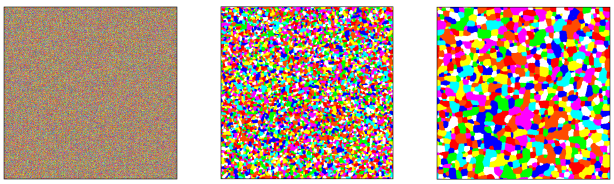


Figure 1.2: Grain boudaries in crystal growth. Three snapshots of the $2d$ ferromagnetic Potts model with $q = 8$ quenched below its (first order) phase transition to $T = T_c/2$. The times at which the images were taken are $t = 0, \ 128, 1024$ MCs. Data from M. P. Loureiro, J. J. Arenzon (Porto Alegre, Brazil, 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 will 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.

1.6 Critical dynamics

In **critical quenches** [6], 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. 1.3 and 1.4.

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

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

with ν the exponent that controls the divergence of the correlation length and z the dynamic critical exponent. This problem has, though, a small parameter (the distance to criticality) that allows for a perturbative treatment and a dynamic renormalisation group approach that is very successful.

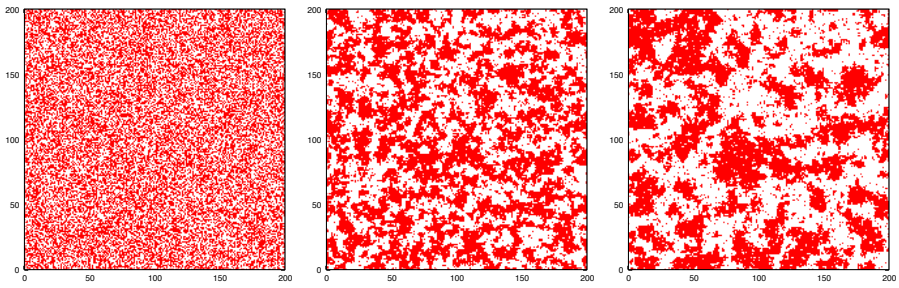


Figure 1.3: Monte Carlo simulations of a $2d$ Ising model. Three snapshots at $t = 1,\ 3 \times 10^5,\ 3 \times 10^6$ MCs after a quench to T_c. Data from T. Blanchard, LFC and M. Picco.

Figure 1.4: 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.

1.7 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 [8].

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.

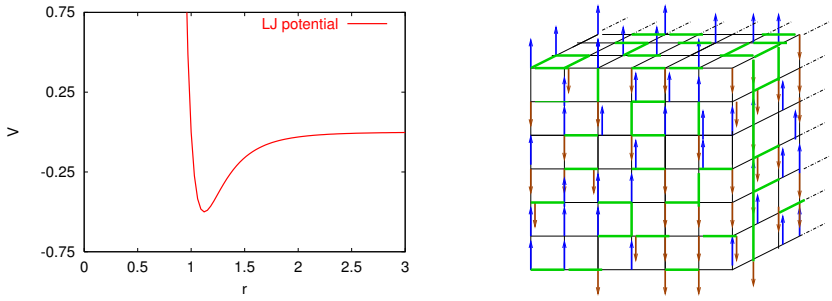


Figure 1.5: Left: The Lennard-Jones potential. Right: the Edwards-Anderson $3d$ spin-glass.

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

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

with usually, $a = 12$ and $b = 6$ (see Fig. 1.5-left) that gives an effective interaction between soft[3] particles in a liquid, has a repulsive and an attractive part, depending

[2]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 $b = 6$.

[3]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.

on the distance between the particles, a set of dynamic variables. In this example, the interactions depend on the positions of the particles and evolve with them.

Figure 1.6: A crystal in a $2d$ colloidal suspension of hard spheres

Figure 1.7: A liquid or a glass in a $2d$ colloidal suspension of hard spheres.

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 no order whatsoever (see Fig. 1.7 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 [8].

There are many types of glasses and they occur over an astounding range of scales from macroscopic to microscopic. See Fig. 1.8 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 $1mm$ 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

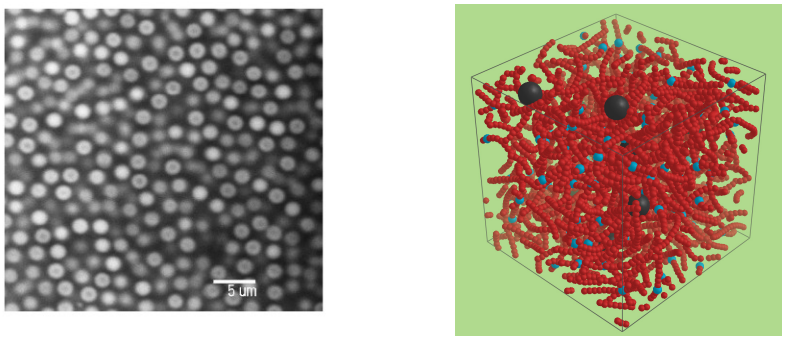


Figure 1.8: Several kinds of glasses. A colloidal suspension observed with confocal microscopy. A polymer melt configuration obtained with molecular dynamics. A simulation box of a Lennard-Jones mixture. A series of photograph of granular matter.

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 80C 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 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 de entropy of the sample by using calorimetric measurements and the thermodynamic relation

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

In some cases the specific volume of the sample is shown as a function of temperature. In numerical simulations the potential energy density can be equally used. Figure 1.9 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.

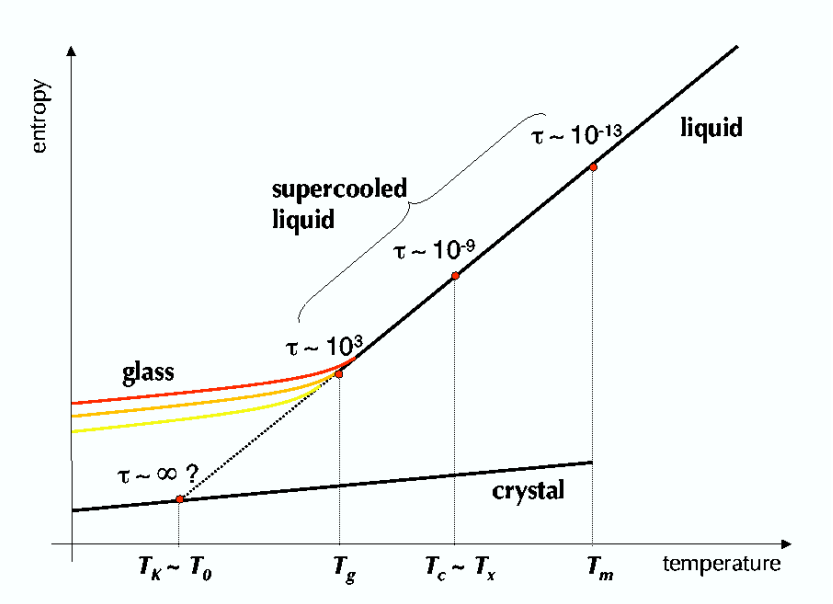


Figure 1.9: The typical plot showing the four 'phases' observed in a cooling experiment: liquid, supercooled liquid, glass and crystal. The characteristic temperatures T_m (a first order phase transition), T_g and the Kauzmann temperature T_K are shown as well as the typical relaxation times in the liquid and super-cooled liquid phases.

The extrapolation of the entropy of the liquid below T_g crosses the entropy of the 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 will 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^2 s/m^2 = 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**:

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

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

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

The **incoherent intermediate or self** correlation:

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

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

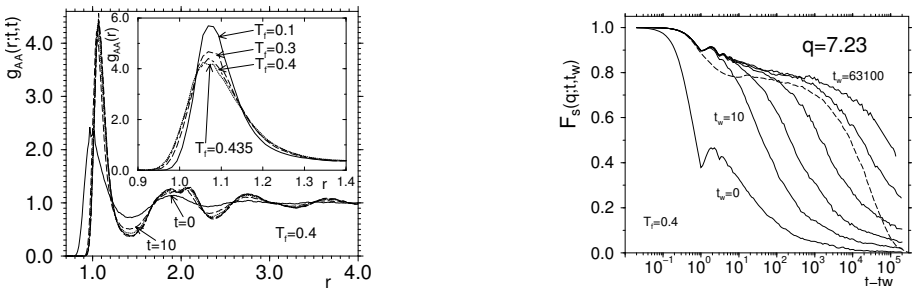


Figure 1.10: Structure and dynamics of a binary Lennard-Jones mixture. Left: the two-point correlation function of the A atoms at different times (main panel) and at different temperatures (inset). Right: the decay of the Fourier transform of the correlation function at the wave-vector associated to the first peak in $g_{AA}(r)$. Data from Kob & J-L Barrat.

In the main panel of Fig. 1.10-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. 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 $T \to T_g$ 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[4] one finds two kinds of fitting laws:

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

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 molecualr, 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) the plateau.

Figure 1.11: Colloidal suspension (data from E. Weeks group) and granular matter (data from O. Pouliquen's group).

Very recently stress has been put on the analysis of the motion of the elements over longer time-scales. Dynamic heterogeneities [14] 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

[4] This is a very naive definition of τ_α, others much more precise are used in the literature.

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 $\rho_0 = N/V$,

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

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 τ_α. 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** [15], will be discussed below.

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

Crytallization at T_m is avoided by cooling fast enough.

Liquid — Supercooled liquid — **Glass**

Exponential relax — Non-exponential relax

Equilibrium — Metastable equilibrium — **Non-equilibrium**

Separation of time-scales &
An exponential number of metastable states!

Stationary — **Aging**

Aging means that correlations and reponses depend on t *and* t_w
ac susceptibilities depend on ω *and* t_w

There might be an **equilibrium transition** to an **ideal glass** at T_s.

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 some 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.

1.8 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:

$$\tau_d \gg \tau_{exp} \gg \tau_0 \ . \tag{1.9}$$

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

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

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 [9] (see Fig. 1.5-right).

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

Hamiltonian then reads

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

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. 1.5, 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. 1.12.

Figure 1.12: Spin-glasses: Susceptibility data (Mydosh). Aging phenomena (Hérisson and Ocio).

1.9 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 [10, 16].

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

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

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 $L^{2\zeta}$. α is the growth exponent, z is the dynamic exponent and ζ 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 will 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.

1.10 Aging

In practice a further complication appears [15]. 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 ρ_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. 1.13 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. 3.42.

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

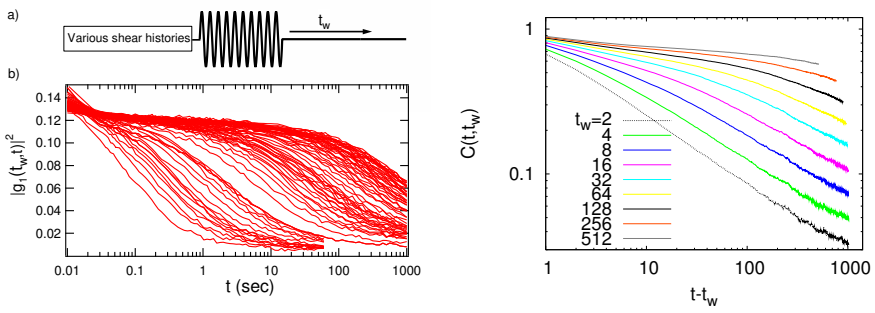


Figure 1.13: Left: two-time evolution of the self-correlation in a colloidal suspension initialized by applying a shearing rate (data from Viasnoff and Lequeux [119]) The longer the waiting time the slower the decay. Right: two-time evolution in the bi-dimensional Ising model quenched below its phase 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 will discuss this feature at length in the lectures.

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

1.11 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.

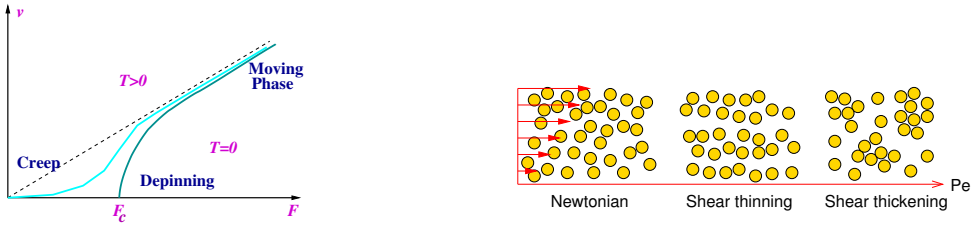


Figure 1.14: Left: Creep and depinning of elastic objects under quenched randomness. Right: Rheology of complex fluids. Shear thinning: τ decreases or thickening τ increases

1.12 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 will discuss here.

1.12.1 Optimization problems

The most convenient area of application is, most probably, the one of **combinatorial optimization** in computer science [11]. 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 will discuss at length is then applicable to these problems with minor (or not so minor) modifications due to the finite connectivity of the networks.

Figure 1.15: Graph partitioning.

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 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 $C_1 : x_1$ OR x_2 made by a single clause C_1 is satisfiable because one can find the values $x_1 =$ true (and x_2 free) or $x_2 =$ true (and x_1 free), which make $C_1 : x_1$ 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 ($\overline{x}$) each, these taken from a pool of N variables. An example in 3-SAT is

$$\mathrm{F} = \begin{cases} C_1 \ : \ x_1 \ \mathrm{OR} \ \overline{x}_2 \ \mathrm{OR} \ x_3 \\ C_2 \ : \ \overline{x}_5 \ \mathrm{OR} \ \overline{x}_7 \ \mathrm{OR} \ x_9 \\ C_3 \ : \ x_1 \ \mathrm{OR} \ \overline{x}_4 \ \mathrm{OR} \ x_7 \\ C_4 \ : \ x_2 \ \mathrm{OR} \ \overline{x}_5 \ \mathrm{OR} \ x_8 \end{cases} \tag{1.13}$$

All clauses have to be satisfied simultaneously so the formula has to be read $\mathrm{F} : C_1$ AND C_2 AND C_3 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. Seconf one decides to require x_i or $\overline{x}_i$ for each of them with probability one half. Third one creates a clause taking the OR of these k literals. Forth 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

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

and the energy function as

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

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.

1.12.2 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 [12] 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,

$$\phi_i(t+1) = f(\sum_{j(\neq i)} J_{ij}\phi_j(t)) \ , \tag{1.16}$$

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 1.16: 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 [13]. 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.

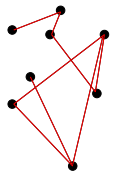


Figure 1.17: Left: random graph with finite connectivity

1.13 Summary and interesting questions

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. 1.17, 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.

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. In these lectures we will only deal with a canonical setting, the microcanonical one being more relevant to quantum systems.

Some 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.
- Could one extend equilibrium statistical mechanics ideas out of equilibrium? *e.g.*, could one use temperature, entropy and other thermodynamic concepts out of equilibrium?

- Related to the previous item, could one construct a non-equilibrium measure that would substitute the Gibbs-Boltzmann one in certain cases.

2 Modeling

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 Canonical setting

In this lecture we always think of the system of interest being coupled to an environment with which it can exchange energy. The total energy of the full system is conserved but the contributions from the system, bath and interaction are not.

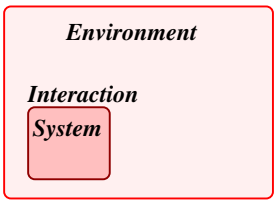


Figure 2.18: Sketch of the system and bath coupling.

2.2 Fluctuations

There are several possible sources of fluctuations:

- **Thermal**: the system is coupled to a classical 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 [18], spins [19], fermions) with chosen distributions of coupling constants and energies.

2.3 The classical reduced partition function

We analyze the statistical **static** properties of a **classical canonical system** in equilibrium at inverse temperature β 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, $Z_{\rm tot}$:

$$Z_{\rm tot}[\eta] = \sum_{\substack{\text{conf env} \\ \text{conf syst}}} \exp(-\beta H_{\rm tot} - \beta\eta x) \tag{2.1}$$

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

$$H_{\rm tot} = H_{\rm syst} + H_{\rm env} + H_{\rm int} + H_{\rm counter} = H_{\rm syst} + \tilde{H}_{\rm env} \ . \tag{2.2}$$

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

$$H_{\rm syst} = \frac{p^2}{2M} + V(x) \ , \tag{2.3}$$

with p and x its momentum and position. $H_{\rm env}$ is the Hamiltonian of a 'thermal bath' that, for simplicity, we take to be an ensemble of N independent harmonic oscillators [17, 18] with masses m_a and frequencies ω_a, $a = 1, \ldots, N$

$$H_{\rm env} = \sum_{a=1}^{N} \frac{\pi_a^2}{2m_a} + \frac{m_a\omega_a^2}{2} q_a^2 \tag{2.4}$$

with π_a and q_a their momenta and positions. This is indeed a very usual choice since it may represent phonons. (These oscillators could be the normal modes of a generic Hamiltonian expanded to quadratic order around its absolute minimum, written in terms of other pairs of conjugate variables; the bath could be, for instance, a chain of harmonic oscillators with nearest-neighbor couplings.) $H_{\rm int}$ is the coupling

between system and environment. We will restrict the following discussion to a linear interaction in the oscillator coordinates, q_a, and in the particle coordinate,

$$H_{\rm int} = x \sum_{a=1}^{N} c_a q_a \ , \tag{2.5}$$

with c_a the coupling constants. The counter-term $H_{\rm counter}$ 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

$$H_{\rm counter} = \frac{1}{2} \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} x^2 \ . \tag{2.6}$$

We note that the addition of the counter-term makes the combination of the environmental, interaction and counter-term Hamiltonians take a rather simple and natural form

$$\tilde{H}_{\rm env} = H_{\rm env} + H_{\rm int} + H_{\rm counter} = \sum_a \frac{m_a \omega_a^2}{2} \left(q_a + \frac{c_a}{m_a \omega_a^2} x \right)^2 \ . \tag{2.7}$$

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 at the expense of modifying the counter-term. 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

$$Z_{\rm red}[\eta] \propto \sum_{\rm conf\ syst} \exp \left[-\beta \left(H_{\rm syst} + H_{\rm counter} + \eta x - \frac{1}{2} \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} \ x^2 \right) \right] \ . \tag{2.8}$$

The 'counter-term' $H_{\rm counter}$ is chosen to cancel the last term in the exponential and it avoids the renormalization of 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 $c_a \to 0$). 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

$$\boxed{Z_{\rm red}[\eta] \propto \sum_{\rm conf\ syst} \exp\left[-\beta\left(H_{\rm syst} + \eta x\right)\right] = Z_{\rm syst}[\eta]\ .} \tag{2.9}$$

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

The interaction with the reservoir does not modify the statistical properties of the particle since $Z_{\rm red} \propto Z_{\rm syst}$, independently of the choices of c_a, m_a, ω_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. 2.4.

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.

2.4 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 modelled as stochastic processes with Langevin equations [28, 29, 30, 31, 32, 33], 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 was originally proposed to model the motion of a colloidal particle in a liquid but it was soon realised that generalisations of it can be used in a much wider context to describe, e.g. the motion of ions in water of the reorientation

of dipolar molecules, or some collective variable of a macroscopic system. It 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 in Sect. 2.4.1 and we derive it in more generality in Sect. 2.4.2.

2.4.1 Langevin's Langevin equation

The Langevin equation[5] for a particle moving in one dimension in contact with a **white-noise** bath reads

$$\boxed{m\dot{v} + \gamma_0 v = F + \xi \;, \qquad v = \dot{x} \;,} \tag{2.10}$$

with x and v the particle's position and velocity.

The fluctuating force ξ is supposed to come from occasional impacts of the Brownian particle with molecules of the surrounding medium. The force during an impact is supposed to vary with extreme rapidity over the time of any observation. Then the effects of the fluctuating force can be summarised by giving its first and second moments, as time averages over an infinitesimal time interval. ξ is then a Gaussian white noise with zero mean $\langle \xi(t) \rangle$ and correlation $\langle \xi(t)\xi(t') \rangle = 2\gamma_0 k_B T \delta(t - t')$. The delta function in time indicates that there is no correlation between impacts in any distinct time intervals around t and t'. $\gamma_0 v$ 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 γ_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 $\langle v^2(t) \rangle \to \langle v^2 \rangle_{eq}$. We will give a different argument for it in the next section.

2.4.2 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

[5] P. Langevin, *Sur la théorie du mouvement brownien*, Comptes-Rendus de l'Académie des Sciences **146**, 530-532 (1908).

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 defined by $H_{\rm tot}$. A derivation of a generalized Langevin equation with memory is very simple starting from Newton dynamics of the full system [17, 33, 20].

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. 2.1**.

Hamilton's equations for the particle are

$$\dot{x}(t) = \frac{p(t)}{m} \ , \qquad \dot{p}(t) = -V'[x(t)] - \sum_{a=1}^{N} c_a q_a(t) - \sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} x(t) \tag{2.11}$$

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

$$\dot{q}_a(t) = \frac{\pi_a(t)}{m_a} \ , \qquad \dot{\pi}_a(t) = -m_a \omega_a^2 q_a(t) - c_a x(t) \ , \tag{2.12}$$

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

$$q_a(t) = q_a(0)\cos(\omega_a t) + \frac{\pi_a(0)}{m_a \omega_a}\sin(\omega_a t) - \frac{c_a}{m_a \omega_a}\int_0^t dt' \sin[\omega_a(t-t')] x(t') \tag{2.13}$$

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. (2.11) yields

$$\boxed{\dot{p}(t) = -V'[x(t)] + \xi(t) - \int_0^t dt' \ \Gamma(t-t')\dot{x}(t') \ ,} \tag{2.14}$$

with the **symmetric and stationary kernel** Γ given by

$$\boxed{\Gamma(t-t') = \textstyle\sum_{a=1}^{N} \frac{c_a^2}{m_a \omega_a^2} \cos[\omega_a(t-t')] \ ,} \tag{2.15}$$

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

$$\boxed{\xi(t) = -\textstyle\sum_{a=1}^{N} c_a \left[\frac{\pi_a(0)}{m_a \omega_a}\sin(\omega_a t) + \left(q_a(0) + \frac{c_a x(0)}{m_a \omega_a^2}\right)\cos(\omega_a t)\right] \ .} \tag{2.16}$$

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

$\xi(t)$ is a sum of oscillating functions of time. The third term on the rhs of eq. (2.14) 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**:

$$\boxed{\gamma(t-t') = \Gamma(t-t')\theta(t-t')\ .} \tag{2.17}$$

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. Two important points can be make here. On the one hand, one can check, by simple numerical generation, that the function ξ at, say, fixed t resembles more and more a random variable as the number of oscillators increases (for incommensurate frequencies ω_a). The initial conditions for the oscillators are the seeds of the random number generator. This is similar to what happens with random number generators in the sense that these are, ultimately, periodic functions with a finite recurrence time that, however, can be made sufficiently long for computational purposes. Therefore, ξ is a **pseudo random number**. On the other hand, one can directly introduce the **statistical element** 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** β. (Note that one needs to assume that the oscillators interacted in the past to establish ergodicity and reach this pdf, though they do not do any longer.) Then, one chooses $\{\pi_a(0), q_a(0)\}$ to be initially distributed according to a canonical phase space distribution:

$$\boxed{P(\{\pi_a(0), q_a(0)\}, x(0)) = 1/\tilde{\mathcal{Z}}_{\rm env}[x(0)]\ e^{-\beta \tilde{H}_{\rm env}[\{\pi_a(0), q_a(0)\}, x(0)]}} \tag{2.18}$$

with $\tilde{H}_{\rm env} = H_{\rm env} + H_{\rm int} + H_{\rm counter}$, that can be rewritten as

$$\tilde{H}_{\rm env} = \sum_{a=1}^{N} \left[\frac{m_a \omega_a^2}{2} \left(q_a(0) + \frac{c_a}{m_a \omega_a^2} x(0) \right)^2 + \frac{\pi_a^2(0)}{2m_a} \right] . \tag{2.19}$$

Again, the presence of $H_{\rm counter}$ here is for convenience. The randomness in the initial conditions gives rise to a random force acting on the reduced system. Indeed, ξ is now a **Gaussian random variable**, that is to say a noise, with

$$\langle \xi(t) \rangle = 0\,, \qquad \langle \xi(t)\xi(t') \rangle = k_B T\ \Gamma(t-t')\ . \tag{2.20}$$

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

$$P[\xi] = \mathcal{Z}^{-1} e^{-\frac{1}{2k_BT}\int_0^t dt \int_0^t dt'\ \xi(t)\Gamma^{-1}(t-t')\xi(t')} \ . \tag{2.21}$$

$\mathcal{Z}$ is the normalization. A random force with non-vanishing correlations on a finite support is usually called a **coloured noise**. Equation (2.14) 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. 2.1** and eq. (2.33).

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_BT. This is a generalized form of the **fluctuation-dissipation relation**, and it applies to the environment.

About the bath

One last comment is in order here. A closed ensemble of harmonic oscillators is an integrable system that does not equilibrate in strict sense. Still, we are using it as a model for a thermal bath. One can argue that the oscillators were in interaction in the past, before being connected to the system, and that this allowed them to reach the Boltzmann probability distribution that is used for their initial states in this calculation. Or else, one can follow the calculations by Mazur & Montroll and see that in the limit of a large number of degrees of freedom the **Poincaré recurrence time** for the system of non-interacting harmonic oscillators becomes so large that it lies beyond any relevant time for the relaxation of the system that is coupled to the oscillator bath[6].

About the counterterm.

Had we not added the counter term the equation would read

$$\dot{p}(t) = -V'[x(t)] + \sum_{a=1}^{N} \frac{c_a^2}{m_a\omega_a^2} x(t) + \xi(t) - \int_0^t dt'\ \Gamma(t-t')\dot{x}(t') \ , \tag{2.22}$$

that is like eq. (2.14) for $V \mapsto V - \frac{1}{2}\sum_{a=1}^{N} \frac{c_a^2}{m_a\omega_a^2} x^2$, as we found with the analysis of the partition sum. Note that, as we will take $c_a = \tilde{c}_a/\sqrt{N}$, with $\tilde{c}_a$ of $O(1)$, the

[6] P. Mazur and E. Montroll, *Poincaré cycles, ergodicity, and irreversibility in assemblies of coupled harmonic oscillators*, J. Math. Phys. **1**, 70 (1960).

constant resulting from the sum over a is $O(1)$. For the distribution of the initial values we can still use $\widetilde{H}_{\rm env}$ or we can choose a Maxwell-Boltzmann distribution with $H_{\rm env} + H_{\rm int}$ alone. The result will be the same, as the supplementary term goes into the normalisation constant for $P_{\rm env}(0)$.

The bath kernel Γ.

Different choices of the environment are possible by selecting different ensembles of harmonic oscillators [7]. 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

$$\boxed{S(\omega) \equiv \frac{1}{N}\sum_{a=1}^{N} \frac{\tilde{c}_a^2}{m_a\omega_a}\,\delta(\omega-\omega_a)} \tag{2.23}$$

a function of ω, of order one with respect to N, and rewrites the kernel Γ as

$$\boxed{\Gamma(t-t') = \int_0^\infty d\omega\, \frac{S(\omega)}{\omega}\,\cos[\omega(t-t')]\,.} \tag{2.24}$$

The spectral density $S(\omega)$ is a weighted sum over the frequencies of the oscillators in the bath. For all finite N it is then just a discrete sum of delta functions. In the limit $N \to \infty$ it can become, instead, a regular function of ω. Assuming this limit is taken, several proposals for the resulting function $S(\omega)$ are made. A common choice is

$$\boxed{\frac{S(\omega)}{\omega} = \frac{2\gamma_0}{\pi}\left(\frac{|\omega|}{\tilde{\omega}}\right)^{\alpha-1} f_c\left(\frac{|\omega|}{\Lambda}\right)\,.} \tag{2.25}$$

The function $f_c(x)$ is a high-frequency cut-off of typical width Λ 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 γ_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 in Sec. 2.4.8. When $\alpha > 1$ ($\alpha < 1$) the bath is **superOhmic** (**subOhmic**). The exponent α is taken to be > 0 to avoid divergencies at low frequency. For the exponential cut-off the integral over ω can be computed for $\alpha = 1$ and $\alpha \neq 1$. In the former Ohmic case one finds

$$\Gamma(t) = \frac{2\gamma_0}{\pi}\,\frac{\Lambda}{[1+(\Lambda t)^2]}\,. \tag{2.26}$$

[7] See, G. W. Ford, M. Kac, and P. Mazur, *Statistical mechanics of assemblies of coupled oscillators*, J. Math. Phys. **6**, 504 (1965), for a detailed analysis.

In the $\Lambda \to \infty$ limit one approaches the Stratonovich limit and $\Gamma(t)$ becomes a delta-function, $\Gamma(t) \to 2\gamma_0\delta(t)$ such that $\int_0^t dt'\ \Gamma(t-t') = 2\gamma_0 \arctan(\Lambda t) \to \gamma_0$ for $\Lambda \to \infty$. In the latter non-Ohmic case the integral over ω yields

$$\Gamma(t) = \frac{2\gamma_0}{\pi}\tilde{\omega}^{-\alpha+1}\ \Gamma_{\rm E}(\alpha)\ \Lambda^\alpha\ \frac{\cos[\alpha \arctan(\Lambda t)]}{[1+(\Lambda t)^2]^{\alpha/2}} \tag{2.27}$$

with $\Gamma_{\rm E}(\alpha)$ the Euler Gamma-function. At long times, for any $\alpha > 0$ and $\alpha \neq 1$, one has

$$\lim_{\Lambda t\to\infty} \Gamma(t) \ = \ \frac{2\gamma_0}{\pi}\tilde{\omega}\ \cos(\alpha\pi/2)\Gamma_{\rm E}(\alpha)\ (\tilde{\omega}t)^{-\alpha}\ , \tag{2.28}$$

a **power law decay**.

Dimensional analysis

The noise ξ is a force and it should have dimensions $[\xi] = ML/T^2$ with $[m_a] = M$, $[q_a] = L$ and the frequencies $[\omega_a] = 1/T$. From their definition one finds $[c_a] = M/T^2$, $[\Gamma] = [S(\omega)] = M/T^2$ and $[\gamma_0] = M/T$.

Exercise 2.1 Prove that for a non-linear coupling $H_{\rm int} = \mathcal{V}[x]\sum_{a=1}^N c_a q_a$ there is a choice of counter-term for which the Langevin equation reads

$$\boxed{\dot{p}(t) = -V'[x(t)] + \xi(t)\mathcal{V}'[x(t)] - \mathcal{V}'[x(t)]\int_0^t dt'\ \Gamma(t-t')\mathcal{V}'[x(t')]\dot{x}(t')} \tag{2.29}$$

with the same Γ as in eq. (2.15) and $\xi(t)$ given by eq. (2.16) with $x(0) \to \mathcal{V}[x(0)]$. The noise appears now **multiplying** a function of the particles' coordinate. Applications of this kind of equations are manifold. For instance, the random motion of a colloid in a confined medium is mimicked with a Langevin equation in which the friction coefficient depends on the position notably close to the walls [91].

Exercise 2.2 Take now a system made of $i = 1, \ldots, n$ variables collected in two n-component vectors $\vec{p}, \vec{x}$. Use $H_{\rm int} = \sum_{i=1}^n \sum_{a=1}^N c_{ai} q_{ai} x_i$ as the coupling between system and bath and an ensemble of n independent sets of harmonic oscillators for the bath. Prove that the stochastic equation is

$$\dot{p}_i(t) = -\frac{\delta V[x(t)]}{\delta x_i(t)} + \xi_i(t) - \int_0^t dt'\ \Gamma_i(t-t')\dot{x}_i(t') \qquad\qquad i = 1, \ldots, n \tag{2.30}$$

where there is no sum over repeated indices and Γ_i and ξ_i are given by

$$\Gamma_i(t-t') = \sum_{a=1}^{N} \frac{c_{ai}^2}{m_{ai}\omega_{ai}^2} \cos[\omega_{ai}(t-t')] \,, \tag{2.31}$$

$$\xi_i(t) = -\sum_{a=1}^{N} c_a \left[\frac{\pi_{ai}(0)}{m_{ai}\omega_{ai}} \sin(\omega_{ai}t) + \left(q_{ai}(0) + \frac{c_{ai}x_i(0)}{m_{ai}\omega_{ai}^2} \right) \cos(\omega_{ai}t) \right] \,. \tag{2.32}$$

The i dependence in Γ_i can be ignored if the ensembles of oscillators are equivalent (i.e. same distribution of parameters). Characterise next the mean $\langle \xi_i(t) \rangle$ and the correlation $\langle \xi_i(t)\xi_j(t') \rangle$ and see under which conditions $\langle \xi_i(t)\xi_j(t') \rangle = \delta_{ij}\Gamma(t-t')$.

Exercise 2.3 Take now a system made of $i = 1, \ldots, n$ variables collected in $\vec{p}, \vec{x}$. Use $H_{\rm int} = \mathcal{V}[x] \sum_{a=1}^{N} c_a q_a$ as the coupling between system and bath, where x is the modulus of the vector $\vec{x}$. Prove that the stochastic equation is

$$\begin{aligned} \dot{p}_i(t) = &-\frac{\delta V[x(t)]}{\delta x_i(t)} + \xi(t)\frac{\delta \mathcal{V}[x(t)]}{\delta x_i(t)} \\ &-\frac{\delta \mathcal{V}[x(t)]}{\delta x_i(t)} \int_0^t dt' \; \Gamma(t-t') \sum_{j=1}^{n} \frac{\delta \mathcal{V}[x(t')]}{\delta x_j(t')} \dot{x}_j(t') \end{aligned} \tag{2.33}$$

with the same Γ and ξ as in eqs. (2.15) and (2.16) with $x(0) \to \mathcal{V}[x(0)]$. There is only one noise component and it appears **multiplying** a function of the particles' coordinate.

Exercise 2.4 The classical phonon Hamiltonian in one dimension is

$$H = \sum_{\ell=-N/2+1}^{N/2} \frac{p_\ell^2}{2} + \sum_{\ell=-N/2+1}^{N/2} \frac{(q_\ell - q_{\ell-1})^2}{2} \tag{2.34}$$

where ℓ is the lattice site index and, for simplicity, we took $m_\ell = \omega_\ell = 1$. The last term is a neares-negihbour coupling. We assume periodic boundary conditions on the chain. Let us also consider a linear coupling of the form $H_I = -q_0 x$ between the central site and the system's coordinate x. Show that going to the Fourier modes $Q_k = N^{-1/2} \sum_{\ell=-N/2+1}^{N/2} e^{ik\ell} q_\ell$ all phonons decouple into independent harmonic oscillators with frequencies $\omega_k^2 = 2(1-\cos ka) = 4\sin^2(ka/2)$, with a the lattice spacing, and the coupling constants between the variable and all Fourier modes are $c_k = N^{-1/2}$. The periodicity $q_N = q_0$ imposes the quantisation of the wave-vectors,

$k = 2\pi n/(Na)$ with $n \in \mathrm{Z}$. Each k describes a normal mode of vibration and within the first Brillouin zone there are N modes.

This calculation can be extended to higher dimensions.

2.4.3 Irreversibility and dissipation.

The friction force $-\gamma_0 v$ in eq. (2.10) – or its retarded extension in the non-Markovian case – explicitly breaks time-reversal ($t \to -t$) 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.

Time reversibility in Newton (or Hamilton) dynamics is the statement that $x(-t)$ (or $\{x(-t), -p(-t)\}$) satisfy the same dynamic equations as $x(t)$ ($\{x(t), p(t)\}$).

The dynamics of the selected variable is still reversible, in the sense that the pair $\{x(-t), -p(-t)\}$ satisfies the same equation as $\{x(t), p(t)\}$, as long as N is kept finite *and* the oscillator positions and momenta are taken as $\{q_a(0), -\pi_a(0)\}$ (instead of $\{q_a(0), \pi_a(0)\}$). In order to prove this statement, we can start from the equation evaluated at $t - t$. The tricky terms, stemming from the integration over the oscillators, evaluated at $-t$ are:

$$
\begin{aligned}
&-\frac{1}{m}\int_0^{-t} dt' \; \frac{c_a^2}{m_a\omega_a^2}\cos[\omega_a(-t-t')]\overline{p}(t') \\
&\qquad -c_a\left[\frac{\overline{\pi}_a(0)}{m_a\omega_a}\sin(-\omega_a t) + \left(\overline{q}_a(0) + \frac{c_a\overline{x}(0)}{m_a\omega_a^2}\right)\cos(-\omega_a t)\right] \\
&-\frac{1}{m}\int_0^{-t} dt' \; \frac{c_a^2}{m_a\omega_a^2}\cos[\omega_a(t+t')]\overline{p}(t') \\
&\qquad -c_a\left[-\frac{\overline{\pi}_a(0)}{m_a\omega_a}\sin(\omega_a t) + \left(\overline{q}_a(0) + \frac{c_a\overline{x}(0)}{m_a\omega_a^2}\right)\cos(\omega_a t)\right] \\
&+\frac{1}{m}\int_0^{t} dt' \; \frac{c_a^2}{m_a\omega_a^2}\cos[\omega_a(t-t')]\overline{p}(-t') \\
&\qquad -c_a\left[-\frac{\overline{\pi}_a(0)}{m_a\omega_a}\sin(\omega_a t) + \left(\overline{q}_a(0) + \frac{c_a\overline{x}(0)}{m_a\omega_a^2}\right)\cos(\omega_a t)\right]
\end{aligned}
\tag{2.35}
$$

where we did not write the sum over a to alleviate the notation. The overlined variables are yet now known, they are the ones that we will later choose to get

the same form for these and the original terms originating in the bath coupling. It is now clear that this aim is attained if one uses $\overline{x}(t) = x(-t)$, $\overline{p}(-t) = -p(-t)$, $\overline{q}_a(t) = q_a(-t)$, $\overline{\pi}_a(-t) = -\pi_a(-t)$, and the last condition implies that $-\pi(0)$ has to be used in the last line.

Even in the case in which all forces derive from a potential, $F = -dV/dx$, the energy of the particle, $H_{\rm cyst} = mv^2/2+V$, is not conserved. This can be easily seen by taking $dH_{\rm cyst}/dt = mv\dot{v}+V'v = v(-\gamma_0 v+\xi)$, say, in the case of additive white noise. The second member does not vanish in general. Its sign is not determined either unless at zero-temperature, when it is negative semi-definite, $-\gamma_0 v^2$, indicating that the dynamics are of gradient descent. On average, in the absence of non-potential energy injecting forces, and for confining potentials, one finds that the energy 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. We will see this mechanism at work in some examples in Sect. 2.5.

Exercise 2.5 Prove the time-irreversibility of the Langevin equation and the fact that the symmetry is restored if $\gamma_0 = 0$. (Show that $\mathbf{v}(-t)$ does not satisfy the same equation as $\mathbf{v}(t)$.)

Exercise 2.5 Show that $d\langle H_{\rm syst}\rangle/dt \neq 0$ when $\gamma_0 \neq 0$. Prove that for a single variable, the non-zero terms can be found from the analysis of $t' \to t^-$ and $t' \to t^+$ limits of $\gamma_0\langle\dot{x}(t)\dot{x}(t')\rangle - 2\gamma_0 T\langle\xi(t)\dot{x}(t')\rangle$. Relate the last term to the linear response function. Discuss the equilibrium case, in which $m\langle\dot{x}^2(t)\rangle = k_B T$ (equipartition).

2.4.4 Stochastic thermodynamics

The energy of the system.

Let's multiply the Langevin equation by $v(t)$[8]. We find

$$\frac{d}{dt}\left[\frac{1}{2}mv^2 + V(x)\right] = v(t)\xi(t) - v(t)\int_0^t dt'\ \Gamma(t-t')v(t') \ . \tag{2.36}$$

Now integrate over time between t_1 and t_2

$$H_{\rm syst}(t_2) - H_{\rm syst}(t_1) = \int_{t_1}^{t_2} dt\ \xi(t)v(t) - \int_{t_1}^{t_2} dt\ \int_0^t dt'\ v(t)\Gamma(t-t')v(t') \ . \tag{2.37}$$

[8]Subtle issues about the chain-rule for derivatives of functions of stochastic variables will be discussed in future Sections. For equations with inertia and/or coloured noise, these problems do not pose.

As there is no reason to suppose that the rhs be identical to zero, one finds that the energy of the system fluctuates and is not constant. Note also that, although the velocity is a Gaussian random variable, the kinetic energy, being given by its square, is not.

Non potential forces.

Time-dependent, $f(t)$, and constant non-potential forces, $f^{\rm np}$ (in higher dimensions), 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.

The energy balance under non-potential forces can be done as above, by multiplying the Langevin equation by $v(t)$. One gets an addition term due to the work done by the non-potential force over the interval $[t_1, t_2]$:

$$\begin{aligned} H_{\rm syst}(t_2) - H_{\rm syst}(t_1) &= \int_{t_1}^{t_2} dt\ f(t)v(t) + \int_{t_1}^{t_2} dt\ \xi(t)v(t) \\ &\quad - \int_{t_1}^{t_2} dt \int_0^t dt'\ v(t)\Gamma(t-t')v(t') \end{aligned} \tag{2.38}$$

The first term on the rhs is the work done by the time-dependent force. The second and third terms can be associated to the heat given or taken from the bath, if a fluctuating energy balance relation

$$\Delta H_{\rm syst} = W^f_{t_1 \to t_2} + \Delta Q \tag{2.39}$$

is proposed. Note that the sign of the last contribution is not fixed and it can be negative meaning that heat can go from the bath to the system. Interest in computing the probability distribution functions of each of these terms is current in the literature. This is part of the so-called **stochastic thermodynamics**, or the idea to extend notions of thermodynamics such as work, heat and entropy, to individual trajectories [21]. These pdfs are of relevance in the study of small systems, especially biological molecules and the like, but also in microfluidics, nanomachines, nano sensing devices, a many other fields. Exact relation for the probability of measuring a positive over the probability of measuring a negative quantity such as the work or heat, have been derived and are special cases of the so-called **fluctuation theorems**.

2.4.5 Smoluchowski (over-damped) limit

In many situations in which friction is very large, the characteristic time for the relaxation of the velocity degrees of freedom to their Maxwell distribution, t_r^v, is very short (see the examples in Sect. 2.5). 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

$$\gamma_0 \dot{x} = F + \xi \tag{2.40}$$

(for simplicity we wrote the white-noise case). Indeed, this **over-damped** 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 γ_0 is small are called **under-damped**.

In the over-damped limit with white-noise the friction coefficient γ_0 can be absorbed in a rescaling of time. One defines the new time τ

$$t = \gamma_0 \tau \ , \tag{2.41}$$

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 $\langle \eta(\tau)\eta(\tau')\rangle = 2k_B T \delta(\tau - \tau')$.

Exercise 2.6 Redefine time as $\tau = k_B T \gamma_0^{-1}\, t$ and $\tilde{x}(\tau) = x(\gamma_0 \beta t)$, and similarly for the other function of time, to transform the Langevin equation into

$$\dot{\tilde{x}} = \beta \tilde{F} + \tilde{\xi} \ , \qquad\qquad \langle \tilde{\xi}(\tau)\tilde{\xi}(\tau')\rangle = 2\delta(\tau - \tau') \ . \tag{2.42}$$

This equation is not well adapted to take the $T \to 0$ limit.

2.4.6 Markov character and generation of memory

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.

The Langevin equation (2.10) 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:

$$m\ddot{x} + \gamma_0 \dot{x} = F + \xi \ . \tag{2.43}$$

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.

A simple solvable example that illustrates this feature is the under-damped white-noise Langevin equation for a harmonic oscillator:

$$m\dot{x} = p \;, \qquad\qquad \dot{p} = -m\omega^2 x - \frac{\gamma_0}{m}\, p + \xi \;, \tag{2.44}$$

with initial condition $p(0) = 0$ and white noise such that $\langle \xi(t)\xi(t')\rangle = 2\gamma k_B T \delta(t-t')$. The second equation can be solved exactly

$$p(t) = \int_0^t dt' \; e^{-\frac{\gamma_0}{m}(t-t')} \; [-m\omega^2 x(t') + \xi(t')] \tag{2.45}$$

and when this solution is put back into the equation for $\dot{x}$ one finds an equation with memory,

$$\dot{x}(t) = -\int_0^t dt' \; K(t-t')x(t') + \xi_x(t) \;, \tag{2.46}$$

with

$$K(t) = \omega^2 \; e^{-\frac{\gamma_0}{m}t} \qquad \text{and} \qquad \xi_x(t) = \frac{1}{m}\int_0^\infty dt' \; e^{-\frac{\gamma_0}{m}(t-t')} \; \xi(t') \;. \tag{2.47}$$

The statistical properties of the new noise can be derived from the ones of the original noise ξ. It keeps the zero average and its correlations are

$$\langle \xi_x(t)\xi_x(t')\rangle = \frac{k_B T}{m\omega^2} \; K(|t-t'|) \;. \tag{2.48}$$

The solution of this problem will be developed in Sect. 2.5.2.

Whenever a variable is integrated out from a Markov set of equations a non-Markov equation is obtain. Proceeding in the reverse sense one can transform a non-Markov equation with exponentially correlated noise into a set of Markov equations that are easier to integrate numerically.

2.4.7 Distinction between relaxation and equilibration

A system coupled to an environment can relax to a non-equilibrium steady state, usually called a ness, that is not the one of thermal equilibrium, $P(v,x;t) \to P_{\rm st}(v,x) \neq P_{\rm GB}(v,x)$.

2.4.8 Phenomenological Langevin equations

In so far we have discussed a system with position and momentum degrees of freedom. Many fields in physics and other sciences use Langevin-like equations to describe the dynamic behavior of a selected set of variables, of different kind, in contact with an environment. Sometimes, these equations look different from the one that we derived above.

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 $V_C = -C^{-1}\int I dt$. The balance between these potentials implies a Langevin type equation for the current circulating across the circuit:

$$L\frac{d^2I}{dt^2} + R\frac{dI}{dt} + C^{-1}I = 0\ . \tag{2.49}$$

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

Classical Ising spins: the soft spin description

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 ± 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 will discuss one when dealing with the $O(N)$ model.

Classical Heisenberg spins

Another example is the **Landau-Lifshitz-Gilbert-Brown equation** for the

stochastic dynamics of a magnetic moment with constant magnitude:

$$\dot{\mathbf{M}} = -\frac{\zeta}{1+\zeta^2\gamma_0^2}\,\mathbf{M}\wedge\left(\mathbf{H}_{\rm eff}+\mathbf{H}+\frac{\gamma_0\zeta}{M_s}\,\mathbf{M}\wedge(\mathbf{H}_{\rm eff}+\mathbf{H})\right)\,, \tag{2.50}$$

in the Landau formulation or

$$\dot{\mathbf{M}} = -\zeta\mathbf{M}\wedge\left(\mathbf{H}_{\rm eff}+\mathbf{H}-\frac{\gamma_0}{M_s}\dot{\mathbf{M}}\right) \tag{2.51}$$

in the Gilbert formulation. $\mathbf{H}$ is a Gaussian white noise with zero mean and delta correlations. γ_0 is friction coefficient. A connection between the two formalisms is possible after the adequate identification of parameters (**Exercise 2.7**). Noise is multiplicative and, as they are written, these equations conserve the modulus of the magnetization only if the Stratonovich calculus is used. Otherwise a drift term has to be added [36]. Note that this is not an irrelevant detail. Numerical codes written with the discretised stochastic differential equation in a different from Stratonovich scheme do not conserve the modulus of the magnetisation.

Classical dipoles

The translational motion of a particle i is characterized by its time-dependent position $\mathbf{r}_i$ and velocity $\mathbf{v}_i$. Imagine that each particle carries an electric dipole orientation $\mathbf{p}_i$. Although constant in modulus, the orientation of the dipole is time-dependent and can be characterized by an angular velocity vector $\boldsymbol{\omega}_i$ such that $d\mathbf{p}_i/dt = \boldsymbol{\omega}_i\times\mathbf{p}_i$. It is subjected to an external force $\mathbf{F}_i$ and to an external torque $\boldsymbol{\Gamma}_i$. For a particle of mass m and inertia tensor I (one can have thin rods in mind) one has

$$m\;\dot{\mathbf{v}}_i = -\gamma_0\mathbf{v}_i+\mathbf{F}_i+\boldsymbol{\eta}_i\,, \tag{2.52}$$

$$I\;\dot{\boldsymbol{\omega}}_i = -\zeta_0\boldsymbol{\omega}_i+\boldsymbol{\Gamma}_i+\boldsymbol{\lambda}_i\,. \tag{2.53}$$

Here $\boldsymbol{\eta}_i$ and $\boldsymbol{\lambda}_i$ are Gaussian random forces and torques, respectively, introduced to account for the thermal exchanges with the surrounding medium. The friction coefficients γ_0 and ζ_0 govern the dissipation into the thermal bath. Just as γ_0 and $\boldsymbol{\eta}_i$ are related by a Stokes-Einstein relation, a similar relation between ζ_0 and $\boldsymbol{\lambda}_i$ exists. The Gaussian random contributions $\boldsymbol{\eta}_i$ and $\boldsymbol{\lambda}_i$ have δ-correlations in time, the amplitude of which is constrained by the condition that for conservative forces the equilibrium distribution should be the standard Boltzmann-Gibbs exponential factor, $\langle\eta_i(t)\eta_j(t')\rangle = 2\gamma_0 k_B T\delta_{ij}\delta(t-t')$, and similarly for $\lambda_i(t)$ with γ_0 replaced

by ζ_0. In physical conditions under which inertial effects can be discarded, at low Reynolds numbers, one obtains a set of over-damped Langevin equations

$$\gamma_0 \, \dot{\mathbf{r}}_i = \mathbf{F}_i + \boldsymbol{\eta}_i \, , \tag{2.54}$$

$$\zeta_0 \, \dot{\mathbf{p}}_i = \boldsymbol{\Gamma}_i \times \mathbf{p}_i + \boldsymbol{\lambda}_i \times \mathbf{p}_i \, , \tag{2.55}$$

in which the latter equation, which features a multiplicative noise, is to be understood with the Stratonovich, mid-point, discretization scheme, that ensures the conservation of the modulus of the dipole, as can be seen directly from (2.55). The ingredients entering the force $\mathbf{F}_i$ felt by particle i include an external force field and possible interactions with other colloids. Similarly, the torque $\boldsymbol{\Gamma}_i$ felt by particle i can include the effect of an external field. In general, the interaction energy $V(\mathbf{r}_i - \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j)$ between particles i and j depends on the distance between these particles and on the orientation of the dipoles they carry, as is the case in the well-known dipole-dipole interaction $V(\mathbf{r}_i - \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j) = \frac{1}{4\pi\epsilon_0}\left[\frac{\mathbf{p}_i \cdot \mathbf{p}_j}{r_{ij}^3} - 3\frac{(\mathbf{p}_i \cdot \mathbf{r}_{ij})(\mathbf{p}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5}\right]$. Both the force $\mathbf{F}_i$ and the torque then derive from the total potential energy $E_{\rm pot} = \frac{1}{2}\sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j, \mathbf{p}_i, \mathbf{p}_j)$ according to

$$\mathbf{F}_i = -\frac{\partial E_{\rm pot}}{\partial \mathbf{r}_i} \, , \qquad \boldsymbol{\Gamma}_i = -\mathbf{p}_i \times \frac{\partial E_{\rm pot}}{\partial \mathbf{p}_i} \, . \tag{2.56}$$

The combination $\boldsymbol{\Gamma}_i \wedge \mathbf{p}_i$ can also be written in the form

$$\boldsymbol{\Gamma}_i \wedge \mathbf{p}_i = \mathbf{E}_i p_i^2 - (\mathbf{p}_i \cdot \mathbf{E}_i)\mathbf{p}_i \, , \qquad \mathbf{E}_i = -\frac{\partial E_{\rm pot}}{\partial \mathbf{p}_i} \, . \tag{2.57}$$

Active dumbbells

In the introduction we mentioned active matter as a field of current research. Active particles can take different forms, activity can also be modelled in various ways, but they are typically in contact with a thermal bath. A simple model of active particle is the one of a dumbbell, that is to say, a diatomic molecule formed by two spherical colloids with diameter $\sigma_{\rm d}$ and mass $m_{\rm d}$ linked together. The atomic positions are noted $\mathbf{r}_1$ and $\mathbf{r}_2$ in a Cartesian system of coordinates fixed to the laboratory. Typically, one assumes that there is an elastic link between the colloids modelled by the finite extensible non-linear elastic form

$$\mathbf{F}_{\rm fene} = -\frac{k\mathbf{r}}{1 - (r^2/r_0^2)} \tag{2.58}$$

with $k > 0$. The denominator ensures that the spheres cannot go beyond the distance r_0 with r the distance between their centres of mass. An additional repulsive force is added to ensure that the two colloids do not overlap. This is the Weeks-Chandler-Anderson (WCA) potential

$$V_{\rm wca}(r) \;=\; \begin{cases} V_{\rm LJ}(r) - V_{\rm LJ}(r_c) & r < r_c \\ 0 & r > r_c \end{cases}$$

with

$$V_{\rm LJ}(r) = 4\epsilon \left[\left(\frac{\sigma_{\rm d}}{r}\right)^{12} - \left(\frac{\sigma_{\rm d}}{r}\right)^{6} \right] \,, \tag{2.59}$$

where ϵ is an energy scale and r_c is the minimum of the Lennard-Jones potential, $r_c = 2^{1/6}\sigma_{\rm d}$. The active forces are polar and act along the main molecular axis $\hat{\mathbf{n}}$, are constant in modulus, and are the same for the two spheres belonging to the same molecule,

$$\mathbf{F}_{\rm act} = F_{\rm act}\ \hat{\mathbf{n}} \,. \tag{2.60}$$

The dynamic equations for one dumbbell are

$$m_d \ddot{\mathbf{r}}_i(t) \;=\; -\gamma_0 \dot{\mathbf{r}}_i(t) + \mathbf{F}_{\rm fene}(\mathbf{r}_{i,i+1}) - \frac{\partial V_{\rm wca}^{i\,i+1}}{\partial r_{i\,i+1}} \frac{\mathbf{r}_{i\,i+1}}{r_{i\,i+1}} + \mathbf{F}_{{\rm act}\,i} + \boldsymbol{\xi}_i \,, \tag{2.61}$$

$$m_d \ddot{\mathbf{r}}_{i+1}(t) \;=\; -\gamma_0 \dot{\mathbf{r}}_{i+1}(t) - \mathbf{F}_{\rm fene}(\mathbf{r}_{i,i+1}) - \frac{\partial V_{\rm wca}^{i+1,i}}{\partial r_{i+1,i}} \frac{\mathbf{r}_{i+1,j}}{r_{i+1,i}} + \mathbf{F}_{{\rm act}\,i} + \boldsymbol{\xi}_{i+1} \,, \tag{2.62}$$

with $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $r_{ij} = |\mathbf{r}_{ij}|$ and $V_{\rm wca}^{ij} \equiv V_{\rm wca}(r_{ij})$ with $V_{\rm wca}$ defined in Eq. (2.59). Once the active force is attached to a molecule a sense of back and forth atoms is attributed to them; $\mathbf{F}_{\rm act}$ is directed from the ith colloid (tail) to the $i+1$th colloid (head). $\mathbf{F}_{\rm act}$ changes direction together with the molecule's rotation. The coupling to the thermal bath is modelled as usual, with a friction and a noise term added to the equation of motion. γ_0 is the friction coefficient. The noise $\boldsymbol{\xi}$ is a Gaussian random variable with

$$\langle \xi_{ia}(t) \rangle \;=\; 0 \,, \tag{2.63}$$

$$\langle \xi_{ia}(t) \xi_{jb}(t') \rangle \;=\; 2\gamma_0 k_B T \delta_{ij} \delta_{ab} \delta(t - t') \,, \tag{2.64}$$

with k_B the Boltzmann constant and T the temperature of the equilibrium environment in which the dumbbells move. a and b label the coordinates in d dimensional space. An effective rotational motion is generated by the random torque due to the white noise acting independently on the two beads.

Fields

Langevin equations are also written for scalar fields

$$m\frac{d^2\phi(x,t)}{dt^2}+\gamma_0\frac{d\phi(x,t)}{dt}=-\frac{\delta V[\phi]}{\delta\phi(x,t)}+\xi(x,t) \tag{2.65}$$

or vector fields.

2.4.9 Discretization of stochastic differential equations

The way in which the stochastic differential equation (2.40) (with no inertia and with white noise) is to be discretized is a subtle matter. Two schemes are the most popular ones, called the Itô and Stratonovich calculus, and are rather well documented in the literature.[9] [35].

Let us try to explain, in a simple way, the origin of the subtleties and how they are controlled. We discretize time according to $t_n = ndt + t_0$ with n an integer running as $n = 0, \ldots, \mathcal{N}$. The continuous time limit will correspond to $dt \to 0$, $\mathcal{N} \to \infty$ while keeping $\mathcal{N}dt = \mathcal{T} - t_0$ fixed and $t_\mathcal{N} = \mathcal{T}$. We now take a single real variable x the dynamics of which is governed by the following stochastic equation

$$\boxed{d_t x(t) = f(x) + g(x)\xi(t)} \tag{2.66}$$

with multiplicative white noise distributed according to a Gaussian pdf with zero mean and variance $\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')$. This stochastic differential equation makes sense only when a discretization rule is explicitly given to define it.

We use the short-hand notation $x_n = x(t_n)$ and $\xi_n = \xi(t_n)$ The white noise statistics correspond to $\langle \xi_n \rangle = 0$ and $\langle \xi_n \xi_m \rangle = 2D/dt\ \delta_{nm}$ that implies $\xi_n^2 \simeq 2D/dt$ and $\xi_n \simeq \mathcal{O}(dt^{-1/2})$ (we use here the step realisation of the Dirac delta function as being identical to 0 away from the interval $[-dt/2, dt/2]$ and equal to $1/dt$ within this interval). We will use the generic α prescription [30]

$$\boxed{x_{n+1} - x_n = f(\overline{x}_n)dt + g(\overline{x}_n)\xi_n dt} \tag{2.67}$$

with

$$\boxed{\overline{x}_n \equiv \alpha x_{n+1} + (1-\alpha)x_n} \tag{2.68}$$

and $0 \leq \alpha \leq 1$ in the following. $\alpha = 0$ is the Itô prescription while $\alpha = 1/2$ is the Stratonovich one.

[9] 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).

Note that

$$\overline{x}_n = x_n + \alpha(x_{n+1} - x_n) \tag{2.69}$$
$$\overline{x}_n = x_{n+1} - (1-\alpha)(x_{n+1} - x_n) \tag{2.70}$$

that implies

$$x_n = \overline{x}_n - \alpha(x_{n+1} - x_n) \tag{2.71}$$
$$x_{n+1} = \overline{x}_n + (1-\alpha)(x_{n+1} - x_n) \tag{2.72}$$

allows one to rewrite the α-prescription equation as

$$\begin{aligned} x_{n+1} - x_n &= [f(x_n) + f'(x_n)\alpha(x_{n+1} - x_n) + \mathcal{O}((x_{n+1} - x_n)^2)]\, dt \\ &\quad + [g(x_n) + \alpha g'(x_n)(x_{n+1} - x_n) + \mathcal{O}((x_{n+1} - x_n)^2)]\, \xi_n dt \\ &\simeq f(x_n)dt + g(x_n)\xi_n dt + \alpha g'(x_n)(x_{n+1} - x_n)\xi_n dt \end{aligned} \tag{2.73}$$

where we used $\xi_n = \mathcal{O}(dt^{-1/2})$ to estimate the relevant contributions up to $\mathcal{O}(dt)$ and we dropped terms $\mathcal{O}(dt^{3/2})$. Replacing $x_{n+1} - x_n$ in the last term by the outcome of the same equation to order $dt^{1/2}$:

$$x_{n+1} - x_n \simeq f(x_n)dt + g(x_n)\xi_n dt + \alpha g'(x_n)g(x_n)(\xi_n dt)^2 \,. \tag{2.74}$$

As $(\xi_n dt)^2 \simeq 2Ddt$, all terms in the rhs are of order dt. We will use this expression to derive the Fokker-Planck equation.

The force term in the stochastic equation is also sometimes written as

$$\begin{aligned} f(\overline{x}_n) &= \alpha f(\overline{x}_n) + (1-\alpha) f(\overline{x}_n) \\ &= \alpha f(x_n + \alpha dx) + (1-\alpha) f(x_{n+1} - (1-\alpha)dx) \\ &= \alpha[f(x_n) + \alpha f'(x_n)dx + \dots] + (1-\alpha)[f(x_{n+1} - (1-\alpha)f'(x_{n+1})dx + \dots] \\ &= \alpha f(x_n) + (1-\alpha) f(x_{n+1}) + O(dx) \end{aligned}$$

and dropping the $O(dx)$ terms that appear multiplied by dt and give rise to negligible terms of $\mathcal{O}(dt^{3/2})$, one has

$$f(\overline{x}_n) = \alpha f(x_n) + (1-\alpha) f(x_{n+1}) \tag{2.75}$$

This is ultimately equivalent to writing the force term as $f(x_n)dt$ in the Langevin equation.

The chain rule

As explained in [30], the chain-rule for the time-derivative of a function V of the variable x depends on the stochastic equation governing the evolution of x; we call it the x-chain rule and for Eq. (2.66) it reads

$$\boxed{d_t V = \dot{x}\, V' + (1-2\alpha) D g^2 V''} \tag{2.76}$$

where $\dot{x} = d_t x = dx/dt$, $v' = \partial_x V$ and $V'' = \partial_x^2 V$. Note that the chain rule is independent of $f(x)$ (that is to say, it will take the same form for a Langevin equation with the drift term, Eq. (2.215), to be discussed below). Somehow surprisingly, the second term is still present for $g = 1$, the additive noise case. It only disappears and one recovers normal calculus for $\alpha = 1/2$.

We now prove Eq. (2.76). Let us write the difference between a generic function V evaluated at x at two subsequent times $n+1$ and n. We expand x_n around the generic α point $\bar{x}_n$ we get

$$\begin{aligned} V(x_{n+1}) - V(x_n) &= V(\bar{x}_n + (1-\alpha)(x_{n+1} - x_n)) - V(\bar{x}_n - \alpha(x_{n+1} - x_n)) \\ &= (x_{n+1} - x_n) V'(\bar{x}_n) + \tfrac{1}{2}(1-2\alpha)(x_{n+1} - x_n)^2 V''(\bar{x}_n) + \mathcal{O}(dt^{3/2}) \end{aligned}$$

where $dx = x_{n+1} - x_n$. Using $\boxed{(x_{n+1} - x_n)^2 = 2Dg(\bar{x}_n)^2 dt + \mathcal{O}(dt^{3/2})}$, from Eq. (2.67) after using $(\xi_n dt)^2 = 2Dt$, where the crucial fact is that this square is of order dt (instead to dt^2) because of the white noise character of the noise, that implies $\xi_n^2 = 2D/dt$, we obtain

$$V(x_{n+1}) - V(x_n) = (x_{n+1} - x_n) V'(\bar{x}_n) + (1-2\alpha) D g(\bar{x}_n)^2 V''(\bar{x}_n) dt + \mathcal{O}(dx^3)$$

and dropping terms of order $dt^{1/2}$ or higher,

$$\boxed{\frac{V(x_{n+1}) - V(x_n)}{dt} = \frac{x_{n+1} - x_n}{dt} V'(\bar{x}_n) + (1-2\alpha) D g(\bar{x}_n)^2 V''(\bar{x}_n)} \tag{2.77}$$

which is the chain-rule. As above, at this order one can replace the $\overline{x}_n$ in g, V' and V'' by any x in the interval. This expression is next written as in Eq. (2.76).

Exercise 2.8. Derive the chain rule for the stochastic equation with multiplicative white noise and inertia.

Influence of the discretisation on the trajectories

One can estimate the importance of the discretisation on the actual trajectories found by computing the difference between the two terms in the right-hand-side of the Langevin equation obtained for a discretisation α and another discretisation $\overline{\alpha}$.

Let us start with the first term, the one equal to f.

$$\begin{aligned} & f(\overline{x}_\alpha(t_t)) - f(\overline{x}_{\overline{\alpha}}(t_k)) \\ & \quad = f(x(t_k)) + f'(x(t_k))\alpha dx - f(x(t_k)) - f'(x(t_k))\overline{\alpha}dx + \mathcal{O}(dx^2) \\ & \quad = f'(x(t_k))(\alpha - \overline{\alpha})dx + \mathcal{O}(dx^2) \to 0 \qquad \text{for} \qquad dt \to 0 \end{aligned} \tag{2.78}$$

the last results being due to the fact that $dx = \mathcal{O}(dt^{1/2})$.

Now, we will find that the difference between the two noise-dependent terms evaluated at different discretisation parameters does not vanish in the same limit:

$$\begin{aligned} & g(\overline{x}_\alpha(t_t))\xi(t_k) - g(\overline{x}_{\overline{\alpha}}(t_k))\xi(t_k) \\ & \quad = [g(x(t_k)) + g'(x(t_k))\alpha dx - g(x(t_k)) - g'(x(t_k))\overline{\alpha}dx + \mathcal{O}(dx^2)]\xi(t_k) \\ & \quad = g'(x(t_k))(\alpha - \overline{\alpha})\xi(t_k)dx + \mathcal{O}(dx^2)\xi(t_k) = \mathcal{O}(dt^0) \end{aligned} \tag{2.79}$$

In consequence, there is a difference of order one in the trajectories found with one and the another discretisation scheme.

Numerical integration of the Langevin equation

The numerical integration of the Langevin equation requires the discretisation of time, $t_k = \epsilon k$ where k is an integer and ϵ the time-step. The choice of the optimal value of ϵ has to be gauged depending on the accuracy of the numerical integration desired (the smallest the ϵ the best) and the length of the time-interval wished to be analysed (one cannot take it to be so small because otherwise only too short time-scales are explored).

In the over-damped limit with additive white noise the most common algorithm used is just the simple iteration of the **Ito relation**

$$x(t_k) = x(t_{k-1}) - \epsilon V'(x(t_{k-1})) + \epsilon\xi(t_{k-1}) \; . \tag{2.80}$$

The only practical issue to stress here is that one needs to consider the time-discretised version of the delta-correlated white noise ξ, see App. :

$$\langle \xi(t_k)\xi(t_n)\rangle = \frac{2k_BT}{\epsilon} \qquad \text{if} \qquad |t_k - t_n| = \epsilon|k-n| < \epsilon/2 \tag{2.81}$$

that implies $\xi(t_k) = \sqrt{2k_BT/\epsilon}\;\eta_k$ with $\langle \eta_k\eta_n\rangle = \delta_{kn}$.

Exercise 2.9 Write an algorithm that integrates the Langevin equation and reproduce the results computed along this Section (for additive noise, in the over-damped limit) with the numerical results.

2.5 The basic processes

We will discuss the motion of the particle in some $1d$ representative potentials: under a constant force, in a harmonic potential, in the flat limit of these two (Fig. 2.19) and the escape from a metastable state and the motion in a double well potential (Fig. 2.29).

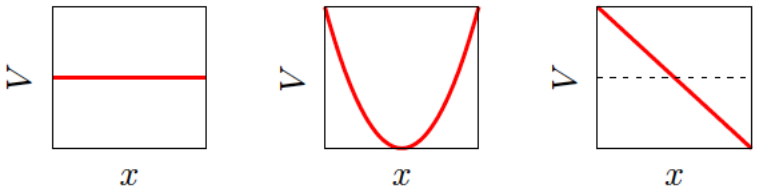


Figure 2.19: Three representative one-dimensional potentials.

2.5.1 A constant force

Let us first consider the case of a **constant force**, F. The first thing to notice is that the Maxwell-Boltzmann measure

$$P_{\rm GB}(v,x) \propto e^{-\beta\left(\frac{v^2}{2m}+V(x)\right)} \tag{2.82}$$

is not normalizable if the size of the line is infinite, due to the $\exp[-\beta V(x)] = \exp(\beta F x)$ term. Let us then study the evolution of the particle's velocity and position to show how these variables behave and the fact that they do very differently.

The problem to solve is a set of two coupled stochastic first order differential equations on $\{v(t), x(t)\}$, one needs two initial conditions v_0 and x_0.

The velocity

The time-dependent velocity follows from the integration of eq. (2.10) over time

$$v(t) = v_0\, e^{-\frac{\gamma_0}{m}t} + \frac{1}{m}\int_0^t dt'\, e^{-\frac{\gamma_0}{m}(t-t')}\,[\,F+\xi(t')\,]\,, \qquad\qquad v_0 \equiv v(t=0)\,.$$

The velocity is a **Gaussian variable** that inherits its average and correlations from the ones of ξ. Using the fact that the noise has zero average

$$\langle v(t)\rangle = v_0\ e^{-\frac{\gamma_0}{m}t} + \frac{F}{\gamma_0}\left(1 - e^{-\frac{\gamma_0}{m}t}\right)\ .$$

In the short time limit, $t \ll t_r^v = m/\gamma_0$, this expression approaches the Newtonian result ($\gamma_0 = 0$) in which the velocity grows linearly in time $v(t) \approx v_0(1 - \gamma_0/m\ t) + F/m\ t = v_0 + (F\gamma_0^{-1} - v_0)\ \gamma_0 m^{-1}\ t$. In the opposite long time limit, $t \gg t_r^v = m/\gamma_0$, for all initial conditions v_0 the averaged velocity decays exponentially to the constant value F/γ_0. The saturation when the bath is active ($\gamma_0 \neq 0$) is due to the friction term.

$$\langle v(t)\rangle = \begin{cases} v_0 + \left(\frac{F}{m} - \frac{v_0\gamma_0}{m}\right)\ t & t \ll t_r^v \\ \frac{F}{\gamma_0} & t \gg t_r^v \end{cases}$$

The **relaxation time** separating the two regimes is

$$\boxed{t_r^v = \tfrac{m}{\gamma_0}} \tag{2.83}$$

The velocity mean-square displacement is

$$\sigma_v^2(t) \equiv \langle (v(t) - \langle v(t)\rangle)^2\rangle = \frac{k_B T}{m}\left(1 - e^{-2\frac{\gamma_0}{m}t}\right) \tag{2.84}$$

independently of F. This is an example of the **regression theorem** according to which the equilibrium fluctuations decay in time following the same law as the average value. The short and long time limits yield

$$\sigma_v^2(t) \equiv \langle (v(t) - \langle v(t)\rangle)^2\rangle \simeq \frac{k_B T}{m}\begin{cases} \frac{2\gamma_0}{m}\ t & t \ll t_r^v \\ 1 & t \gg t_r^v \end{cases} \tag{2.85}$$

and the two expressions match at $t \simeq t_r^v/2$. The asymptotic limit is the result expected from equipartition of the velocity mean-square displacement, $\langle (v(t) - \langle v(t)\rangle)^2\rangle \to \langle (v(t) - \langle v\rangle_{\rm stat})^2\rangle_{\rm stat}$ that implies for the 'kinetic energy' $\langle K\rangle_{\rm stat} = k_B T/2$ only if the velocity is measured with respect to its average. In the heuristic derivation of the Langevin equation for $F = 0$ the amplitude of the noise-noise correlation, say A, is not fixed. The simplest way to determine this parameter is to require that equipartition for the kinetic energy holds $A/(\gamma_0 m) = T/m$ and hence $A = \gamma_0 T$. This relation is known under the name of **fluctuation–dissipation theorem** (fdt)

of the second kind in Kubo's nomenclature. It is important to note that this fdt characterizes the surrounding fluid and not the particle, since it relates the noise-noise correlation to the friction coefficient. In the case of the Brownian particle this relation ensures that after a transient of the order of t_r^v, the bath maintains the fluctuations of the velocity, σ_v^2, constant and equal to its equilibrium value.

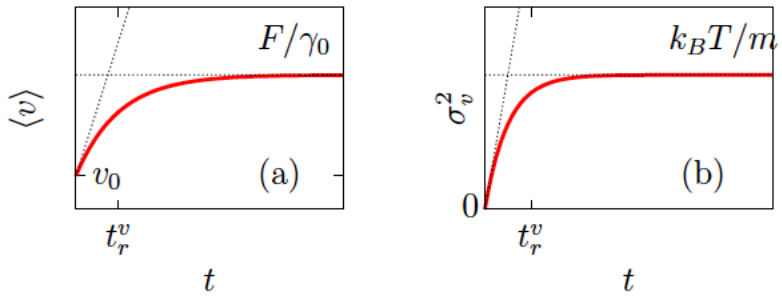


Figure 2.20: Results for the constant force problem. (a) Mean velocity as a function of time. (b) Velocity mean-square displacement as a function of time. In both cases the linear behavior at short times, $t \ll t_r^v$, and the saturation values are shown. The slopes are F/m and $k_BT/m \times 2\gamma_0/m$, respectively.

The velocity **two-time connected correlation** reads

$$\langle [v(t) - \langle v(t) \rangle][v(t') - \langle v(t') \rangle] \rangle = \frac{k_BT}{m} \left[e^{-\frac{\gamma_0}{m}|t-t'|} - e^{-\frac{\gamma_0}{m}(t+t')} \right] .$$

This is sometimes called the **Dirichlet correlator**. This and all other higher-order velocity correlation functions approach a **stationary limit** when the shortest time involved is longer than t_r^v. At $t = t'$ one recovers the mean-square displacement computed in eq. (2.84). When both times are short compared to t_r^v the two-time correlator behaves as $\sim 2k_BT\gamma_0/m^2 \ \max(t, t')$. When at least one of the two times is much longer than t_r^v the second term vanishes and one is left with an exponential decay as a function of time delay:

$$C_{vv}^c(t, t') \equiv \langle [v(t) - \langle v(t) \rangle][v(t') - \langle v(t') \rangle \rangle \to \frac{k_BT}{m} e^{-\frac{\gamma_0}{m}|t-t'|} \qquad t, t' \gg t_r^v \ . \quad (2.86)$$

The two-time connected correlation falls off to, say, $1/e$ in a **decay time**

$$\boxed{t_d^v = m/\gamma_0} \quad (2.87)$$

In this simple case $t_r^v = t_d^v$ but this does not necessarily happen in more complex cases.

More generally one can show that for times $t_1 \geq t_2 \geq \cdots \geq t_n \geq t_r^v$:

$$\boxed{\langle \delta v(t_1 + \Delta) \dots \delta v(t_n + \Delta) \rangle = \langle \delta v(t_1) \dots \delta v(t_n) \rangle \quad \text{(TTI)}} \tag{2.88}$$

with $\delta v(t) = v(t) - \langle v \rangle(t)$, for all delays Δ. **Time-translation invariance (TTI)** or **stationarity** is one generic property of **equilibrium dynamics**. Another way of stating (2.88) is

$$\langle v(t_1) \dots v(t_n) \rangle = f(t_1 - t_2, \dots, t_{n-1} - t_n) \; . \tag{2.89}$$

Another interesting object is the linear response of the averaged velocity to a small perturbation applied to the system in the form of $V \to V - fx$, i.e. a change in the slope of the potential in this particular case. One finds

$$R_{vx}(t,t') \equiv \left. \frac{\delta \langle v(t) \rangle_f}{\delta f(t')} \right|_{f=0} = \frac{1}{m} \; e^{-\frac{\gamma_0}{m}(t-t')} \; \theta(t-t') \tag{2.90}$$

$$\simeq \frac{1}{k_B T} \langle [v(t) - \langle v(t) \rangle][v(t') - \langle v(t') \rangle] \rangle \; \theta(t-t') \tag{2.91}$$

the last identity being valid in the limit t or $t' \gg t_r^v$. This is an fdt relation between a linear response, $R_{vx}(t,t')$, and a connected correlation, $C_{vv}^c(t,t')$, that holds for one of the particle variables, its velocity, when this one reaches the stationary state.

$$\boxed{k_B T \; R_{vx}(t,t') = C_{vv}^c(t,t') \; \theta(t-t') \qquad \text{(FDT)} \; .} \tag{2.92}$$

In conclusion, the velocity is a Gaussian variable that after a characteristic time t_r^v verifies 'equilibrium'-like properties: its average converges to a constant (determined by F), its multi-time correlation functions become stationary and a fluctuation-dissipation theorem links its linear response to the connected correlation at two times.

The position

The particle's position, $x(t) = x_0 + \int_0^t dt' v(t')$ is still a Gaussian random variable:

$$\begin{aligned} x(t) \;\; &= \;\; x_0 + v_0 \; t_r^v + \frac{F}{\gamma_0}(t - t_r^v) + t_r^v \left(\frac{F}{\gamma_0} - v_0 \right) e^{-\frac{\gamma_0}{m} t} \\ &\quad + \frac{1}{m} \int_0^t dt' \int_0^{t'} dt'' \; e^{-\frac{\gamma_0}{m}(t'-t'')} \; \xi(t'') \; . \end{aligned} \tag{2.93}$$

Its noise-average behaves as the Newtonian result, **ballistic motion**,

$$\boxed{\langle x(t)\rangle \simeq x_0 + v_0 t + \frac{\gamma_0}{2m}\left(\frac{F}{\gamma_0} - v_0\right) t^2 \qquad \text{for} \qquad t \ll t_r^v} \tag{2.94}$$

at short times and it crossover to

$$\boxed{\langle x(t)\rangle \to x_0 + v_0\ t_r^v + \frac{F}{\gamma_0}(t - t_r^v) \qquad \text{for} \qquad t \gg t_r^v} \tag{2.95}$$

at long times. Note the reduction with respect to ballistic motion ($x \propto Ft^2$) due to the friction drag and the fact that this one-time observable does not saturate to a constant.

An interesting result, that we will use later, is the fact that the coordinate and the noise have vanishing correlation at equal times: $\langle x(t)\xi(t)\rangle = 0$. This can be easily proven by multiplying the expression for $x(t)$ by $\xi(t)$ and taking the average.

The position mean-square displacement approaches

$$\boxed{\sigma_x^2(t) \equiv \langle (x(t) - \langle x(t)\rangle)^2\rangle \to 2D_x t \quad \text{with} \quad D_x \equiv \frac{k_B T}{\gamma_0} \quad \text{(Diffusion)}} \tag{2.96}$$

in the usual $t \gg t_r^v$ limit, that is to say **normal diffusion** with the **diffusion constant** D_x. This expression can be computed using $x(t) - \langle x(t)\rangle$ as obtained from the $v(t) - \langle v(t)\rangle$ above (and it is quite a messy calculation) or one can simply go to the Smoluchowski limit, taking advantage of the knowledge of what we have just discussed on the behaviour of velocities, and obtain diffusion in two lines.

Exercise 2.10 Do the calculation sketched above.

When the friction coefficient γ_0 is given by the Stokes law, $\gamma_0 = 6\pi\eta a$ for spherical particle with radius a in a liquid with dynamic viscosity η, the diffusion constant is given by the **Stokes-Einstein** relation $D_x = k_B T/(6\pi\eta a)$.

Figure 2.21: Left panel: five runs of the Langevin equation in the over-damped limit with no external force and a Gaussian white noise at temperature T. Right panel: the average $\langle x^2\rangle$ computed with $n = 10^2,\ 10^3,\ 10^4,\ 10^5$ runs. The straight line represents the normal diffusion $\langle x^2\rangle \simeq 2k_B T t$.

The searched result can also be found as follows. Multiply the Langevin equation evaluated at t by x evaluated at the same instant and use an obvious identity to find

$$m x\dot{v} = m\left(\frac{d}{dt}(xv) - v^2\right) = -\gamma_0 v x + xF + x\xi \tag{2.97}$$

Take now the noise average. Use the fact that the average of $x\xi$, when the two factors are evaluated at the same time, vanishes identically, and exchange time-derivative and noise-average (assuming this operation is permitted). The resulting equation is

$$\frac{d}{dt}\langle xv\rangle = -\frac{\gamma_0}{m}\langle vx\rangle + \frac{F}{m}\langle x\rangle + \langle v^2\rangle \ . \tag{2.98}$$

The last two terms in the right-hand-side are a known time-dependent function, $A(t)$:

$$A \equiv \frac{F}{m}\langle x\rangle + \langle v^2\rangle \ , \tag{2.99}$$

$$\frac{F}{m}\langle x\rangle = \frac{F}{m}\left[x_0 + v_0 t_r^v + \frac{F}{\gamma_0}\left(t - t_r^v\right) + t_r^v\left(\frac{F}{\gamma_0} - v_0\right)e^{-\frac{\gamma_0}{m}t}\right] \ , \tag{2.100}$$

$$\langle v^2\rangle = \frac{k_B T}{m}\left(1 - e^{-2\frac{\gamma_0}{m}t}\right) + \left[v_0 e^{-\frac{\gamma_0}{m}t} + \frac{F}{\gamma_0}\left(1 - e^{-\frac{\gamma_0}{m}t}\right)\right]^2 \ . \tag{2.101}$$

One can now integrate eq. (2.98) over time

$$\langle xv\rangle = x_0 v_0 \ e^{-\frac{\gamma_0}{m}t} + \int_0^t dt' e^{-\frac{\gamma_0}{m}(t-t')}A(t') \tag{2.102}$$

to find a rather lengthy expression. In the long time limit, $t \gg t_r^v$, we drop all exponentially decaying terms to obtain

$$\langle xv\rangle \ \rightarrow \ \frac{k_B T}{\gamma_0} + \frac{F}{\gamma_0}\left(t_r^v v_0 + x_0\right) + \frac{F^2}{\gamma_0^2}\left(t - t_r^v\right) \tag{2.103}$$

Now, using $\langle xv\rangle = \frac{1}{2}\frac{d}{dt}\langle x^2\rangle$ one finally finds

$$\langle x^2\rangle \rightarrow 2\frac{k_B T}{\gamma_0}t + 2\frac{F}{\gamma_0}\left(t_r^v v_0 + x_0\right)t + \frac{F^2}{\gamma_0^2}\left[\left(t - t_r^v\right)^2 - t_r^2\right] \tag{2.104}$$

The last two terms are $\langle x\rangle^2$ in the same regime of times. Therefore, eq. (2.96) is recovered.

Another way to measure the diffusion coefficient directly from the velocity that is commonly used in the literature is

$$\boxed{D_x = \lim_{\tau\to\infty}\lim_{t'\to\infty}\int_0^\tau dt' \ \langle \delta v(\tau + t')\delta v(t')\rangle \ .} \tag{2.105}$$

One can check that it gives the same result.

In contrast to the velocity mean-square displacement this quantity does not saturate at any finite value. Similarly, the particle displacement between two different times t and t' is

$$\Delta_{xx}(t,t') \equiv \langle [x(t) - x(t')]^2 \rangle \to 2D_x|t - t'| \,. \tag{2.106}$$

It is interesting to note that the force dictates the mean position but it does not modify the fluctuations about it (similarly to what it did to the velocity). Δ_{xx} is stationary for time lags longer than t_r^v.

The two-time position-position connected correlation reads

$$C^c_{xx}(t,t') = \langle (x(t) - \langle x(t) \rangle)(x(t') - \langle x(t') \rangle) \rangle = \dots \tag{2.107}$$

Exercise 2.11 compute this correlation function.

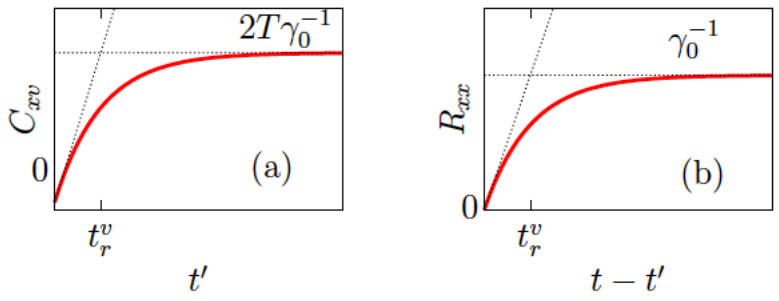


Figure 2.22: Results for the constant force problem. (a) The correlation between the position and the velocity of the particle measured at different times. (b) The linear response of the position to a kick applied linearly to itself at a previous time. In both cases the linear behavior at short times, $t \ll t_r^v$ and the saturation values are shown.

The linear response of the particle's position to a kick linearly applied to itself at a previous time, in the form $V \to V - fx$ at $t' < t$, is

$$R_{xx}(t,t') \equiv \left. \frac{\delta \langle x(t) \rangle_f}{\delta f(t')} \right|_{f=0} = \frac{1}{\gamma_0} \left[1 - e^{-\frac{\gamma_0}{m}(t-t')} \right] \theta(t - t') \,, \tag{2.108}$$

with the limits

$$R_{xx}(t,t') \to \begin{cases} m^{-1}\ (t-t')\ \theta(t-t') & t-t' \ll t_r^v\ , \\ \gamma_0^{-1}\ \theta(t-t') & t-t' \gg t_r^v\ . \end{cases} \tag{2.109}$$

A simple calculation proves that in the short time-differences limit this is the result for Newton dynamics.

Exercise 2.12 show the property mentioned above.

The correlation between the position and the velocity reads

$$\begin{aligned} \langle (x(t) - \langle x(t)\rangle)(v(t') - \langle v(t')\rangle)\rangle &= \frac{2k_BT}{m}\left[\frac{m}{\gamma_0} - \left(1+\frac{m}{\gamma_0}\right)e^{-\frac{\gamma_0}{m}t'}\right] \\ &\to \frac{2k_BT}{\gamma_0} \end{aligned} \tag{2.110}$$

and it is only a function of t'. One notices that in the asymptotic limit in which both sides of the equation saturate

$$\boxed{2k_BT\ R_{xx}(t,t') = C^c_{xv}(t,t') \quad \text{for } t-t' \gg t_r^v \text{ and } t' \gg t_r^v\ ,} \tag{2.111}$$

with a factor of 2 different from the relation in eq. (2.92).

In conclusion, the position is also a Gaussian variable but it is explicitly out of equilibrium. Its average and variance grow linearly in time, the latter as in normal diffusion, and the fluctuation-dissipation relation has an additional factor of 1/2 (or 2, depending on on which side of the equality one writes it) with respect to the form expected in equilibrium.

A measure for the time dependent fluctuating position and velocity can be written down, taking advantage of the fact that both variables are Gaussian:

$$P(v,x) \propto \exp\left[-\frac{1}{2}\int dt \int dt'\ \delta y^t(t) A(t,t') \delta y(t')\right] \tag{2.112}$$

with the 2×2 matrix A being the inverse of the matrix of correlations, ${A^{-1}}_{ij}(t,t') = \langle \delta y_i(t) \delta y_j(t')\rangle$ with $i,j = 1,2$, $\delta y^t(t) = (\delta v(t)\ \ \delta x(t))$ and $\delta v(t) = v(t) - \langle v(t)\rangle$ (similarly for x). The correlations are given above so the dynamic pdf can be easily constructed. There will be elements in the matrix that remain time-dependent for all times.

Exercise 2.13 Confront

$$\langle v^m(t) x^n(t) x^k(t')\rangle \qquad \text{and} \qquad \langle v^m(t) x^n(t) k x^{k-1}(t') v(t')\rangle\ ; \tag{2.113}$$

conclude.

The energy

The averaged kinetic energy can be computed using $\langle v^2(t)\rangle = \sigma_v^2(t) + \langle v(t)\rangle^2$ and the results already derived. It reaches, in the $t \gg t_r^v$ limit, a constant value: $\langle K(t)\rangle \to k_B T/2 + F/(2\gamma_0)$. The averaged potential energy diverges in the long-time limit if $F \neq 0$ since the potential is unbounded in the $x \to \infty$ limit: $\langle V(t)\rangle = -F\langle x(t)\rangle \simeq -F^2/\gamma_0 t$ for $t \gg t_r^v$. In the particular case $F = 0$ the total energy is just kinetic and it approaches the constant expected from equipartition asymptotically $\langle K(t)\rangle \to k_B T/2$.

It is also interesting to investigate the sign of dE/dt on the mean, $\langle dE/dt\rangle = -\gamma_0\langle v^2\rangle + \langle v\xi\rangle$. The first term tends to $-\gamma_0 k_B T/m - F$. The second term also yields a non-trivial contribution $\langle v\xi\rangle \to m^{-1}\int_0^t dt' e^{-\gamma_0(t-t')/m}\langle \xi(t)\xi(t')\rangle = \gamma_0 k_B T/m$. Adding these two together one finds $\langle dE/dt\rangle \to -F$ asymptotically, for $t \gg t_r^v$.

Two kinds of variables

This example shows that even in this very simple problem the velocity and position variables have distinct behavior: the former is in a sense trivial, after the transient t_r^v and for longer times, all one-time functions of $v - F/\gamma_0$ saturate to their equilibrium-like values and the correlations are stationary. Instead, the latter remains non-trivial and evolving out of equilibrium. One can loosely ascribe the different behavior to the fact that the velocity feels a confining kinetic energy $K = mv^2/2$ while the position feels an unbounded potential $V = -Fx$ in the case in which a force is applied, or a flat potential $V = 0$ if F is switched off. In none of these cases the potential is able to take the particle's position to equilibrium with the bath. The particle slides on the slope and its excursions forward and backward from the mean get larger and larger as time increases.

Over-damped (Smoluchowski) limit

Quite generally, the classical problems we are interested in are such that the friction coefficient γ_0 is large and the inertia term can be neglected, in other words, all times are much longer than the characteristic time t_r^v. We will do it in the rest of the lectures.

Ergodicity

The ergodic hypothesis states that, in equilibrium, one can exchange ensemble averages by time averages and obtain the same results. Out of equilibrium this hypothesis is not expected to hold and one can already see how dangerous it is

to take time-averages in these cases by focusing on the simple velocity variable. Ensemble and time averages coincide only if the time-averaging is done over a time-window that lies after t_r^v but it does not if the integration time-interval goes below t_r^v. Moreover, in the case of the position variable, there is no finite t_r^x.

Tests of equilibration have to be done very carefully in experiments and simulations. One can be simply mislead by, for instance, looking just at the velocities statistics.

Effect of a colored bath: anomalous diffusion

The **anomalous diffusion** ($F = 0$) of a particle governed by the generalized Langevin equation, eq. (2.14), with colored noise characterized by power-law correlations as the ones given in eq. (2.15), a problem also known as **fractional Brownian motion**, was studied in detail by N. Pottier [24]. The particle's velocity equilibrates with the environment although it does at a much slower rate than in the Ohmic case: its average and mean-square displacement decay as a power law - instead of exponentially - to their asymptotic values (still satisfying the regression theorem). The particle's mean square displacement is determined by the exponent of the noise-noise correlation,

$$\Gamma(t) \simeq t^{-\alpha} \qquad \text{and} \langle x^2(t) \rangle \simeq t^{\alpha} \ , \tag{2.114}$$

the dynamics is **subdiffusive** for $\alpha < 1$, **diffusive** for $\alpha = 1$ and **superdiffusive** for $\alpha > 1$. A time-dependent diffusion coefficient verifies $D_x(t) \equiv 1/2 \ d\langle x^2(t) \rangle / dt \propto t^{\alpha-1}$: it is finite and given by eq. (2.106) for normal diffusion, it diverges for superdiffusion and it vanishes for subdiffusion. The ratio between the linear response and the time-derivative of the correlation ratio reads $TR_{xx}(t,t')/\partial_{t'} C_{xx}(t,t') = D_x(t-t')/[D_x(t-t') + D_x(t')]$. It approaches $1/2$ for normal diffusion and the two-time dependent function $1/[1 + (t'/(t-t'))^{\alpha-1}]$ in other cases.

Exercise 2.14 Work out these results.

Perrin's experiment

Jean-Baptiste Perrin used these results to measure the Avogadro number experimentally and, more importantly, give evidence for the discrete character of matter[10]. The idea is already described in Lucretius's poem *De rerum natura, On the nature of things*. The reasoning goes as follows. Take a spherical tracer particle with radius a and immerse it in a liquid with viscosity η. These two quantities can be measured.

[10] J. B. Perrin, *Brownian motion and molecular reality*, Annales de Chimie et de Physique **18**, 5 (1909).

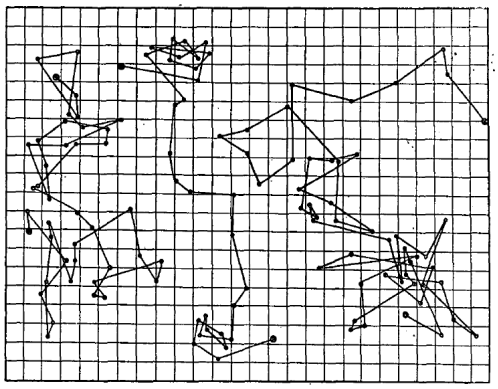


Figure 2.23: Colloidal particle trajectories. The radius of the particles is $0.53\,\mu$m, the points are successive positions taken at intervals of 30 s. The grid has spacing $3.2\,\mu$m. Image taken from Perrin's original article.

Assume that the liquid behaves as a white noise. Stokes law states that the friction coefficient for this particle is

$$\gamma_0 = 6\pi\eta a \ . \tag{2.115}$$

The Boltzmann constant k_B is given by the gas constant R, that is also known, divided by the Avogadro number since $k_B = nR/N = R/N_A$ with n the number of moles and N the number of atoms in a gas. Therefore

$$\sigma_x^2(t) \simeq 2D_x t = \frac{R}{3\pi\eta a}\frac{T}{N_A}t \tag{2.116}$$

and, by measuring the tracer's diffusion one can extract N_A.

2.5.2 Relaxation in a quadratic potential: full analysis

The Hamiltonian of a one-dimensional harmonic oscillator of mass m and spring constant k is

$$H_{\rm syst} = \frac{p^2}{2m} + \frac{kx^2}{2} \ . \tag{2.117}$$

The Langevin equation of motion reads

$$m\ddot{x}(t) = -\gamma_0\dot{x}(t) - kx(t) + h(t) + \xi(t) \ . \tag{2.118}$$

with $h(t)$ a time-dependent deterministic force. By setting $k = 0$ one recovers the motion of a Brownian particle, see Sect. 2.4. ξ is the white noise with zero mean and correlations $\langle \xi(t)\xi(t')\rangle = 2k_B T\gamma_0 \delta(t-t')$.

Qualitative analysis: time-scales

From an order of magnitude analysis of the the three terms in the homogeneous equation one can extract the time-scales that rule the dynamics of this problem. The easiest way to determine these time scales is to first Fourier transform the homogeneous equation that determines the Green function

$$-m\omega^2\tilde{x}(\omega) - i\gamma_0\omega\tilde{x}(\omega) + k\tilde{x}(\omega) \; . \tag{2.119}$$

For the sake of completeness, we present this analysis for a coloured noise with power-law correlations, Eq. (2.25), in the limit in which the cut-off has been sent to infinity, for which the equation above generalises to

$$-m\omega^2\tilde{x}(\omega) - i\gamma_0\omega^\alpha\tilde{\omega}^{\alpha-1}\tilde{x}(\omega) + k\tilde{x}(\omega) \; . \tag{2.120}$$

In the absence of dissipation ($\gamma_0 = 0$) the particle oscillates within the harmonic well, and the parameter dependence of the frequency and period of oscillation is determined with an order of magnitude argument

$$m\omega_{\rm osc}^2 \approx k \qquad \Rightarrow \qquad \omega_{\rm osc}^2 \approx \frac{k}{m} \qquad \Rightarrow \qquad \boxed{t_{\rm osc} \approx \left(\frac{m}{k}\right)^{1/2}} \tag{2.121}$$

Under the action of the dissipative force new time-scales appear. First, one can expect that the competition between inertia and dissipation gives rise to the velocity relaxation time, t_r^v. Therefore,

$$m\omega_r^{v2} \approx \gamma_0\omega_r^{v\alpha}\tilde{\omega}^{\alpha-1} \qquad \Rightarrow \qquad \omega_r^v \approx \left(\frac{\gamma_0}{m}\,\tilde{\omega}^{1-\alpha}\right)^{1/(2-\alpha)} \tag{2.122}$$

and

$$\boxed{t_r^v \approx \left(\frac{m}{\gamma_0}\,\tilde{\omega}^{\alpha-1}\right)^{1/(2-\alpha)}} \tag{2.123}$$

In the particular case $\alpha = 1$ the bath becomes Ohmic and $t_r^v \approx m/\gamma_0$ as in Eq. (2.83).

Second, the comparison between dissipation and harmonic force yields

$$\gamma_0\omega_r^{x\alpha}\tilde{\omega}^{\alpha-1} \approx k \qquad \Rightarrow \qquad \omega_r^x \approx \left(\frac{k}{\gamma_0}\tilde{\omega}^{1-\alpha}\right)^{1/\alpha} \tag{2.124}$$

and

$$\boxed{t_r^x \approx \left(\frac{\gamma_0}{k}\,\tilde{\omega}^{\alpha-1}\right)^{1/\alpha}} \tag{2.125}$$

that for $\alpha = 1$ becomes $t_r^x \approx \gamma_0/k$ a time-scale that we will see appearing in the exact calculation below.

Now, we can compare these time-scales and conclude about the possible types of particle motion. If $t_{\rm osc} < t_r^x$ the particle continues to oscillate during its dissipative evolution while, on the contrary, if $t_{\rm osc} > t_r^x$, the oscillations are damped and the relaxation of observables is monotonic. One has

$$\begin{array}{lcll} t_{\rm osc} & < & t_r^x & \text{Underdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)}k^{2-\alpha}m^{\alpha} > \gamma_0^2\ , \\ t_{\rm osc} & > & t_r^x & \text{Overdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)}k^{2-\alpha}m^{\alpha} < \gamma_0^2\ . \end{array} \tag{2.126}$$

The crossover occurs at parameters such that $\gamma_0^2 \approx km$ for $\alpha = 1$, see below.

Finally, the comparison between the oscillation time, $t_{\rm osc}$, and the velocity relaxation time, t_r^v, yields

$$\begin{array}{lcll} t_{\rm osc} & < & t_r^v & \text{Underdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)}k^{2-\alpha}m^{\alpha} > \gamma_0^2\ , \\ t_{\rm osc} & > & t_r^v & \text{Overdamped motion} \qquad \tilde{\omega}^{2(1-\alpha)}k^{2-\alpha}m^{\alpha} < \gamma_0^2\ , \end{array} \tag{2.127}$$

exactly the same conditions as for the position, as it should. The difference in behaviour between position and velocity is decided by the comparison between the relaxation time of the velocity and position. If $t_r^v \ll t_r^x$ the velocity equilibrates with the environment well before the position.

Quantitative analysis in the white noise case

The full differential equation (2.118) can be easily solved by first evaluating the Green function $G(t)$ from

$$m\ddot{G}(t) + \gamma_0\dot{G}(t) + kG(t) = \delta(t)\ , \tag{2.128}$$

that, after Fourier transforming, implies

$$\tilde{G}(\omega) = 1/(-m\omega^2 - i\gamma_0\omega + k)\ . \tag{2.129}$$

The right-hand-side has two poles:

$$\omega_{\pm} = -\frac{i\gamma_0}{2m} \pm \sqrt{\frac{k}{m} - \frac{\gamma_0^2}{4m^2}}\ , \tag{2.130}$$

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

$$4km - \gamma_0^2 > 0 \qquad \omega_\pm \text{ complex (under-damped case) ,} \tag{2.131}$$

$$4km - \gamma_0^2 \leq 0 \qquad \omega_\pm \text{ imaginary (over-damped) .} \tag{2.132}$$

It is important to note that in both cases the poles are located in the lower half complex plane.

Using Cauchy's formula to transform back in time one finds that, for $t > 0$, the Green function reads

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

and it vanishes identically for $t < 0$. Two other important properties of $G(t)$ are $G(0) = 0$ and $m\dot{G}(0) = 1$ that follow from integrating (2.128) between $t = -\delta$ and $t = \delta$ and taking $\delta \to 0$. One also checks $2|\omega_I|\dot{G}(0) + \ddot{G}(0) = 0$ in the under-damped case.

In the under-damped case the time-dependent position of the particle is given by

$$\begin{aligned} x(t) = e^{-|\omega_I|t}\left\{[\dot{x}(0) + x(0)|\omega_I|]\;\frac{\sin\omega_R t}{\omega_R} + x(0)\cos\omega_R t\right\} \\ + \int_0^\infty dt'\; G(t-t')\,[\xi(t') + h(t')] \end{aligned} \tag{2.133}$$

and this can be rewritten as

$$\begin{aligned} x(t) = [\dot{x}(0) + x(0)|\omega_I|]mG(t) + x(0)[m\dot{G}(t) + |\omega_I|mG(t)] \\ + \int_0^\infty dt'\; G(t-t')\,[\xi(t') + h(t')] \end{aligned} \tag{2.134}$$

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 $t' = t$. One can find corresponding expression for the over-damped case.

Let us first dicuss the asymptotic values of one-time quantities. The simplest cases are the averaged position and momentum themselves. In the absence of an external field, the potential is symmetric with respect to $x \to -x$ and $p \to -p$.

Since the noise ξ has zero average, after a characteristic-time needed to forget the initial conditions, the average of both x and p vanish if $k \neq 0$. This is consistent with the result expected in equilibrium, $\langle x \rangle_{eq} = \langle p \rangle_{eq} = 0$, though it is not sufficient to prove that the particle equilibrates with its environment. The way in which this zero limit is approached depends strongly on the value of $4km - \gamma_0^2$ and we shall discuss it later.

When $k = 0$ the result is different. In the absence of external forces, while the average momentum vanishes, the average coordinate approaches a non-zero value for $t \gg t_c^v$, $\langle x(t) \rangle \to x(0) + p(0)/\gamma_0$: the initial condition is remembered forever by the particle's motion. It is a first indication of the non-equilibration of the coordinate for a flat potential.

Independently of the parameters k, γ_0 and T and as long as $m \neq 0$, after a tedious but straighforward calculation one finds that

$$\lim_{t \gg t_c^v} C_{pp}(t,t) = \lim_{t \gg t_c^v} \langle p(t)p(t) \rangle = m k_B T = \langle p^2 \rangle_{eq} \ , \qquad t_c^v \equiv \frac{m}{\gamma_0}$$

where the last term indicates the static average. The same kind of calculation can be pursued to show that the average of any function of the momentum approaches its equilibrium limit asymptotically. This is good evidence for establishing the equilibration of the momentum. [Note that even if one of the characteristic times that determine the relaxation of the Green function diverges when $k = 0$, the velocity-velocity correlation is well-behaved since it only involves $\dot{G}(t)$.]

The observables that are functions of the position depend on the value of k. As long as $k > 0$ there is a confining harmonic potential for the position and all equal-time functions of it approach an asymptotic limit that coincides with the one dictated by the equilibrium distribution. For instance,

$$\lim_{t \gg t_c^v} C_{xx}(t,t) = \lim_{t \gg t_c^v} \langle x(t)x(t) \rangle = \frac{k_B T}{k} = \langle x^2 \rangle_{eq} \ .$$

Instead, if $k = 0$ there is no confining potential and the particle diffuses to infinity. If $k < 0$ the potential pushes the particle away from the origin towards $\pm\infty$ depending on the sign of the initial position. In none of these cases one can define a normalisable measure over the full infinite space and the position of the particles does not equilibrate with its environment. We discuss these two cases in detail below focusing on the study of the temporal evolution of correlation functions that depend on two times. We analyse the auto-correlation

$$C_{xx}(t,t') = \text{Effect of initial cond} + 2k_B T \gamma_0 \int_0^\infty ds \ G(t-s)G(t'-s) \ ,$$

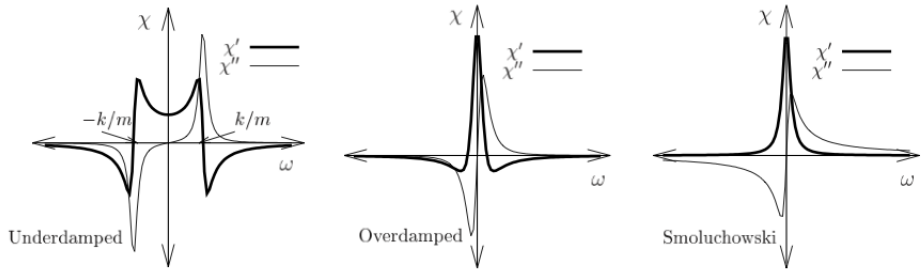


Figure 2.24: Green functions of the damped harmonic oscillator in different limits.

and the linear response of the position of the particle at time t after a kick to this same variable has been applied at a previous time t'. From eqn (2.134), this is given by the Green function itself:

$$R_{xx}(t,t') \equiv \delta\langle x(t)\rangle/\delta h(t')|_{h=0} = G(t-t') \tag{2.135}$$

We distinguish the relaxation with different damping arising from different values of the parameters.

Relaxation in the under-damped limit.

When $\omega_R \neq 0$, see eqn (2.131), the self correlation and linear response *oscillate* with frequency $\omega_R = \sqrt{k/m - \gamma_0^2/(4m^2)}$ and *decay exponentially* with a characteristic time $t_c = |\omega_I|^{-1} = 2m/\gamma_0$. They are displayed with dashed lines in Fig. **??**. The Fourier representation of the response function is shown in Fig. 2.24-left where we plot χ'_{xx} and χ''_{xx} as functions of ω. We observe that χ' changes sign at $\omega = \pm k/m$ and $\chi''(\omega)$ has peaks at $\omega = \pm\sqrt{k^2/m^2 - \gamma_0^2/4}$ with half-width at half maximum equal to $\gamma_0/2$. If $\gamma_0 \to 0$ these peaks approach the frequencies $\pm k/m$ of the undamped oscillator.

Relaxation in the over-damped limit.

If, instead, we take the case in eqn (2.132) for which $\omega_R = 0$ (and $k \neq 0$) the self correlation and linear response have *pure exponential* decays with two time constants:

$$\begin{aligned} t_{fast} = \omega_-^{-1} &= \frac{2m}{\gamma_0 + \sqrt{\gamma_0^2 - 4km}} \to \frac{m}{\gamma_0} \equiv t_c^v \\ t_{slow} = \omega_+^{-1} &= \frac{2m}{\gamma_0 - \sqrt{\gamma_0^2 - 4km}} \to \frac{\gamma_0}{k} \equiv t_c^x \end{aligned} \quad \text{when } 4km \ll \gamma_0^2 \tag{2.136}$$

When $km \ll \gamma_0^2$ the fast decay time, which is the caracteristic time for relaxation of the velocity correlations, is much shorter than the slow one, $t_{fast} \ll t_{slow}$. For long observation times compared to t_{slow} one can neglect the fast mode. This is equivalent to neglecting the inertial term in the original Langevin equation and using the Smoluchowski limit to construct the properties of the coordinate.

The real and imaginary parts of the Fourier transform of the linear response are usually called χ' and χ''. χ' is peaked at the origin. In the extreme over-damped limit in which one can neglect inertia χ''/ω is a Lorentzian centered at the origin with width t_{slow}^{-1}.

Relaxation in the Smoluchowski limit.

In this purely viscous case, where $m = 0$, there is only one characteristic time left, $t_c^x = \gamma_0/k$. The response decays exponentially, $R(t) = \gamma_0^{-1} e^{-t/t_c^x}$ and the susceptibility is then given by

$$\tilde{\chi}(\omega) = \frac{1}{-i\gamma_0\omega + k} = \frac{k}{k^2 + \gamma_0^2\omega^2} + i\frac{\gamma_0\omega}{k^2 + \gamma_0^2\omega^2} \ .$$

Its real part is positive for all values of ω and the imaginary part is usually said to take a *Debye* form. See the right panel in Fig. 2.24.

Diffusion in the random walk limit.

When $k \to 0$ the coordinate x does not have a confining potential and a normalized equilibrium distribution cannot be defined for this degree of freedom. In this case there is no reason to expect that any equilibrium property will apply to this variable. Indeed, when $k \to 0$ the characteristic time t_{slow} diverges: there is no relaxation and a Brownian particle diffuses. The Green function approaches, exponentially in $t - t'$, a finite limit:

$$G(t - t') \sim \frac{1}{\gamma_0} \left(1 - e^{-\frac{\gamma_0}{m}(t-t')}\right) \ . \tag{2.137}$$

For any fixed time-difference, the correlation function diverges linearly with the shorter time. If $t' \leq t$, for $t' \gg t_c^v$ and $t - t'$ fixed, choosing the simplest initial condition $x(0) = p(0) = 0$, we have

$$\lim_{t' \gg t_c^v,\ t-t' \text{ fixed}} C_{xx}(t, t') = -\frac{2mk_BT}{\gamma_0^2}\left(1 - \frac{1}{2}e^{-\frac{\gamma_0}{m}|t-t'|}\right) + \frac{2k_BT}{\gamma_0}\min(t, t')$$

In particular, at equal long times $t = t' \gg m/\gamma_0$, $C_{xx}(t, t) \sim 2k_BT/\gamma_0\ t$. This demonstrates the breakdown of stationarity and hence the fact that the system is

far from equilibrium. For $\min(t,t')$ fixed, $C_x x(t,t')$ decays exponentially with the time-difference towards the constant $2k_BT/\gamma_0(\min(t,t') - m/\gamma_0)$.

The displacement Δ_{xx} instead is a simpler function of $t-t'$, and for long time-differences it becomes the usual diffusion law.

2.5.3 Relaxation in a quadratic potential: over-damped limit

Another relevant example is the relaxation of a particle in a harmonic potential, with its minimum at $x^* \neq 0$:

$$V(x) = \frac{k}{2}(x - x^*)^2 \ , \tag{2.138}$$

in contact with noise that we take to be white as the simpler starting case. The potential confines the particle and one can then expect the coordinate to reach an equilibrium distribution.

This problem can be solved exactly keeping inertia for all values of γ_0 but the calculation is slightly tedious. The behavior of the particle velocity has already been clarified in the constant force case. We now focus on the over-damped limit,

$$\gamma_0 \dot{x} = -k(x - x^*) + \xi \ , \tag{2.139}$$

with k the spring constant of the harmonic well, that can be readily solved,

$$x(t) = x_0 \ e^{-\frac{k}{\gamma_0}t} + \gamma_0^{-1} \int_0^t dt' \ e^{-\frac{k}{\gamma_0}(t-t')} \ [\xi(t') + kx^*] \ , \qquad x_0 = x(0) \ . \tag{2.140}$$

This problem becomes formally identical to the velocity dependence in the previous example.

Convergence of one-time quantities

The averaged position is

$$\boxed{\langle x(t) - x^* \rangle = (x_0 - x^*) e^{-\frac{k}{\gamma_0}t} \to 0 \qquad t_r^x \gg \gamma_0/k \quad \text{(Convergence)}} \tag{2.141}$$

Of course, one-time quantities should approach a constant asymptotically if the system equilibrates with its environment.

Two-time quantities

Figure 2.25: Left panel: five runs of the Langevin equation in the over-damped limit with a quadratic external potential (oscillator) and a Gaussian white noise at temperature T. Central panel: the average $\langle x \rangle$ computed with $n = 10^2,\ 10^3,\ 10^4,\ 10^5$ runs. Right panel: the variance $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = k_B T/k$.

The two-time connected correlation (where one extracts, basically, the asymptotic position x^*) reads

$$\langle \delta x(t) \delta x(t') \rangle = k_B T\ k^{-1}\ e^{-\frac{k}{\gamma_0}(t+t')} \left[e^{2\frac{k}{\gamma_0}\min(t,t')} - 1 \right] . \tag{2.142}$$

Again, the **Dirichlet correlator** ($\delta x(t) = x(t) - \langle x(t) \rangle$). For at least one of the two times going well beyond the position relaxation time $t_r^x = \gamma_0/k$ the memory of the initial condition is lost and the connected correlation becomes **stationary**:

$$C_c(t,t') = \langle \delta x(t) \delta x(t') \rangle \to k_B T\ k^{-1}\ e^{-\frac{k}{\gamma_0}|t-t'|} \qquad \min(t,t') \gg t_r^x . \tag{2.143}$$

For time-differences that are longer than $t_d^x = \gamma_0/k$ the correlation decays to $1/e$ and one finds $t_d^x = t_r^x$. Interestingly enough, the relaxation and decay times diverge when $k \to 0$ and the potential becomes flat.

Note that when the time-difference $t - t'$ diverges the average of the product factorizes, in particular, for the correlation one gets

$$\langle x(t) x(t') \rangle \to \langle x(t) \rangle \langle x(t') \rangle \to x^* \langle x(t') \rangle \tag{2.144}$$

for any t', even finite. We will see this factorization property at work later in more complicated cases.

Fluctuation-dissipation theorem (FDT)

One can also compute the linear response to an infinitesimal perturbation that couples linearly to the position changing the energy of the system as $H \to H - fx$ at a given time t':

$$R(t,t') = \left. \frac{\delta \langle x(t) \rangle_f}{\delta f(t')} \right|_{f=0} . \tag{2.145}$$

The explicit calculation yields

$$\begin{aligned} & R(t,t') = \gamma_0^{-1}\ e^{-k\gamma_0^{-1}(t-t')}\ \theta(t-t') \\ & \boxed{R(t,t') = \tfrac{1}{k_B T}\ \tfrac{\partial C_c(t,t')}{\partial t'}\ \theta(t-t') \quad \text{(FDT)}} \end{aligned} \tag{2.146}$$

The last equality holds for times that are longer than t_r^x. It expresses the **fluctuation-dissipation theorem (fdt)**, a model-independent relation between the two-time linear response and correlation function. Similar - though more complicated - relations for higher-order responses and correlations also exist in equilibrium. There are many ways to prove the fdt for stochastic processes. We will discuss one of them in Sect. 2.4.2 that is especially interesting since it applies easily to problems with correlated noise.

It is instructive to examine the relation between the linear response and the correlation function in the limit of a flat potential ($k \to 0$). The linear response is just $\gamma_0^{-1}\theta(t-t')$. The Dirichlet correlator approaches the diffusive limit:

$$\langle \delta x(t)\delta x(t')\rangle = 2\gamma_0^{-1}k_BT\ \min(t,t') \qquad \text{for} \qquad k\to 0 \tag{2.147}$$

and its derivative reads $\partial_{t'}\langle \delta x(t)\delta x(t')\rangle = 2\gamma_0^{-1}k_BT\ \theta(t-t')$. Thus,

$$R(t,t') = \frac{1}{2k_BT}\ \partial_{t'}\langle \delta x(t)\delta x(t')\rangle\ \theta(t-t')$$
$$\boxed{R(t,t') = \tfrac{1}{2k_BT}\ \partial_{t'}C_c(t,t')\ \theta(t-t') \qquad \text{(FDR for diffusion)}} \tag{2.148}$$

A factor $1/2$ is now present in the relation between R and C_c. It is another signature of the fact that the coordinate is not in equilibrium with the environment in the absence of a confining potential.

Exercise 2.15 Evaluate the two members of the FDT, eq. (2.146), in the case of the tilted potential $V(x) = -Fx$. Conclude.

Exercise 2.16 Compute $\langle x^n(t)x(t')\rangle$ and $\delta\langle x^n(t)\rangle/\delta h(t')|_{h=0}$ and compare. Discuss.

Exercise 2.17 Take the diffusive problem in the over-damped limit, $\dot{x} = \xi$, where the friction coefficient has been absorbed with a redefinition of time. Compute the linear response of the n-th moment of the coordinate position $\langle x^n(t)\rangle_h$ under a perturbation that modifies the energy according to $V \mapsto V - hx$. Compute the time-derivative of the correlation $\langle x^n(t)x(t')\rangle$. Compare the two and conclude about the pre factor that relates them. Does it depend on n? Is it equal to $(k_BT)^{-1}$?

Reciprocity or Onsager relations

Let us compare the two correlations $\langle x^3(t)x(t')\rangle$ and $\langle x^3(t')x(t)\rangle$ within the harmonic example. One finds $\langle x^3(t)x(t')\rangle =$
$3\langle x^2(t)\rangle\langle x(t)x(t')\rangle$ and $\langle x^3(t')x(t)\rangle = 3\langle x^2(t')\rangle\langle x(t')x(t)\rangle$. Given that $\langle x^2(t)\rangle =$

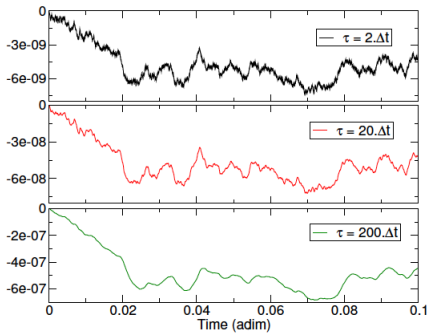


Figure 2.26: Random walk under the effect of a noise with exponential decaying correlations controlled by the parameter τ_D given as labels in the figure, see Eqs. (2.152). The time-step for the integration is $\Delta t = 10^{-4}$, temperature fixed by $2k_BT = 0.5$, and the damping parameter is $\lambda = 10^{-2}$. Figure taken from [39].

$\langle x^2(t')\rangle \to \langle x^2\rangle_{eq}$ and the fact that the two-time self-correlation is symmetric,

$$\langle x^3(t)x(t')\rangle = \langle x^3(t')x(t)\rangle \ . \tag{2.149}$$

With a similar argument one shows that for any functions A and B of x:

$$\begin{aligned} &\langle A(t)B(t')\rangle = \langle A(t')B(t)\rangle \\ &\boxed{C_{AB}(t,t') = C_{AB}(t',t) \quad \text{(Reciprocity)}} \end{aligned} \tag{2.150}$$

This equation is known as **Onsager relation** and applies to A and B that are even under time-reversal (e.g. they depend on the coordinates but not on the velocities or they have an even number of verlocities).

All these results remain unaltered if one adds a linear potential $-Fx$ and works with connected correlation functions.

Colored noise with exponential correlation

Exercise 2.18 Solve the stochastic dynamics of a particle in a harmonic potential with a exponentially decaying memory kernel $\Gamma(t-t') = \gamma_0 e^{-|t-t'|/\tau_D}$. Hint: use Laplace transform techniques.

Figure 2.26 shows the solution to the Langevin equations:

$$\dot{x} = -\lambda x + \eta \ , \tag{2.151}$$

$$\dot{\eta} = -\eta/\tau + \xi \ , \tag{2.152}$$

with $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2k_B T/\tau_D \ \delta(t-t')$. This white noise induces an exponentially decaying correlation function of the noise η that appears in the first equation. (Note, however, that this first equation lacks the memory kernel that should be present in the left-hand-side to ensure the approach to equilibrium of such an equation under a potential.) The three panels in the equation show the trajectories $x(t)$ for the same realization of the white noise ξ. The smoothing effect of correlation is quite clear.

Colored noise with power law correlation

Let us now take a power-law correlated noise. The Langevin equation can be solved by using the Laplace transform. Correlation and linear responses can be computed. As the system should equilibrate – there is confining potential – the FDT holds. However, the decay of these two functions (and more complex ones involving more times) are not trivial in the sense that their temporal dependence is not exponential. Instead, the position correlation function and its linear response are given by the Mittag-Leffer function

$$C_{xx}(t,t') = \frac{1}{k} E_{\alpha,1}\left(\frac{k|t-t'|^\alpha}{\overline{\gamma}_0}\right) , \tag{2.153}$$

$$R_{xx}(t,t') = \frac{1}{\overline{\gamma}_0} E_{\alpha,\alpha}\left(\frac{k|t-t'|^\alpha}{\overline{\gamma}_0}\right) \theta(t-t') , \tag{2.154}$$

where $\overline{\gamma}_0$ is a constant that is proportional to γ_0 and all other pre-factors in $\Gamma(t-t')$. For the Ohmic $\alpha = 1$ case the Mittag-Leffer function becomes an exponential, as expected. For $\alpha \neq 1$ the decay is algebraic, $E_{\alpha,1}(x) \simeq x^{-1}$ that implies $C_{xx}(t-t') \simeq |t-t'|^{-\alpha}$. The ratio between linear response and time derivative of the correlation function is

$$\frac{k_B T R_{xx}(t-t')}{\partial_{t'} C_{xx}(t-t')} = 1 + \left(\frac{t}{t'} - 1\right)^{1-\alpha} \frac{E_{\alpha,1}(-kt^\alpha/\overline{\gamma}_0) E_{\alpha,\alpha}(-kt'^\alpha/\overline{\gamma}_0)}{E_{\alpha,\alpha}(-k(t-t')^\alpha/\overline{\gamma}_0)} \tag{2.155}$$

In the long time limit, $t \geq t' \gg 1$, the second term vanishes as long as $k > 0$ and one recovers the equilibrium result.

Figure 2.27: Sketch of the experiment. Correlation function measured in [40] and [41], $\alpha = 0.51 \pm 0.07$.

Colored noise and active forces

The description of the motion of a tracer (e.g. a silica bead) attached to an active cell is done with an over-damped Langevin equation with coloured noise and active (non-potential forces [42]).

2.5.4 A two-dimensional example

Take a point-like particle with mass m moving in a two dimensional space. The position of this particle is $\vec{r} = (x, y) = x\hat{i} + y\hat{j}$ in a Cartesian coordinate system. The particle feels a potential $V(x, y) = kx^2/2$ and it is in contact with a generic environment in thermal equilibrium at temperature T.

Using what we have already computed for one dimensional problems we can guess the asymptotic behaviour of the phase space variables $(\vec{p}, \vec{r})$. For simplicity, we will use a white bath with friction coefficient γ_0. The momentum (or velocity) should equilibrate to its Maxwellian form, $\propto \exp(-\beta m v^2/2)$, after a characteristic time $\tau_r^v = m/\gamma_0$. The position $\vec{r} = (x, y)$ will have different behaviour in the x (confined) and y (flat) directions. The x component should reach equilibrium after a characteristic time $\tau_r^x = \gamma_0/k$. This means that it will reach a pdf $\propto \exp(-\beta k x^2/2)$. The y component of the position, instead, should undergo normal diffusion and it will not equilibrate.

The expectations exposed in the previous paragraph can be shown analytically. Take the over-damped (Smoluchowski) limit in which the inertia term in the dynamic equation is neglected. In this limit the Langevin equation becomes

$$\begin{aligned} \gamma_0 \dot{x}(t) &= -kx(t) + \xi_x(t) \ , \\ \gamma_0 \dot{y}(t) &= \xi_y(t) \ . \end{aligned}$$

The solutions are

$$\begin{aligned} x(t) &= x(0)e^{-kt/\gamma_0} + \gamma_0^{-1} \int_0^t dt' \ e^{-k(t-t')/\gamma_0} \ \xi_x(t') \ . \\ y(t) &= y(0) + \gamma_0^{-1} \int_0^t dt' \ \xi_y(t') \ . \end{aligned}$$

The four correlations are given by

$$\begin{aligned} C_{xx}(t, t') &= \langle x(t)x(t') \rangle = x^2(0)e^{-k(t+t')/\gamma_0} + k_B T \gamma_0^{-1} \ [e^{-k|t-t'|/\gamma_0} - e^{-k(t+t')/\gamma_0}] \ , \\ C_{xy}(t, t') &= \langle x(t)y(t') \rangle = x(0)y(0)e^{-kt/\gamma_0} \ , \\ C_{yx}(t, t') &= \langle y(t)x(t') \rangle = x(0)y(0)e^{-kt'/\gamma_0} \ , \\ C_{yy}(t, t') &= \langle y(t)y(t') \rangle = y^2(0) + 2k_B T \gamma_0^{-1} \min(t, t') \ , \end{aligned}$$

where we used $\langle \xi_x(t)\xi_x(t')\rangle = \langle \xi_y(t)\xi_y(t')\rangle = 2k_BT\gamma_0\delta(t-t')$, and the fact that different noise components are uncorrelated, $\langle \xi_x(t)\xi_y(t')\rangle = 0$. As already announced, in the long times limit, $t \gg \gamma_0/k$ and $t' \gg \gamma_0/k$, one finds stationarity for the xx correlation, $C_{xx}(t,t') \to k_BT\gamma_0^{-1}e^{-k|t-t'|/\gamma_0}$, decorrelation of the crossed functions, $C_{xy}(t,t') \to 0$ and $C_{yx}(t,t') \to 0$, and diffusion along the y direction, $C_{yy}(t,t') \to 2k_BT\gamma_0^{-1}\min(t,t')$.

Apply now a small perturbation to the particle that modifies the potential V according to $V \to V - \vec{h}\cdot\vec{r}$. The solutions under the perturbation are

$$\langle x\rangle_{\vec{h}} = x(0)e^{-kt/\gamma_0} + \gamma_0^{-1}\int_0^t dt'\ e^{-k(t-t')/\gamma_0}\ [\xi_x(t') + h_x(t')]\ ,$$
$$\langle y\rangle_{\vec{h}} = y(0) + \gamma_0^{-1}\int_0^t dt'\ [\xi_y(t') + h_y(t')]\ ,$$

and these imply

$$R_{xx}(t,t') = \delta\langle x(t)\rangle_{\vec{h}}/\delta h_x(t')|_{\vec{h}=\vec{0}} = \gamma_0^{-1}\ e^{-k(t-t')/\gamma_0}\ \theta(t-t')\ ,$$
$$R_{yy}(t,t') = \delta\langle y(t)\rangle_{\vec{h}}/\delta h_y(t')|_{\vec{h}=\vec{0}} = \gamma_0^{-1}\ \theta(t-t')\ ,$$
$$R_{xy}(t,t') = \delta\langle x(t)\rangle_{\vec{h}}/\delta h_y(t')|_{\vec{h}=\vec{0}} = R_{yx}(t,t') = \delta\langle y(t)\rangle_{\vec{h}}/\delta h_x(t')|_{\vec{h}=\vec{0}} = 0\ .$$

The comparison to the time-derivatives of the associated correlation functions yields

$$k_BTR_{xx}(t,t') = \partial_{t'}C_{xx}(t,t')\theta(t-t') \qquad \text{and FDT holds}\ ,$$
$$k_BTR_{yy}(t,t') = \frac{1}{2}\partial_{t'}C_{yy}(t,t')\theta(t-t') \qquad \text{there is a factor of } 1/2\ ,$$
$$k_BTR_{xy}(t,t') = \partial_{t'}C_{xy}(t,t')\theta(t-t') = 0\ ,$$
$$k_BTR_{yx}(t,t') = 0 \ \text{ and } \ \partial_{t'}C_{yx}(t,t')\theta(t-t') \to 0 \ \text{ for } t' \gg \gamma_0/k\ .$$

2.5.5 Non-quadratic potentials: perturbation theory

For the moment we only treated cases in which the potential was, at most, quadratic, and the Langevin equation was, therefore, linear in the variable. Quite generally one faces non-linear stochastic differential equations that cannot be solved exactly.

In some fortunate cases, perturbation theory can be easily formulated in this context. Take, for instance, the case of a quartic potential $V(x) = kx^2/2 + \lambda x^4/2$ with $k > 0$ and $\lambda > 0$ and let us focus on the over-damped dynamics of a particle that starts from the position x_0 initially. The Langevin equation for $\lambda = 0$ has

already been solved. Let us then take the trajectory (2.140) as the zero-th order of a systematic expansion in powers of the coupling constant λ:

$$x(t) = \sum_{n=0} x_n(t)\lambda^n \tag{2.156}$$

with

$$x(0) = x_0 = \sum_{n=0} x_n(0)\lambda^n \ . \tag{2.157}$$

Quite naturally, we choose

$$x_0(0) = x_0 \qquad \text{and} \qquad x_{n>0}(0) = 0 \ . \tag{2.158}$$

Order by order in λ we then have

$$O(\lambda^0): \qquad \gamma_0 \dot{x}_0(t) = -kx_0(t) + \xi(t) \tag{2.159}$$

$$O(\lambda^1): \qquad \gamma_0 \dot{x}_1(t) = -kx_1(t) - x_0^3(t) \tag{2.160}$$

$$O(\lambda^2): \qquad \gamma_0 \dot{x}_2(t) = -kx_2(t) - 3x_0^2(t)x_1(t) \tag{2.161}$$

$$O(\lambda^3): \qquad \gamma_0 \dot{x}_3(t) = -kx_3(t) - 3x_2(t)x_0^2(t) - 3x_1^2(t)x_0(t) \tag{2.162}$$

etc. The structure of these equations is the same, with a linear operator $\gamma_0 d_t + k$ acting on the unknown functions at each order and a source term that is known (as a functional of ξ) from the previous orders. Their solutions are

$$x_n(t) = x_n(0)e^{-kt/\gamma_0} + \int_0^t dt' \ e^{-k(t-t')/\gamma_0} \ \text{source}(t') \tag{2.163}$$

Note that the power expansion in λ transforms into a power expansion in ξ. The averages can be easily computed by using the factorization properties of the noise averages for Gaussian statistics (Wick's theorem).

Figure 2.28: Dynamics in a quartic potential $V(x) = kx^2/2 + \lambda x^4/4$ with $k = 0$ and $\lambda = 1$ (left) and $k = 1$ and $\lambda = 0.1$ (right). In both cases $\gamma_0 = 1$ and $k_B T = 0.15$. Different curves are for different number of samples as explained in the key.

Exercise 2.19 Compute the first terms in the expansion above. Compare the outcome for σ^2 to the numerical result shown in Fig. 2.28 generated with $\gamma_0 = 1$ and $k_B T = 0.15$ for a pure quartic potential with $\lambda = 1$ and for a potential with $k = -1$. and $\lambda = 0.1$.

With this perturbative method one cannot, however, access non-perturbative processes as the ones leading to the thermal activation over barriers discussed below.

2.5.6 A particle in a harmonic potential under multiplicative white noise

Take the equation

$$\frac{dx(t)}{dt} = -kx(t) + x(t)\xi(t) \tag{2.164}$$

with zero average Gaussian white noise. Use the **Stratonovich** convention in which usual rules of calculus apply. In order to solve this stochastic differential equation, first absorb the first term in the rhs with the redefinition $y(t) = e^{kt}x(t)$ and write

$$\frac{dy}{dt} = y(t)\xi(t) \tag{2.165}$$

with the solution

$$y(t) = y(0)\ e^{\int_0^t dt'\ \xi(t')} \qquad \Rightarrow \qquad x(t) = x(0)\ e^{-kt+\int_0^t dt'\ \xi(t')} \tag{2.166}$$

For a Gaussian noise the average yields

$$\langle x(t)\rangle = x(0)\ e^{-kt}\ e^{\frac{1}{2}\langle(\int_0^t dt'\ \xi(t'))^2\rangle} = x(0)\ e^{-kt}e^{k_BTt} = x(0)e^{-(k-k_BT)t} \tag{2.167}$$

interestingly enough, the average particle position vanishes or diverges depending upon $k > k_BT$ or $k < k_BT$. It is clear from this example that in the latter case the particle does not equilibrate with the potential $V(x) = x^2/2$ as one could have expected. We will see how the departing equation has to be modified, by an additional drift term, to ensure equilibration to a quadratic potential, after discussing the Fokker-Planck equation for the stochastic process with multiplicative noise. The equation ensuring this fact is

$$\frac{dx(t)}{dt} = Dx(t) - kx^3(t) + x(t)\xi(t) \tag{2.168}$$

but this one is no longer solvable analytically.

One can still compute the linear response by using the solution under a perturbation linearly coupled to the particle's position ($-kx \mapsto -kx + h$)

$$x(t) = x_0\ e^{-kt+\int_0^t dt'\ \xi(t')} + \int_0^t dt'\ e^{-k(t-t')+\int_{t'}^t dt''\ \xi(t'')}\ h(t') \tag{2.169}$$

from where

$$\begin{aligned} R(t,t') &= e^{-k(t-t')}\langle e^{\int_{t'}^{t} dt''\ \xi(t'')}\rangle = e^{-k(t-t')}\ e^{\frac{1}{2}\langle(\int_{t'}^{t} dt''\ \xi(t''))^2\rangle} \\ &= e^{-k(t-t')}\ e^{k_B T(t-t')} = e^{-(k-k_B T)(t-t')} \end{aligned} \tag{2.170}$$

where we ignored the $\theta(t-t')$ factor assuming $t \geq t'$. The linear response is a stationary function, in the sense that it only depends upon $t-t'$. What about the position-position correlation and mean-share displacement? They read

$$\begin{aligned} C(t,t') &= \langle x_t x_{t'}\rangle = x_0^2\ e^{-k(t+t')}\ e^{k_B T[\max(t,t')]} \\ \Delta(t,t') &= \langle (x_t - x_{t'})^2\rangle \end{aligned} \tag{2.171}$$

and they both behave very weirdly.

2.5.7 Thermally activated processes

The phenomenological **Arrhenius law**[11] yields the typical time needed to escape from a potential well as an exponential of the ratio between the height of the barrier and the thermal energy scale $k_B T$, (with prefactors that can be calculated explicitly, see below). This exponential is of crucial importance for understanding slow (glassy) phenomena, since a mere barrier of $30 k_B T$ is enough to transform a microscopic time of 10^{-12}s into a macroscopic time scale. See Fig. 2.29-right for a numerical study of the Coulomb glass that demonstrates the existence of an Arrhenius time-scale in this problem. In the glassy literature such systems are called **strong** glass formers as opposed to **weak** ones in which the characteristic time-scale depends on temperature in a different way.

In 1940 Kramers estimated the **escape rate** from a potential well as the one shown in Fig. 2.29-center due to thermal fluctuations that give sufficient energy to the particle to allow it to surpass the barrier[12]. After this seminal paper this problem has been studied in great detail [22] given that it is of paramount importance in many areas of physics and chemistry. An example is the problem of the dissociation of a molecule where x represents an effective one-dimensional **reaction coordinate** and the potential energy barrier is, actually, a **free-energy barrier**.

Kramers assumed that the reaction coordinate is coupled to an equilibrated environment with no memory and used the probability formalism in which the parti-

[11] S. A. Arrhenius, *On the reaction velocity of the inversion of cane sugar by acids*, Zeitschrift für Physikalische Chemie **4**, 226 (1889).

[12] H. A. Kramers, *Brownian motion in a field of force and the diffusion model of chemical reactions*, Physica **7**, 284 (1940).

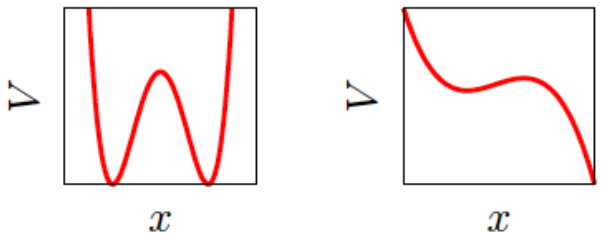


Figure 2.29: Left: sketch of a double-well potential. Center: sketch of a potential with a local minimum. Right: correlation function decay in a classical model of the $3d$ Coulomb glass at nine temperatures ranging from $T = 0.1$ to $T = 0.05$ in steps of 0.05 and all above T_g. In the inset the scaling plot $C(t) \sim f(t/t_A)$ with a characteristic time-scale, t_A, that follows the Arrhenius activated law, $t_A \simeq 0.45/T$. Figure due to Kolton, Domínguez and Grempel [25].

cle motion is described in terms of the time-dependent probability density $P(x, v, t)$ (that for such a stochastic process follows the Kramers partial differential equation).

If the thermal energy is at least of the order of the barrier height, $k_B T \sim \Delta V$, the reaction coordinate, x, moves freely from the vicinity of one well to the vicinity of the other.

The treatment we discuss applies to the opposite weak noise limit in which the thermal energy is much smaller than the barrier height, $k_B T \ll \Delta V$, the random force acts as a small perturbation, and the particle current over the top of the barrier is very small. Most of the time x relaxes towards the minimum of the potential well where it is located. Eventually, the random force drives it over the barrier and it escapes to infinity if the potential has the form in Fig. 2.29-center, or it remains in the neighbourhood of the second well, see Fig. 2.29-left.

Figure 2.30: Left panel: five runs of the Langevin equation in the over-damped limit with a double well external potential (oscillator) and a Gaussian white noise at temperature T. Central panel: the average $\langle x \rangle$ computed with $n = 10^2,\ 10^3,\ 10^4,\ 10^5$ runs. Right panel: the variance $\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$.

The treatment is simplified if a constant current can be imposed by injecting

particles within the metastable well and removing them somewhere to the right of it. In these conditions Kramers proposed a very crude approximation whereby P takes the stationary canonical form

$$P_{\rm st}(x,v) = \mathcal{N} e^{-\beta\frac{v^2}{2} - \beta V(x)} \ . \tag{2.172}$$

($m = 1$ for simplicity here.) If there is a sink to the right of the maximum, the normalization constant $\mathcal{N}$ is fixed by further assuming that $P_{\rm st}(x,v) \sim 0$ for $x \geq \tilde{x} > x_{\rm max}$. The resulting integral over the coordinate can be computed with a saddle-point approximation justified in the large β limit. After expanding the potential about the minimum and keeping the quadratic fluctuations one finds

$$\mathcal{N}^{-1} = \frac{2\pi}{\beta\sqrt{V''(x_{\rm min})}}\, e^{-\beta V(x_{\rm min})} \ .$$

The escape rate, r, over the top of the barrier can now be readily computed by calculating the outward flow across the top of the barrier:

$$\boxed{r \equiv \tfrac{1}{t_A} \equiv \int_0^\infty dv\ v P(x_{\rm max}, v) = \tfrac{\sqrt{V''(x_{\rm min})}}{2\pi}\, e^{-\beta(V(x_{\rm max}) - V(x_{\rm min}))}} \tag{2.173}$$

Note that we here assumed that no particle comes back from the right of the barrier. This assumption is justified if the potential quickly decreases on the right side of the barrier.

The crudeness of the approximation (2.172) can be grasped by noting that the equilibrium form is justified only near the bottom of the well. Kramers estimated an improved $P_{\rm st}(x,v)$ that leads to

$$r = \frac{\left(\frac{\gamma^2}{4} + V''(x_{\rm max})\right)^{1/2} - \frac{\gamma}{2}}{\sqrt{V''(x_{\rm max})}}\ \frac{\sqrt{V''(x_{\rm min})}}{2\pi}\ e^{-\beta(V(x_{\rm max}) - V(x_{\rm min}))} \ . \tag{2.174}$$

This expression approaches (2.173) when $\gamma \ll V''(x_{\rm max})$, *i.e.* close to the under-damped limit, and

$$r = \frac{\sqrt{V''(x_{\rm max})V''(x_{\rm min})}}{2\pi\gamma}\, e^{-\beta(V(x_{\rm max}) - V(x_{\rm min}))} \tag{2.175}$$

when $\gamma \gg V''(x_{\rm max})$, *i.e.* in the over-damped limit (see Sect. 2.4.5 for the definition of these limits).

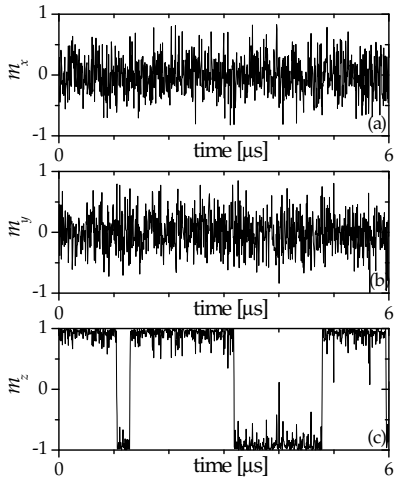


Figure 2.31: Magnetization reversal (an activated process) in the LLGB equation (picture taken from Romá, LFC & Lozano 14).

The inverse of (2.174), t_A, is called the **Arrhenius time** needed for **thermal activation** over a barrier $\Delta V \equiv V(x_{\max}) - V(x_{\min})$. The prefactor that characterises the well and barrier in the harmonic approximation is the **attempt frequency** with which the particles tend to jump over the barrier. In short,

$$\boxed{t_A \simeq \tau \, e^{\beta|\Delta V|} \qquad \text{(Arrhenius time)}} \tag{2.176}$$

The one-dimensional reaction coordinate can be more or less easily identified in problems such as the dissociation of a molecule. In contrast, such a single variable is much harder to visualize in an interacting problem with many degrees of freedom. The Kramers problem in higher dimensions is highly non-trivial and, in the infinite-dimensional **phase-space**, is completely out of reach.

The Arrhenius time can be derived within the path-integral formalism that we will discuss later [26, 27].

2.5.8 Driven systems

In the introduction we mentioned that systems can be externally maintained out of equilibrium We list here two solvable examples, in the form of exercises, that illustrate this point.

Exercise 2.20 Study the Langevin equation for a single particle moving in $d = 1$ under no external potential, in a case in which the friction kernel is $\gamma_1(t - t')$ and the noise-noise correlation in $\Gamma_2(t - t')$.

Exercise 2.21 Take a harmonic oscillator, in its over-damped limit to make the calculations simpler, and couple it to two external reservoirs, at different temperatures, T_1 and T_2, and different memory kernels, for instance, a delta function (white noise) and an exponential decay (Ornstein-Uhlenbeck process). The Langevin relaxation of the particle can be solved exactly and it is quite interesting. The particle inherits the two time-scales ($\tau_1 \to 0$ and τ_2 finite) from the baths as can be seen from the decay, in two steps, of the position correlation function or linear response. The temperatures of the environments appear in the fluctuation dissipation relation between these two functions in the corresponding time regimes [37, 38].

Exercise 2.22 Take now a symmetric two-dimensional harmonic oscillator $V(x, y) = k(x^2 + y^2)/2$ and apply the non-potential force $\vec{f}(x, y) = a(y, -x)$ on it, with a a parameter. This force makes a particle turn within the potential well. Describe the trajectories and compute mean-square displacement, correlation function and linear response. One can check, by direct calculation, that the fluctuation-dissipation theorem does not hold.

2.6 The Fokker-Planck approach

The Kramers or Fokker-Planck approach is useful to prove that a given Langevin equation with **white noise** takes the system to equilibrium at the working temperature. It is a deterministic partial differential equation on the probability distribution for the stochastic variable at time t to take a given value, say y, that can be closed as such for problems with white (additive or multiplicative) noise. The stichastci variables can be both velocity and position and then one speaks about the **Kramers equation** or just the position variables, in the Smoluchowski $t \gg t_I$ limit and one speaks about the **Fokker-Planck equation**. here, for the sake of simplicity, we focus on the latter case.

We start from the identity for **Markov processes**,

$$P(y, t + dt) = \int dx_0 \; P(y, t + dt|x_0, t) \; P(x_0, t) \; , \tag{2.177}$$

where $P(y, t + dt|x_0, t)$ is the **conditional probability** of finding y at time $t + dt$ provided the system was in the state x_0 at the previous time t (note that x_0 is not necessarily the initial value here). The integral runs over all accessible values of x_0.

This equation holds for any value of the time increment dt but we will later focus on infinitesimal ones. It is also called the **Chapman-Kolmogorov** equation.

To make contact with the stochastic process in the Langevin description, it is convenient to define the conditional probability in the following way:

$$P(y, t+dt|x_0, t) = \langle \delta(y - x(t+dt)) \rangle \tag{2.178}$$

where the mean value is taken over the noise ξ, and $x(t+dt)$ is determined by the Langevin equation with the 'initial condition' $x(t) = x_0$. Expanding Eq. (2.178) in powers of $\Delta x \equiv x(t+dt) - x(t) = y - x_0$ we immediately obtain

$$P(y, t+dt|x_0, t) = \delta(y-x_0) - d_y\delta(y-x_0)\langle \Delta x \rangle + \frac{1}{2} d_y^2 \delta(y-x_0)\langle (\Delta x)^2 \rangle + \dots \tag{2.179}$$

where the ellipsis indicate terms involving higher order moments of Δx. The idea is to compute the averages $\langle \Delta x \rangle$ and $\langle (\Delta x)^2 \rangle$ to leading order in dt and then take the limit $dt \to 0$. To do this, we need to use the Langevin equation of motion and it is at this point that its form (additive or multiplicative noise) will play a role.

We recall the discretization of the stochastic different equations with white noise discussed in Sec. :

$$\gamma_0(x_{n+1} - x_n) = f(\overline{x}_n)dt + g(\overline{x}_n)\xi_n dt \tag{2.180}$$

where we reintroduced the friction coefficient γ_0. The overline variables are defined as $\overline{x}_n = \alpha x_{n+1} + (1-\alpha)x_n$, and $\langle \xi_n dt \rangle = 0$ and $\langle (\xi_n dt)^2 \rangle = 2Ddt$, with $D = k_B T \gamma_0$.

2.6.1 Additive white noise

We will here present an evaluation of Δx obtained from the integration of the Langevin equation over the interval $[t, t+dt]$. It reads

$$\Delta x \equiv x(t+dt) - x(t) = x_{n+1} - x_n = -\frac{1}{\gamma_0} V'(\overline{x}_n) + \frac{1}{\gamma_0}\xi_n dt \tag{2.181}$$

and x_n being set to the 'reference value' x_0. From here the averages are readily computed:

$$\langle \Delta x \rangle = -\frac{dt}{\gamma_0} V'(x_0) \tag{2.182}$$

$$\langle (\Delta x)^2 \rangle = \frac{2Ddt}{\gamma_0^2} + O(dt^2) \tag{2.183}$$

where, in the second line, we identified the contribution from the deterministic force as being $O(dt^2)$ and we used the fact that $x(t) = x_n$ will be fixed to x_0 to set to zero

the contribution from the cross product. Interestingly enough, the mean value as well as the second moment are of order dt. Higher momenta of the distribution such as $\langle(\Delta x)^3\rangle$ and so on and so forth are of higher order in dt and do not contribute to the expansion for sufficiently small dt. It is important to note that these results depend on x_0. Replacing now these averages in (2.179), next in (2.177),

$$\begin{aligned} P(y,t+dt) &= P(y,t) + \frac{dt}{\gamma_0}\partial_y \int dx_0\ V'(x_0)\ \delta(y-x_0)\ P(x_0,t) \\ &\quad + \frac{2Ddt}{2\gamma_0^2}\partial_y^2 \int dx_0\ \delta(y-x_0)\ P(x_0,t)\ , \end{aligned} \tag{2.184}$$

performing the integrals over x_0, and taking the $dt \to 0$ limit

$$\gamma_0 \partial_t P(y,t) = \partial_y[V'(y)\ P(y,t)] + \frac{D}{\gamma_0}\partial_y^2 P(y,t) \tag{2.185}$$

This is the Fokker-Planck (or Smoluchowski) equation for a one variable Langevin process with white additive noise. Note that if $D = k_B T \gamma_0$ the factor in the last term becomes $k_B T$ and this equation takes the usual form. The limit γ_0 can then be safely taken to recover the dissipation-less limit.

Stationary solution

We look now for a solution that is time-independent, $P_{\rm st}(y)$, and normalizable. We have

$$0 = \partial_y[V'(y)\ P_{\rm st}(y)] + \frac{D}{\gamma_0}\partial_y^2 P_{\rm st}(y)\ . \tag{2.186}$$

A first integration over y implies

$$\text{cst} = V'(y)\ P_{\rm st}(y) + \frac{D}{\gamma_0}\ \partial_y P_{\rm st}(y)\ . \tag{2.187}$$

To ensure the normalization of the pdf it is natural to impose $\lim_{y\to\infty} P_{\rm st}(y) = 0$ and $\lim_{y\to\infty} \partial_y P_{\rm st}(y) = 0$. Therefore, the constant must vanish and we find

$$\frac{\partial_y P_{\rm st}(y)}{P_{\rm st}(y)} = -\frac{\gamma_0 V'(y)}{D} \qquad \Rightarrow \qquad P_{\rm st}(y) \propto e^{-\gamma_0 V(y)/D} = e^{-V(y)/(k_B T)} \tag{2.188}$$

Approach to the stationary solution

The question remains as to whether the dynamics of the system takes it to this stationary solution asymptotically or not. An elegant way to prove this fact is to consider the 'dynamic free-energy functional'

$$\mathcal{F}[P] = \int dy\ P(y,t)\ [k_B T \ln P(y,t) + V(y)] \tag{2.189}$$

where P is a generic solution of the Fokker-Planck equation. The time derivative of $\mathcal{F}$ reads

$$d_t \mathcal{F}[P] = \int dy\ \partial_t P(y,t)\ \ [k_B T \ln P(y,t) + V(y) + k_B T] \tag{2.190}$$

Using now the FP equation to replace $\partial_t P(y,t)$

$$\begin{aligned} d_t \mathcal{F}[P] \ &= \ \int dy\ \left\{ \frac{1}{\gamma_0} \partial_y [V'(y) P(y,t)] + \frac{D}{\gamma_0^2} \partial_y^2 P(y,t) \right\} \\ &\quad [k_B T \ln P(y,t) + V(y) + k_B T] \end{aligned} \tag{2.191}$$

We now integrate by parts and drop the border terms as P and $\partial_y P$ are expected to vanish at infinity to obtain

$$\begin{aligned} d_t \mathcal{F}[P] \ &= \ -\frac{1}{\gamma_0} \int dy\ \ [V'(y) P(y,t) + k_B T \partial_y P(y,t)] \\ &\qquad \times \partial_y \left[k_B T \ln P(y,t) + V(y) + k_B T \right] \\ &= \ -\frac{1}{\gamma_0} \int dy\ \ [V'(y) P(y,t) + k_B T \partial_y P(y,t)]^2 \ \frac{1}{P(y,t)} \leq 0 \end{aligned} \tag{2.192}$$

Moreover, one sees that the numerator in the integrand vanishes identically only for $P_{\rm eq} = N e^{-V/(k_B T)}$. For the Boltzmann equilibrium distribution function, therefore, $d_t \mathcal{F}[P_{\rm eq}] = 0$.

As V is bounded from below for a potential that may lead to equilibrium, $\mathcal{F}$ is also bounded from below. In the course of time, for any $P \neq P_{\rm eq}$, its derivative is always negative. Therefore, $\mathcal{F}$ has to approach its asymptotic value where $d_t \mathcal{F}$ must vanish. As we also showed that $d_t \mathcal{F}[P_{\rm eq}] = 0$ then

$$\lim_{t \to \infty} P(y,t) = P_{\rm eq}(y)\ . \tag{2.193}$$

Connection to the Schrödinger equation

The FP equation looks very similar to the Schrödinger equation for imaginary time, apart from a term proportional to $V'(y) \partial_y P(y,t)$. One can, however, eliminate it by introducing the function

$$P(y,t) = \psi_0(y) \rho(y,t) \qquad \text{with} \qquad \psi_0(y) = \text{ct}\ e^{-\frac{\beta}{2} V(y)} \tag{2.194}$$

with $\beta = (k_B T)^{-1}$. After a simple calculation one finds

$$\gamma_0 \partial_t \rho(y,t) = \left[k_B T \partial_y^2 - U_{\rm FP}(y)\right] \rho(y,t) \tag{2.195}$$

with

$$U_{\rm FP}(y) = -\frac{1}{2} V''(y) + \frac{\beta}{4} (V'(y))^2 \tag{2.196}$$

where FP stands for Fokker-Planck. This is a Schrödinger equation in imaginary time, with the linear Schrödinger operator

$$H_{\rm FP}(y) = k_B T \partial_y^2 - U_{\rm FP}(y) \tag{2.197}$$

that is a symmetric operator on the space of real functions ($\int dx\ (H_{\rm FP}\Phi_1(x))\Phi_2(x) = \int dx\ \Phi_1(x)(H_{\rm FP}\Phi_2(x))$). A number of properties follow:
– The eigenvalues of $H_{\rm FP}$ are real.
– If $U_{\rm FP}$ grows rapidly to infinity for $y \to \pm\infty$ the spectrum of $H_{\rm FP}$ is discrete.
– It is easy to check that $\psi_0(y)$ is an eigenvector of $H_{\rm FP}$ with zero eigenvalue, $H_{\rm FP}(y)\psi_0(y) = E_0\psi_0(y) = 0$, implying $E_0 = 0$.
– $\psi_0(y)$ is non-negative (cst is taken to be positive). Hence, it must be the ground state of $H_{\rm FP}$. All other eigenvalues E_n are strictly positive, $E_n > 0$ for $n > 0$.
– The eigenvectors of $H_{\rm FP}$ associated to different eigenvalues are orthogonal.
– The solution is

$$\rho(y,t) = \sum_{n=0}^{\infty} c_n \psi_n(y) e^{-E_n t} \tag{2.198}$$

(where we absorbed the γ_0 in a redefinition of time, for simplicity) with $H_{\rm FP}\psi_n(y) = E_n\psi_n(y)$ and $c_n = \int dy\ \psi_n(y)\rho(y,0)$.
– When $t \to \infty$ all terms vanish exponentially apart from the one associated to $n = 0$. Thus,

$$\lim_{t\to\infty} \rho(y,t) = c_0\psi_0(y) = \psi_0(y) \tag{2.199}$$

since $c_0 = \int dy\ \psi_0(y)\rho(y,0) = \int\ dy\ P(y,0) = 1$.
– The property above implies

$$\lim_{t\to\infty} P(y,t) = \psi_0^2(y) = {\rm cst}^2 e^{-\beta V(y)} \tag{2.200}$$

– One can easily show that the probability is normalized at all times

$$\begin{aligned} \int dy\ P(y,t) &= \int dy\ \psi_0(y)\rho(y,t) = \int dy\ \psi_0(y) \sum_n c_n \psi_n(y) e^{-E_n t} \\ &= \sum_n c_n e^{-E_n t} \int dy\ \psi_0(y)\psi_n(y) = \sum_n c_n e^{-E_n t}\delta_{n0} = c_0 = 1 \end{aligned} \tag{2.201}$$

– Finally,

$$\lim_{t\to\infty} P(y,t) = \frac{e^{-\beta V(y)}}{\int dx\ e^{-\beta V(x)}} \tag{2.202}$$

and this is another way of proving the approach to Boltzmann equilibrium.

Relaxation time

The longest relaxation time is then the inverse of the energy of the first excited state

$$\tau_{\rm eq} = E_1^{-1}\ . \tag{2.203}$$

This time can, however, diverge. In particular, if it scales with the size of the system.

2.6.2 Multiplicative white noise

In this calculation we will be more careful with the discrete time analysis. We rely heavily on the fact that $\langle \xi_n \xi_m \rangle = 2D/dt\ \delta_{nm}$ implies $\xi_n \simeq \mathcal{O}(dt^{-1/2})$ and $\xi_n dt \simeq \mathcal{O}(dt^{1/2})$. We work with the generic equation $\gamma_0 d_t x = f(x) + g(x)\xi$.

As discussed in Sec. the discretized equation reads

$$\gamma_0 \Delta x \equiv x_{n+1} - x_n = f(x_n)dt + g(x_n)\xi_n dt + g'(x_n)\alpha \Delta x \xi_n dt\ . \tag{2.204}$$

We replace Δx in the last term by this very same equation to get

$$\begin{aligned} \gamma_0 \Delta x \ &= \ f(x_n)dt + g(x_n)\xi_n dt \\ &\quad + g'(x_n)\alpha \xi_n dt \gamma_0^{-1}[f(x_n)dt + g(x_n)\xi_n dt + g'(x_n)\alpha \Delta x \xi_n dt]\ . \end{aligned} \tag{2.205}$$

Keeping now all terms that will contribute to the average up to $\mathcal{O}(dt)$

$$\gamma_0 \Delta x = f(x_n)dt + g(x_n)\xi_n dt + \alpha g(x_n) g'(x_n) \gamma_0^{-1} (\xi_n dt)^2 \tag{2.206}$$

If we fix x_n to take the value $x(t) = x_0$ in the expansion for $P(y, t+dt|x_0, t)$, x_n is not correlated with the noise ξ_n. Therefore, under the noise average the third term vanishes. Using $\langle (\xi_n dt)^2 \rangle = 2Ddt$,

$$\gamma_0 \langle \Delta x \rangle = f(x_n)dt + 2D\gamma_0^{-1} \alpha g(x_n) g'(x_n) dt\ . \tag{2.207}$$

Let us examine $(\Delta x)^2$. Keeping terms that will contribute to the average up to $\mathcal{O}(dt)$ we have

$$\gamma_0^2 \langle \Delta x^2 \rangle \simeq \langle [g(x_n)\xi_n dt]^2 \rangle = 2D g^2(x_n)\ dt \tag{2.208}$$

Once again, the mean value as well as the two point correlation are of order dt. These results depend on $x_n = x_0$. Replacing now in (2.179), next in (2.177),

$$\gamma_0 P(y,t+dt) = \gamma_0 P(y,t) - dt\ \partial_y \int dx_0\ [f(x_0) + 2\frac{D}{\gamma_0}\alpha g(x_0)g'(x_0)]\ \delta(y-x_0)\ P(x_0,t) + \frac{2Ddt}{2\gamma_0}\partial_y^2 \int dx_0\ \delta(y-x_0)\ g^2(x_0)\ P(x_0,t)\ , \tag{2.209}$$

and performing the integrals over x_0, in the $dt \to 0$ limit

$$\boxed{\gamma_0 \partial_t P(y,t) = -\partial_y\{[f(y) + 2\frac{D}{\gamma_0}\alpha g(y)g'(y)]\ P(y,t)\} + \frac{D}{\gamma_0}\partial_y^2[g^2(y)P(y,t)]} \tag{2.210}$$

This is the Fokker-Planck (or Smoluchowski) equation for the stochastic process $\gamma_0 d_t x = f(x) + g(x)\xi$ with white noise. For $g(x) = 1$ we recover Eq. (2.185) for additive noise.

Stationary solution

The stationary solution to Eq. (2.210) with vanishing current, $J = 0$, is

$$P_{\rm st}(x) = \frac{N}{g^2(x)} \exp\left[\frac{\gamma_0}{D}\int_x dx'\ \frac{f(x') + 2D\gamma_0^{-1}\alpha g(x)g'(x))}{g^2(x')}\right] \tag{2.211}$$

with N a normalization constant. This stationary probability depends upon α and $g(x)$. In order to get rid of this undesired feature, we chose to work with the drifted force

$$\boxed{f(x) = -g^2(x)V'(x) + 2D\gamma_0^{-1}(1-\alpha)g(x)g'(x)}\ . \tag{2.212}$$

The associated FP equation reads

$$\begin{aligned}\partial_t P(x,t) &= -\partial_x[-g^2(x)V'(x) + 2D\gamma_0^{-1}g(x)g'(x))P(x,t)] \\ &\quad + D\gamma_0^{-1}\,\partial_x^2[g^2(x)P(x,t)] \\ &= \partial_x\{[(g^2(x)V'(x) - 2D\gamma_0^{-1}g(x)g'(x))P(x,t)] \\ &\quad + D\gamma_0^{-1}\,\partial_x[g^2(x)P(x,t)]\} \\ &= \partial_x\{g^2(x)[V'(x)P(x,t) + D\gamma_0^{-1}\,\partial_x P(x,t)]\}\ .\end{aligned} \tag{2.213}$$

It is still independent of α though it depends on $g(x)$. However, its asymptotic solution with vanishing current does not and it reads

$$P_{\rm st}(x) = P_{\rm GB}(x) = N\exp\left[-\frac{\gamma_0}{D}\ V(x)\right] \tag{2.214}$$

independently of α and g, the desired result. Note that the effect of the extra term is to correct the prefactor in the measure, not what goes in the exponential, that would be the same $-\gamma_0 V/D$ even without the additional $2D\gamma_0^{-1} g g'$ term in the drift.

Therefore, meaning physical applications in the sense that the stochastic dynamics tends to equilibrium at the Boltzmann measure, need the drifted Langevin equation

$$\boxed{d_t x(t) = -g^2 V'(x) + 2D\gamma_0^{-1}(1-\alpha) g(x) g'(x) + g(x)\xi(t)} \tag{2.215}$$

Note that with this force, there is a drift in the Langevin equation even in the Stratonovich convention. The extra term *is not* the one needed to build the generalized derivative appearing in the chain rule (2.76), since the factor $2D(1-\alpha)$ in the drift is different from the factor $D(1-2\alpha)$ in the chain-rule (in these two last expression we have absorbed γ^{-1} in a redefinition of D as in the section where we derived the chain rule γ_0 was set to one.). The Fokker-Planck equation takes a simple form given in Eq. (2.213).

The Langevin equation (2.215) is equivalent to (again with $\gamma_0 = 1$)

$$\boxed{g^{-2}(x) d_t x(t) = -V'(x) + 2D(1-\alpha) g'(x) g^{-1}(x) + g^{-1}(x)\xi(x)} \tag{2.216}$$

that has the form claimed in [94] in the sense that the term responsible for dissipation (lhs) is proportional to g^{-2} while the noise is accompanied by just one factor g^{-1} and there is no g factor in the deterministic force along the gradient descent direction. The second term in the rhs is the drift that was not discussed in [94] since the approach to equilibrium was not studied in this paper.

2.6.3 Kramers equation and colored noise

In the previous section we worked in the Smoluchowski limit. A partial differential equation for $P(v, x, t)$ can also be derived.

Exercise 2.23 Derive the Kramers equation.

The coloured noise case is more tricky. As no Markov property can be used there is no closed partial differential equation for $P(y, t)$.

2.7 Master equation

For the moment we have only treated problems with continuous variables and in the rest of the notes we will stick to this kind of problems as well. However,

here, we wish to present the master equation that is, basically, the partner of the Fokker-Planck equation for discrete Markov stochastic processes.

The Chapman-Kolmogorox equation (2.177) applies also to problems with discrete variables with the simplification of replacing the integral by a sum over discrete states. The conditional or **transition probability** over an infinitesimal time interval dt can be written as

$$P(y,t+dt|x_0,t) = \underbrace{\left(1 - dt\sum_z W_{zy}\right)}_{\text{probabilty of no transition}} \delta_{zy} + dtW_{yx_0} \tag{2.217}$$

The possibility of there being more than one transition in the interval dt has been neglected; a conjecture that is valid in the limit $dt \to 0$. The first term represents the probability for the system to stay in the state x_0 between t and dt while the second term is the probability that the system leaves the state x_0 to go to y in this same interval. Consistently, this expression satisfies $\sum_y P(y,t+dt|x_0,t) = 1$.

Replacing now (2.217) in (2.177) and arranging terms in such a way to have a time-derivative in the left-hand-side,

$$\frac{dP_x}{dt} = \sum_z (W_{xz}P_z - W_{zx}P_x) \tag{2.218}$$

The first term in the right-hand-side is a gain, in the sense that it increases the probability P_x while the second term in the right-hand-side is a loss since it contains the contribution of all processes that take from x to any z and makes P_x diminish. This is the **master equation**.

2.8 Concluding remarks

The Langevin equation and its relation to the Fokker-Planck formalism have been described in many textbooks on stochastic processes including Risken's [29], Gardiner's [30] and van Kampen's [31]. Many applications can be found in Coffrey et al.'s [32]. Another derivation of the Langevin equation uses collision theory and admits a generalization to relativistic cases [22]. The alternative master equation description of stochastic processes, more adapted to deal with discrete variables, is also very powerful but we will not use it is these lectures.

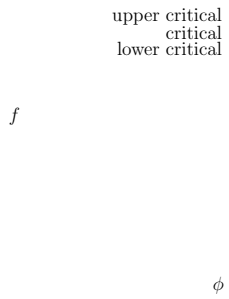
3 Dynamics at or through a phase transition

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 will 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 metallurgy terminology. We will investigate how the system evolves by trying to accommodate to the new conditions and equilibrate with its environment. We will 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 will 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.

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. 3.32 for a sketch. We will discuss quenches to the phase transition and below it. In the former case, the system can get to a critical point (Fig. 3.32-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. 3.32-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. 3.32-left) or **metastable**, that is to



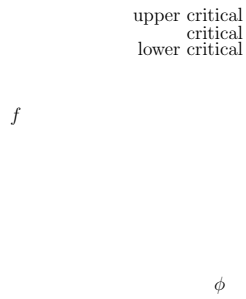


Figure 3.32: Left: second-order phase transition. Right: first order phase transition.

say a local minimum, and the phase transition is of first order (see Fig. 3.32-right) in the final externally imposed conditions.[13] 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 materials (with equal overall concentration) 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. An example is the easy-axis magnetization reversal under an abrupt change of the sign of the applied field or phase separation across first order phase transitions.

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 inmiscible liquids. Ferromagnetic domain growth is an example of the **non-conserved** case.

The kinetics of systems undergoing critical dynamics [6] or an ordering process [4] is an important problem for material science but also for our generic understanding of pattern formation in non-equilibrium systems and the approach to equilibrium in systems with slow dynamics that are yet not well understood. 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

[13] Strictly speaking metastable states with infinite life-time exist only in the mean-field limit.

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 growth of order is an open question.

Exercise 3.1 Take the d-dimensional Ising Hamiltonian, $H = -J \sum_{\langle ij \rangle} s_i s_j + h \sum_i s_i$ for spins $s_i = \pm 1$ and transform it into a Hamiltonian for occupation variables of two interacting species A and B, apt to describe phase separating problems. Relate the exchange parameter J to the interaction energy between neighbouring particles, ϵ_{AA}, ϵ_{AB} and ϵ_{BB}. See, e.g. [5].

Exercise 3.2 Treat the Ising and binary-mixture models in the mean-field approximation (called Curie-Weiss or Bragg-Williams or, equivalently, replace the sum over nearest-neighbours on the lattice by a sum over all pair of spins in the sample) and obtain their equilibrium phase diagrams, free-energy densities as function of the relevant order parameters, and the dependence of the latter on the external parameters (temperature and magnetic field in the magnetic system, and temperature and density difference of the two kinds of particles in the unary mixture case). Compare the free-energy density to the form in Fig. 3.32.

Exercise 3.3 Take a ferromagnetic Ising model with four spin interactions $H = -J \sum_{ijkl} s_i s_j s_k s_l$, and study it with the mean-field approximation. Is the transition of second or first order? Discuss.

3.1 Summary of static critical phenomena and scaling

In equilibrium, when a critical point is approached in parameter space, the assumption is that the correlation length is the only relevant length scale, and that it depends upon the distance from the critical point as

$$\xi_{eq} \simeq |T - T_c|^{-\nu} \tag{3.1}$$

The emerging long-range correlations are fully specified by the symmetry properties of the model under consideration and do not depend on details of the microscopic interactions. The notion of universality was originally introduced by experimentalists in order to describe the observation that several apparently unrelated physical systems may be characterized by the same type of singular behaviour near the transition.

In equilibrium the dynamics are stationary. One-time quantities should be independent of absolute time. Two-time quantities should depend upon the time difference, and time-delay dependent correlation functions characterise the temporal decorrelation of equilibrium fluctuations.

Critical scaling states that the correlation function should be an homogenous function

$$G(\vec{r}, t-t') = \mu^{d-2+\eta}\, \mathcal{G}(\mu\vec{r}, (t-t')\mu^z, |T-T_c|\mu^{1/\nu}), \tag{3.2}$$

and its structure factor

$$S(\vec{k}, t-t') = k^{-2+\eta}\, \Sigma(\vec{k}/\mu, (t-t')\mu^z, |T-T_c|\mu^{1/\nu}) \tag{3.3}$$

as well, with μ a momentum scale. The exponents and scaling functions can be derived with the RG analysis of an effective field theory, valid in the vanishing lattice spacing limit. By universality, the critical behaviour of continuous theory and discrete system should be the same. This statement is also expected to hold in the equilibrium dynamics, in the sense that its aspects should not depend on the details of the microscopic updates used (as long as they respect the same conservation laws).

3.2 The kinetic Ising model

The Ising spin variables do not have intrinsic dynamics, as is seen by constructing the relevant Poisson bracket. In order to associate kinetics with the Ising model, one assumes that it is placed in contact with a heat bath that generates stochastic spin-flips, $s_i \mapsto -s_i$. These updates are appropriate to describe the non-conserved order parameter dynamics of the paramagnetic - ferromagnetic transition. The heat bath can be interpreted as consisting of phonons that induce spin-flips via a spin-lattice coupling. The probability of a jump depends on the configuration of all other spins and the heat-bath temperature and it is chosen to satisfy **detailed balance** so as to ensure the asymptotic approach to equilibrium. A realisation of this dynamics is given by the Glauber model [45].

In the case in which the Ising model describes a lattice gas or a binary (AB) mixture the appropriate microscopic kinetics involves the diffusion of atoms. For example, atomic jumps to vacant sites in the lattice gas, or A and B interchanges in the binary mixture. Thus, the heat bath causes the exchange of neighbouring spins that point in opposite directions, or the exchange of two neighbouring particles and satisfies the detailed balance condition. This process mimics phonon-induced atomic jumps. The resultant model is referred to as the spin-exchange or Kawasaki model [46].

3.3 Snapshots

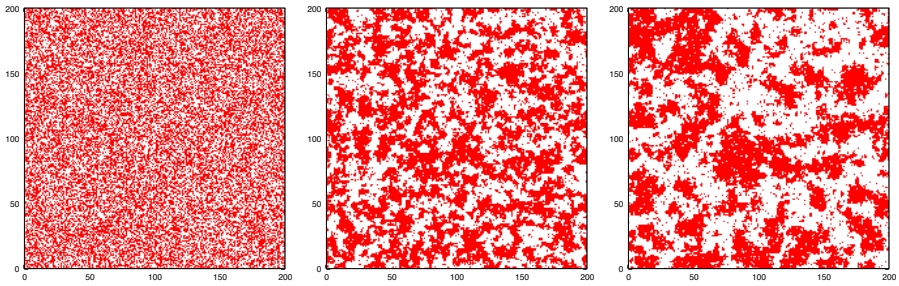


Figure 3.33: Monte Carlo simulations of a $2d$ Ising model. Three snapshots at $t = 1,\ 3 \times 10^5,\ 3 \times 10^6$ MCs after a quench to T_c. Note that $m_{eq} = 0$.

Figure 3.34: Monte Carlo simulations of a $2d$ Ising model. Three snapshots at $t = 1,\ 3\times10^5,\ 3\times10^6$ MCs after a quench to $0.5\ T_c$. Thermal fluctuations within the domains are visible. They are like equilibrium fluctuations leading to $0 < m_{eq} < 1$ at $T < T_c$.

Take a magnetic system, such as the ubiquitous Ising model with ferromagnetic uniform interactions, and quench it to its Curie point or into the low temperature phase starting from a random initial condition. Classically, the spins do not have an intrinsic dynamics; it is defined via a stochastic rule of Glauber, Metropolis, Langevin (when soft-spins are used) or similar type with or without locally conserved magnetization. For the purpose of the following discussion it is sufficient to focus on non-conserved local microscopic dynamics. Three snapshots taken after times 1, 3×10^5 and 3×10^6 MCs in a critical and two sub-critical quenches at different T below T_c are shown in Figs. 3.33, 3.34, and 3.35, respectively.

Time-dependent macroscopic observables are then expressed in terms of the values of the spins at each time-step. For instance, the magnetization density and its two-time self correlation function are defined as

$$m(t) \equiv N^{-1} \sum_{i=1}^{N} \langle\, s_i(t) \,\rangle \ , \qquad C(t,t') \equiv N^{-1} \sum_{i=1}^{N} \langle\, s_i(t) s_i(t') \,\rangle \ , \tag{3.4}$$

where the angular brackets indicate an average over many independent runs (i.e. random numbers) starting from identical initial conditions and/or averages over different initial configurations.

In **critical quenches**, patches with equilibrium critical fluctuations grow in time but their linear extent never reaches the equilibrium correlation length that diverges, $R_c(t) \ll \xi_{eq}(T_c) \to \infty$. Clusters of aligned neighbouring spins 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. The equilibrium magnetization vanishes, $m_{eq}(T_c) =$ and $\langle s_i(t) \rangle = 0$ at all t.

In **quenches into the ordered phase through a second order phase transition** the ferromagnetic interactions tend to align the neighbouring spins in parallel direction and in the course of time domains of the two ordered phases form and grow, see Figs. 3.34, 3.35 and 3.36. At any finite time after the quench the configuration is such that the two types of domains co-exist. If one examines the configurations in more detail one reckons that there are some spins reversed within the domains. These 'errors' are due to thermal fluctuations and are responsible of the fact that the magnetization of a given configuration within the domains is smaller than one and close to the equilibrium value at the working temperature (apart from fluctuations due to the finite size of the domains), $0 < m_{eq}(T)$. The total magnetization, computed over the full system, is zero (up to fluctuating time-dependent corrections that scale with the square root of the inverse system size). The thermal averaged spin, $\langle s_i(t) \rangle$ vanishes for all i and all finite t, see below for a more detailed discussion of the time-dependence. As time passes the typical size of the domains $R(t)$ increases and the interfaces get flatter in a way that we will also discuss below.

Quenches across first order phase transitions will be discussed separately in Sec. 3.16.

Figure 3.35: Monte Carlo simulations of the $2d$ Ising model. Three snapshots at $t = 1,\ 3 \times 10^5, 3 \times 10^6$ MCs after a quench to 0.01 T_c. There is almost perfect order within the domains ($m_{eq} \simeq 1$).

3.4 Relaxation, equilibration and reversal times

We wish to distinguish the **relaxation time**, t_r, defined as the time needed for a given initial condition to reach equilibrium in one of the (possibly many equivalent)

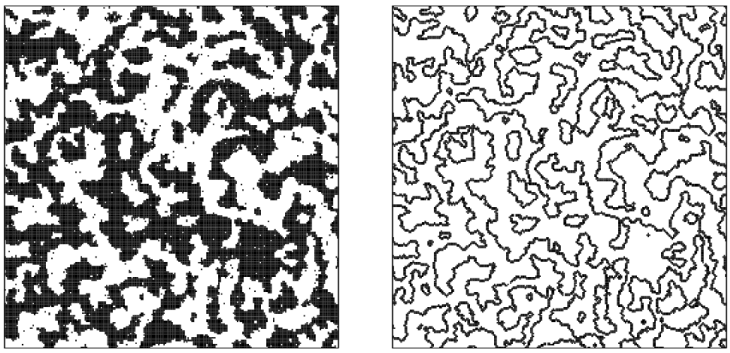


Figure 3.36: Snapshot of the $2d$ Ising model at a number of Monte Carlo steps after a quench from infinite to a subcritical temperature. Left: the up and down spins on the square lattice are represented with black and white sites. Right: the domain walls are shown in black.

phases, from the **decorrelation time**, t_d, defined as the time needed for a given configuration to decorrelate from itself. To lighten the notation we do not signal out the variable that we use to study these typical times (as we did with the velocity and position in the examples of Sect. 2.5). We further define the **reversal time**, t_R, as the time needed to go from one to another of the equivalent equilibrium phases. We focus on a second-order phase transition with broken symmetry between two equilibrium states here.

3.4.1 Quench from $T \gg T_c$ to $T > T_c$

If one quenches the system to $T > T_c$ the relaxation time, t_r, needed to reach configurations sampled by the Boltzmann measure depends on the system's parameters but, most importantly, remains finite even for an infinite-size system. Once a short transient overcome, the average of a local spin approaches the limit given by the Boltzmann measure, $\langle s_i(t) \rangle \to \langle s_i \rangle_{eq} = m = 0$, for all i and all other more complex observables satisfy equilibrium laws. The relaxation time is estimated to behave as $t_r \simeq |T - T_c|^{-\nu z_{eq}}$ close to T_c, with ν the critical exponent characterizing the divergence of the equilibrium correlation length, $\xi_{eq} \sim (T - T_c)^{-\nu}$, and z_{eq} the dynamic equilibrium exponent that links times and lengths, $R_c(t) \sim t^{1/z_{eq}}$.

The relaxation of the two-time self-correlation at $T > T_c$, when the time t' is

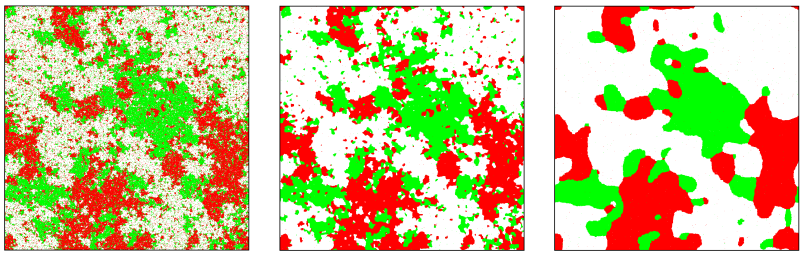


Figure 3.37: Snapshot of the $2d$ Potts model with $q = 3$ at a number of Monte Carlo steps after a quench from the critical to a subcritical temperature.

chosen to be longer than t_r, decays exponentially

$$\lim_{t' \gg t_r} \langle s_i(t) s_i(t') \rangle \simeq e^{-(t-t')/t_d} \tag{3.5}$$

with a decorrelation time that increases with decreasing temperature and close to (but still above) T_c diverges as the power law, $t_d \sim (T - T_c)^{-\nu z_{eq}}$. The divergence of t_d is the manifestation of **critical slowing down**. The asympotic value verifies

$$\lim_{t-t' \gg t' \gg t_r} \langle s_i(t) s_i(t') \rangle = \lim_{t \gg t_r} \langle s_i(t) \rangle \lim_{t' \gg t_r} \langle s_i(t') \rangle = \langle s_i \rangle_{eq} \langle s_i \rangle_{eq} = m_{eq}^2 = 0 \ , \tag{3.6}$$

cfr. eq. (2.144).

Grosso modo the behavior of the spin degree of freedom is equivalent to the one derived for the position of a particle in a harmonic potential centered at zero with non vanishing positive spring constant in Sec. 2.5.2.

3.4.2 Quench from $T \gg T_c$ to $T \leq T_c$

At or below T_c, coarsening from an initial condition that is **not correlated with the equilibrium state** and with no bias field does not take the system to equilibrium in finite times with respect to a function of the system's linear size, L. More explicitly, if the growth law is a power law [see eq. (3.33)] one needs times of the order of $L^{z_{eq}}$ (critical) or L^{z_d} (subcrititcal) to grow a domain of the size of the system. This gives a rough idea of the time needed to take the system to one of the two equilibrium states (subcritical). For any shorter time, domains of the two types exist and the system is **out of equilibrium**.

The self-correlation of such an initial state evolving at $T \leq T_c$ involves power laws or logarithms and although one cannot associate to it a decay time as one does

to an exponential, one can still define a characteristic time that, quite generally, turns out to be related to the age of the system, $t_d \simeq f(t')$ [see eq. (3.32)], where t' is the first time at which the configuration of the system is measured to compute the correlation function.

In contrast, the relaxation time of an **equilibrium** magnetized configuration at temperature T vanishes since the system is already equilibrated while the decorrelation time t_d is a finite function of T.

The relaxation of the two-time fluctuation self-correlation at $T < T_c$, when the time t' is chosen to be longer than t_r, that is to say, once the system has thermalized in one of the two equilibrium states, decays exponentially

$$\lim_{t' \gg t_r} \langle \delta s_i(t) \delta s_i(t') \rangle \simeq e^{-(t-t')/t_d} \tag{3.7}$$

with a decorrelation time that decreases with decreasing temperature and close to T_c (but below it) also diverges as a power law, $t_d \sim (T - T_c)^{-\nu z_{eq}}$. The asympotic value verifies

$$\lim_{t-t' \gg t' \gg t_r} \langle s_i(t) s_i(t') \rangle = \lim_{t \gg t_r} \langle s_i(t) \rangle \lim_{t' \gg t_r} \langle s_i(t') \rangle = \langle s_i \rangle_{eq} \langle s_i \rangle_{eq} = m_{eq}^2 \geq 0 \ , \tag{3.8}$$

cfr. eqs. (2.144) and (3.6), depending on $T = T_c$ or $T > T_c$. Again, *grosso modo* the behavior of the spin degree of freedom for an ordered initial condition at $T < T_c$ is equivalent to the one derived for the position of a particle in a harmonic potential centered at a non-vanishing position with non vanishing positive spring constant in Sec. 2.5.2.

3.4.3 Summary

The lesson to learn from this comparison is that the relaxation time and the decorrelation time not only depend upon the working temperature but they also depend upon the initial condition.

In all critical or low-temperature cases we will study the relaxation time also depends on the system size L – and diverges in the infinite size limit. In short, for a random initial condition and an infinite system, $L \to \infty$, one has

$$t_r^\phi \simeq \begin{cases} \text{finite} & T > T_c \ , \\ |T - T_c|^{-\nu z_{eq}} & T \gtrsim T_c \ , \\ \infty & T \leq T_c \end{cases}$$

while for a finite system, $L < +\infty$, one finds

$$t_r^\phi \simeq \begin{cases} L^{z_{eq}} & T = T_c \ , \\ L^{z_d} & T < T_c \ . \end{cases}$$

For a random initial condition quenched to the critical or sub-critical temperature the decorrelation time grows (and diverges) with the waiting time t' but does not diverge with the system size. For a system quenched above the critical temperature this time saturates to a waiting-time independent value. A system that evolves from an ordered initial condition at sub-critical temperature has a finite decorrelation time.

Still another time scale is given by the time needed to reverse an equilibrium configuration in the low-T phase. This one is expected to be given by an Arrhenius law, with the height of the barrier being determined by the extensive free-energy barrier between the two minima, i.e. $\Delta F \simeq L^d f$, therefore,

$$\boxed{t_R^\phi \simeq e^{\beta L^d f} \qquad \text{Reversal time-scale .}} \tag{3.9}$$

The Ginzburg-Landau description allows for a pictorial interpretation of these results. The dynamics of the full system is visualized as the motion of its representative point in the Ginzburg-Landau potential. At high T the potential is harmonic in the deterministic Allen-Cahn equation, or the double-well structure in the time-dependent stochastic Ginzburg-Landau equation is completely ignored. The relaxation is similar to the one of a particle in a harmonic potential studied in Sect. 2.5.2. At low T, the initial position in the double-well potential depends on the type of initial condition $\phi(\vec{x}, 0) = 0$ or $\phi(\vec{x}, 0) \neq 0$. In the first case, the point sits on top of the central barrier and it does not detach from it in finite times with respect to a function of L. In the second case, the point starts from within one well and it simply rolls (on average) to the bottom of the well. This relaxation is similar to the one in the harmonic case. To reverse the configuration from, say, positive to negative magnetization the point needs to jump over the barrier in the double well potential and it does via thermal activation ruled by the Arrhenius law. The height of the barrier is extensive and diverges with L.

Note, however, that the phase-space of the system is actually N-dimensional while the description that is given here is projected onto one single coordinate, the one of the order-parameter. This reduction might lead to some misunderstandings and one should be very careful with it.

3.5 Correlation functions

In this Subsection we present several correlation functions that are instructive in this context.

The space-time correlation function is the average overlap between any two spins placed at distance r

$$\boxed{L^d C(r,t) = \sum_{ij/|\vec{r}_i - \vec{r}_j|=r} \langle s_i(t) s_j(t) \rangle}$$

The time-dependent structure factor is defined as the Fourier transform of the space displaced correlation function

$$\boxed{S(\vec{q},t) \equiv \sum_{\vec{r}} e^{i\vec{q}\cdot\vec{r}}\ C(\vec{r},t)}$$

where $C(\vec{r},t)$ is the averaged space-time correlation function defined above. The sum runs over lattice sites. A continuous space version can be given.
The two-time correlation function is a local in space correlation that is non-local in time

$$\boxed{C(t,t') = \langle s_i(t) s_i(t') \rangle}$$

where i is any spin in the sample. A sum over all spins in the sample should yield the same result, if the system is *a priori* space homogeneous.

A general time-delayed and space-dependent correlation can also be defined as

$$\boxed{L^d G(r,t-t') = \sum_{ij/|\vec{r}_i - \vec{r}_j|=r} \langle s_i(t) s_j(t') \rangle}$$

and its Fourier transform with respect to space, the delayed structure factor.

3.6 Growing length and dynamic scaling

In coarsening systems the dynamics are not stationary. In usual cases, the averaged space-time correlation function $C(r,t)$ allows for the identification of a growing length from, for example,

$$R_{\rm a}(T,t) \equiv \int d^d r\ r^{\rm a+1} C(r,t) / \int d^d r\ r^{\rm a} C(r,t) \tag{3.10}$$

(a is a parameter chosen to weight preferentially short or long distances; the time-dependence of $R_{\rm a}(t)$ should not depend on a. However, in a simulation various sources of error make the choice of a important. Heuristically, $a = 1$ is reocmmended as a trade-off between systematic errors for low wave-vectors and statistical errors for large wave vectors.) Here and in the following $\langle \ldots \rangle$ stands for an average over different realizations of thermal histories at heat-bath temperature T and/or initial conditions. In presence of quenched disorder one adds an average over it and denotes

it [...]. The stochastic time-dependent function $N^{-1}\sum_{ij/|\vec{r}_i-\vec{r}_j|=r} s_i(t)s_j(t)$ after a quench from a random initial condition does not fluctuate in the thermodynamic limit. Therefore, the averages are not really necessary but they are usually written down. In spin-glasses and glasses this observable does not yield information on the existence of any growing length as we will discuss below.

The spherically averaged structure factor $S(k,t)$ – the Fourier transform of $C(r,t)$ – can be measured experimentally with small-angle scattering of neutrons, x-rays or light and from it $R_{\rm a}(T,t)$ can be extracted. Numerically it is measured as

$$S(\vec{k},t) = \langle \phi(\vec{k},t)\phi^*(\vec{k},t)\rangle \tag{3.11}$$

where $\phi(\vec{k},t)$ is the Fourier transform of the field $\phi(\vec{r},t)$. In a finite size simulation box, the wave-vector takes discrete values $\vec{k} = 2\pi(k_1,\dots k_d)/L$. $S(\vec{k},t)$ is then averaged over a spherical coquille to give the scalar function $S(k,t)$. The characteristic domain size is then defined as the reciprocal of the first moment of the scalarized structure factor, $R(t) = \langle k\rangle^{-1}(t)$, with

$$\langle k\rangle(t) = \frac{\int_0^{k_{\rm max}} dk\ S(k,t)}{\int_0^{k_{\rm max}} dk\ S(k,t)}\ , \tag{3.12}$$

where $k_{\rm max}$ is the magnitude of the largest wave-vector that one considers, typically, half the magnitude of the largest wave-vector in the Brillouin zone of the lattice. The resulting length scale is measured in units of the lattice spacing.

For ferromagnetic spin systems on a lattice, another, very simple way, of extracting the growing length is to measure the inverse number of defects, $D(t)$, defined as the number of spins with at least one antiparallel neighbour, and estimate $R(t)$ as $N/D(t)$.

The ordering process is characterized by the growth of a **typical length**, $R(T,t)$. The growth regimes are summarized in the following equation and in Fig. 3.43:

$$\left\{\begin{array}{lll} R_c(t) \to \xi_{eq}(T) < +\infty & T > T_c & \text{saturation,} \\ R_c(t) \to \xi_{eq}(T) \to \infty & T = T_c & \text{critical coarsening,} \\ R_c(t) \to R(T,t) \to L & T < T_c & \text{sub-critical coarsening.} \end{array}\right. \tag{3.13}$$

and $\xi_{eq}(T) \ll R(t)$ for $T < T_c$. (Note that ξ_{eq} is defined from the connected static correlation function while R is defined from the dynamic correlation function. They measure different lengths as indicated below.) After a quench to the high temperature phase $T > T_c$ the system first grows equilibrium regions until reaching the equilibrium correlation length ξ_{eq} and next relaxes in equilibrium as explained

in the previous section. The correlation length could be very short and the transient non-equilibrium regime be quite irrelevant ($T \gg T_c$). In the critical region, instead, the equilibrium correlation length is very long and it becomes important. In a critical quench the system never orders sufficiently and $R(T_c, t) < \xi_{eq}$ for all finite times. Finally, a quench into the subcritical region is characterized by two growth regimes: a first one in which the critical point dominates and the growth is as in a critical quench; a second one in which the proper sub-critical ordering is at work. The time-dependence of the growth law is different in these two regimes as we will see below. (Note that below T_c the equilibrium correlation length ξ_{eq} does not measure the size of ordered regions but the typical distance until which a fluctuation has an effect.)

In the asymptotic time domain, when $R(T, t)$ has grown much larger than any microscopic length in the system, a **dynamic scaling symmetry** sets in, similarly to the usual scaling symmetry observed in equilibrium critical phenomena. According to this hypothesis, the growth of $R(T, t)$ is the only relevant process and the whole time-dependence enters only through $R(T, t)$.

3.7 Critical coarsening

The scaling behavior of binary systems quenched to the critical point is quite well understood. It can be addressed with scaling arguments and renormalization group approaches [6] which give explicit expressions for many of the quantities of interest up to two loops order. Numerical simulations confirm the analytic results and probe exponents and scaling functions beyond the available perturbative orders. In this case the system builds correlated critical Fortuin-Kasteleyn clusters[14] with fractal dimension[15] $D_{FK} = (d + 2 - \eta)/2$, where η is the usual static critical exponent, in regions growing algebraically as $R_c(T_c, t) \equiv R_c(t) \sim t^{1/z_{eq}}$; henceforth we simplify the notation and avoid writing T_c within R. [As an example, for the bidimensional critical Ising class $\eta = 1/4$ and $D_{FK} = (2 + 2 - 1/4)/2 = 15/8$.]

Importantly enough, the dynamic exponent z_{eq} is the same that characterises the dynamic fluctuations of equilibrium fluctuations. Therefore, the relaxation to

[14] The Fortuin-Kasteleyn clusters are constructed as follows. Starting with a spin domain, one first draws all bonds linking nearest-neighbor spin on the cluster and then erases bonds with a temperature dependent probability $e^{-\beta J}$. In such a way, the original bond-cluster typically diminishes in size and may even get disconnected.

[15] A possible definition of the fractal dimension is given by the box counting construction in which one counts the number of boxes of linear size ϵ that are needed to cover the set and computes $D = \lim_{\epsilon \to 0} [\ln N(\epsilon) / \ln(1/\epsilon)]$.

Figure 3.38: Sketch of the construction of a FK cluster. A domain is identified. The bonds between nearest-neighbor aligned spins (represented with black dots on the lattice sites) are erased using the FK procedure. Two FK disconnected clusters remain. The surviving bonds are highlighted on the edges of the lattice.

equilibrium is governed by the same exponent as the de-correlation in equilibrium.

One-time quantities

A critical point can be identified by the **kurtosis of the order parameter** – also called **Binder parameter** – that measures the deviation from Gaussianity of its fluctuations. A time-dependent similar object is

$$g_L(t) = 2 - \frac{\langle [M^2(t)]^2 \rangle}{\langle M^2(t) \rangle^2} \tag{3.14}$$

with $M(t) = \sum_i s_i(t)$ the total magnetisation at time t. Critical dynamics scaling states that $g_L(t)$ can only depend upon the ratio between the growing length $R_c(t)$ and the linear size of the sample L:

$$g_L(t) = G\left(\frac{R_c(t)}{L}\right) \tag{3.15}$$

provided that $a \ll R_c(t) \ll L$. This proposal allows one to determine $R_c(t)$ from the finite size analysis of the time-dependent Binder parameter.

Correlation functions

In the asymptotic time regime the space-time correlation function has the scaling form

$$\boxed{C(r,t) = C_{eq}(r)\ C_{ag}(r,t) \qquad \text{Multiplicative separation}} \tag{3.16}$$

The first factor describes the equilibrium correlation, $C_{eq}(r) \simeq r^{2-d-\eta}$ while the second one takes into account the out of equilibrium relaxation and scales as $f(r/R_c(t))$. One has

$$C(r,t) = r^{-2(d-D_{FK})}\ f\left(\frac{r}{R_c(t)}\right) \tag{3.17}$$

$$\boxed{C(r,t) = r^{2-d-\eta}\ f\left(\frac{r}{R_c(t)}\right)}$$

The pre-factor $r^{-2(d-D_{FK})}$ takes into account that the growing domains have a **fractal nature** (hence their *density* decreases as their size grows) and the fact that the order parameter vanishes at the second order critical point. The dependence on $r/R_c(t)$ in $f(x)$ expresses the similarity of configurations at different times once lengths are measured in units of $R_c(t)$. At distances and times such that $r/R_c(t) \ll 1$ the equilibrium power-law decay, $C_{eq}(r) \simeq r^{2-d-\eta}$, should be recovered, thus $f(x) \simeq 1$ at $x \to 0$. $f(x)$ falls off rapidly for $x \gg 1$ to ensure that spins are uncorrelated at distances larger than $R_c(t)$, and $f(x \to \infty) = 0$. The actual way in which $f(x)$ decays to zero is non-trivial and can be computed with dynamic RG methods.

For two-time quantities, when t' is sufficiently large one has

$$\boxed{C(t,t') = C_{st}(t-t')\; C_{ag}(t,t') \qquad \text{Multiplicative separation}} \tag{3.18}$$

with $C_{st}(t-t')$ characterising the decor relation within an equilibrated patch and C_{ag} representing the out of equilibrium dynamics. One has

$$\boxed{C(t,t') = R_c(t-t')^{2-d-\eta}\; f_c\left(\frac{R_c(t)}{R_c(t')}\right) \qquad \text{Multiplicative separation.}}$$

Here $C_{st}(t-t') \simeq R_c(t-t')^{-2(d-D_{FK})} = R_c(t-t')^{2-d-\eta}$. The scaling function $f_c(x)$ describes the non-equilibrium behavior. It satisfies $f_c(1) = 1$ and $f_c(x \to \infty) = 0$, see the sketch in Fig. 3.39 (a). The former condition ensures that equilibrium is established up to the length $R_c(t)$. The latter decorrelation occurs faster than what the equilibrium relaxation tells beyond this length. In the scaling forms the equilibrium and non-equilibrium contributions enter in a **multiplicative** structure. Non-equilibrium effects are taken into account by taking ratios between the sizes of the correlated domains at the observation times t' and t in the scaling functions. Note that the reason why the equilibrium results are recovered for $t \simeq t'$ is that for very similar times one does not let the system realize that it is out of equilibrium.

The limiting values of f and f_c are given by

$$\begin{aligned} f(x) &= \begin{cases} 1 & x \ll 1 \\ 0 & x \gg 1 \end{cases} \qquad x = \frac{r}{R_c(t)} \\ f_c(x) &= \begin{cases} 1 & x \to 1 \\ 0 & x \gg 1 \end{cases} \qquad x = \frac{R_c(t)}{R_c(t')} \end{aligned} \tag{3.19}$$

In the case of non-conserved scalar order-parameter dynamics the growing length behaves as

$$\boxed{R_c(t) \sim t^{1/z_{eq}}} \tag{3.20}$$

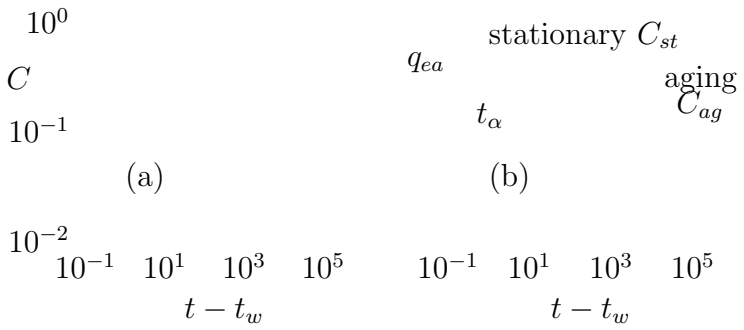


Figure 3.39: Sketch of the decay of the two-time correlation at T_c (a) and $T < T_c$ (b) for different values of the waiting-time, increasing from left to right.

with z_{eq} the equilibrium dynamics exponent (note that z_{eq} is different from z_d). We will not discuss critical dynamics in detail; this problem is treated analytically with dynamic renormalization group techniques and it is very well discussed in the literature [6, 7]. In short, the exponent z_{eq} is given by [43]

$$z_{eq} = 2 + \frac{N+2}{(N+8)^2}\left[3\ln\frac{4}{3} - \frac{1}{2}\right]\epsilon^2 + O(\epsilon^3) \tag{3.21}$$

where N is the dimension of the possibly vector field, $N = 1$ for a scalar one, and $\epsilon = 4 - d$ with d the dimension of space. Note that z_{eq} is larger than 2 for all finite N and it approaches 2 in the large N limit (at least up to this order in perturbation theory). In particular, one finds

$$z_{eq} \simeq \begin{cases} 2.0538 & d = 2 \\ 2.0134 & d = 3 \\ 2 & d = 4 \end{cases}$$

for $N = 1$. $d = 4$ is the upper critical dimension in this problem. Numerical simulations indicate $z_{eq} \simeq 2.13$ in $d = 2$. These results are valid for white noise dynamics. The effect of colored noise is to change the value of the exponent z_{eq} when it is sufficiently long-range correlated (sub-Ohmic noise with a power-law decay with an exponent smaller than a critical value that depends on the dimension of space) [44].

The multiplicative scaling is also obtained with the dynamic RG method.

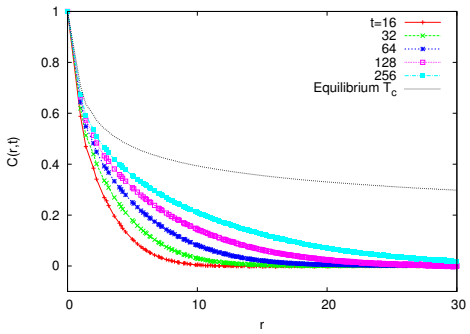


Figure 3.40: The space-time correlation function in the $2d$ Ising model after a quench to its critical point (MC data). With color data points the dynamic measurements. With a dashed black line the equilibrium power-law decay.

3.8 Sub-critical coarsening

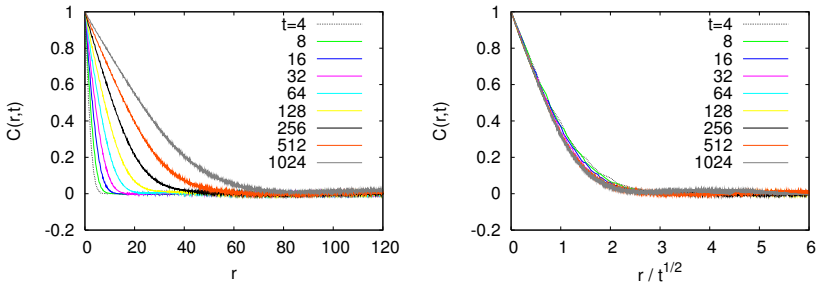


Figure 3.41: The equal-time correlation as a function of distance in the $2d$IM quenched below T_c. Raw (left) and scaled (right) data. These numerical simulations were performed by A. Sicilia.

3.8.1 Dynamic scaling hypothesis

The **dynamic scaling hypothesis** states that at late times and in the scaling limit

$$r \gg \xi_{eq}(g) \,, \qquad R(g,t) \gg \xi_{eq}(g) \,, \qquad r/R(g,t) \;\text{ arbitrary} \,, \tag{3.22}$$

where r is the distance between two points in the sample, $r \equiv |\vec{x} - \vec{x}'|$, and $\xi_{eq}(g)$ is the equilibrium correlation length that depends on all parameters (T and possibly others) collected in g, there exists a **single characteristic length**, $R(g,t)$, such that the domain structure is, in statistical sense, independent of time when lengths are scaled by $R(g,t)$. Time, denoted by t, is typically measured from the instant when the critical point is crossed. In the following we ease the notation and write only the time-dependence in R. This hypothesis has been proved analytically in very simple models only, such as the one dimensional Ising chain with Glauber dynamics or the Langevin dynamics of the d-dimensional $O(N)$ model in the large N limit (see Sect. 3.11). But, as in critical coarsening, this regime sets in only after an "equilibrium-like" regime has died out. We are more precise below.

The late stage of phase-ordering in binary systems is characterized by a patchwork of large domains the interior of which is basically thermalized in one of the two equilibrium phases while their boundaries are slowly moving. This picture suggests the splitting of the degrees of freedom (spins) into two categories, providing statistically independent contributions to observables such as correlation or response functions. More precisely, a quasi-equilibrium stationary contribution arises as due to bulk spins, while boundaries account for the non-equilibrium part. Then asymptotically one has

$$\boxed{C(r,t) \simeq C_{eq}(r) + C_{ag}(r,t) \qquad \text{Additive separation.}} \tag{3.23}$$

The first term describes the distance dependence of the equilibrium fluctuations in the low temperature broken symmetry pure states

$$C_{eq}(r) = (1 - \langle s_i \rangle_{eq}^2)\; g\left(\frac{r}{\xi_{eq}}\right), \tag{3.24}$$

where $\langle s_i \rangle_{eq}$ is the equilibrium expectation value of the local spin in one of the two symmetry breaking states, $\langle s_i \rangle_{eq} = m$, and $g(x)$ is a function with the limiting values $g(0) = 1$, $\lim_{x\to\infty} g(x) = 0$. (We choose to have $C_{eq}(0) = 1 - m^2$ and we leave the missing m^2 contribution to ensure $C(0) = 1$ to the second term.) The second term takes into account the motion of the domain walls through

$$C_{ag}(r,t) = \langle s_i \rangle_{eq}^2\; f\left(\frac{r}{R(t)}\right), \tag{3.25}$$

with $f(0) = 1$ and $\lim_{x\to\infty} f(x) = 0$. Both C_{eq} and C_{ag} obey (separately) scaling forms with respect to the equilibrium and the non-equilibrium lengths ξ_{eq} and $R(t)$,

respectively. In particular, eq. (3.25) expresses the fact that system configurations at different times are statistically similar provided that lengths are measured in units of $R(t)$, namely the very essence of dynamical scaling.

The limiting values of the functions f and g are given by

$$g(x) = \begin{cases} 1 & x \ll 1 \\ 0 & x \gg 1 \end{cases} \qquad x = \frac{r}{\xi_{eq}}$$
$$f(x) = \begin{cases} 1 & x \ll 1 \\ 0 & x \gg 1 \end{cases} \qquad x = \frac{R(t)}{R(t')} \tag{3.26}$$

Monte Carlo simulations of the Ising model and other systems quenched below criticality and undergoing domain growth demonstrate that in the long waiting-time limit $t' \gg t_0$, the spin self-correlation $\langle s_i(t) s_i(t') \rangle$ separates into two additive terms

$$\boxed{C(t,t') \sim C_{st}(t-t') + C_{ag}(t,t') \quad \text{Additive separation}} \tag{3.27}$$

see Fig. 3.42, with the first one describing equilibrium thermal fluctuations within the domains,

$$C_{st}(t-t') = (1 - \langle s_i \rangle^2)\ g_c\left(\frac{t-t'}{\tau_{eq}}\right) \tag{3.28}$$

and

$$g_c(x) = \begin{cases} 1 & x \ll 1 \\ 0 & x \gg 1 \end{cases} \qquad x = \frac{t-t'}{\tau_{eq}} \tag{3.29}$$

and the second one describing the motion of the domain walls

$$C_{ag}(t,t') \;\; = \;\; \langle s_i \rangle_{eq}^2\ f_c\left(\frac{R(t)}{R(t')}\right) \tag{3.30}$$

with

$$f_c(x) = \begin{cases} 1 & x \to 1 \\ 0 & x \gg 1 \end{cases} \tag{3.31}$$

To ease the notation we have not written the explicit T-dependence in R that, as we will see below, is less relevant than t. Note that by adding the two contributions one recovers $C(t,t) = 1$ as expected and $C(t,t') \to 0$ when $t \gg t'$. The first term is identical to the one of a system in equilibrium in one of the two ordered states, see eq. (3.8) for its asymptotic $t - t' \gg t'$ limit; the second one is inherent to the out of equilibrium situation and the existence and motion of domain walls.

Separation of time scales. The first and second term vary in completely different two-time scales. The first one changes when the second one is fixed to $\langle s_i \rangle_{eq}^2$, at times such that $R(t)/R(t') \simeq 1$. The second one varies when the first one decayed to zero. The mere existence of the second term is the essence of the aging phenomenon with older systems (longer t') having a slower relaxation than younger ones (shorter t'). The scaling of the second term as the ratio between 'two lengths' is a first manifestation of **dynamic scaling**. Recall the sketch shown in Fig. 3.39.

A decorrelation time can also be defined in this case by expandind the argument of the scaling function around $t' \simeq t$. Indeed, calling $\Delta t \equiv t - t'$ one has $R(t)/R(t') \simeq R(t' + \Delta t)/R(t') \simeq [R(t') + R'(t')\Delta t]/R(t') \simeq 1 + \Delta t/[d \ln R(t')/dt']^{-1}$ and one identifies a **t'-dependent decorrelation time**

$$\boxed{t_d \simeq [d \ln R(t')/dt']^{-1} \quad \text{decorrelation time}} \tag{3.32}$$

which is, in general, a growing function of t'.

The main effect of temperature is to change the value of m, that is the equilibrium one. This can be seen in Fig. 3.42 where simulations of the $2d$Im at $T = 0.5$ and $T = 2$ (both below T_c) are displayed. Increasing temperature the 'extent' of the equilibrium relaxation is larger as the equilibrium correlation decays to a lower value.

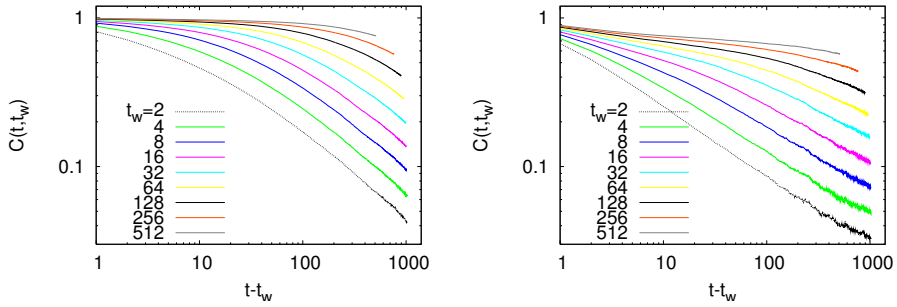


Figure 3.42: The two-time self-correlation in the $2d$IM with non-conserved order parameter dynamics at several waiting-times given in the key at temperature $T = 0.5$ (left) and $T = 2$ (right). Data obtained with Monte Carlo simulations. Note that the plateau is located at a lower level in the figure on the right consistently with the fact that $\langle \phi \rangle_{eq}$ decreases with increasing temperature. Data from A. Sicilia et al.

In order to fully characterise the correlation functions one then has to determine the typical growing length, R, and the scaling functions, g, f, g_c, f_c, *etc.* It turns out

that the former can be determined with semi-analytic arguments and the predictions are well verified numerically – at least for clean system. The latter, instead, are harder to obtain. We will give a very brief state of the art report in Sect. 3.10.8. For a much more detailed discussion of these methods see the review articles in [4].

The time-dependent typical domain length, $R(t)$, is determined numerically by using several indirect criteria or analytically within certain approximations. The most common ways of measuring R are with numerical simulations of lattice models or the numerical integration of the continuous partial differential equation for the evolution of the order parameter. In both cases one

– Computes the 'inverse perimeter density' $R(t) = -\langle H \rangle_{eq} / [\langle H(t) \rangle - \langle H \rangle_{eq}]$ with $\langle H(t) \rangle$ the time-dependent averaged energy and $\langle H \rangle_{eq}$ the equilibrium energy both measured at the working temperature T.

– Puts the dynamic scaling hypothesis to the test and extracts R from the analysis.

3.8.2 $R(t)$ in clean one dimensional cases with non-conserved order parameter

In one dimension, a space-time graph allows one to view coarsening as the diffusion and annhilitation upon collision of point-like particles that represent the domain walls. In the Glauber Ising chain with non-conserved dynamics [45] one finds that the typical domain length grows as $t^{1/2}$ while in the continuous case the growth is only logarithmic, $\ln t$ [47].

3.8.3 $R(t)$ in non-conserved order parameter curvature dynamics in $d > 2$

In this case the growth law scales as $\lambda(T) t^{1/2}$ as we will show in Sec. using the time-dependent Ginzburg-Landau equation.

There are a number of ways to find the growth law

$$\boxed{R(t) = \lambda \; t^{1/z_d}} \tag{3.33}$$

with z_d the **dynamic exponent**, in **pure and isotropic** systems (see [4]). The effects of temperature enter only in the parameter λ and, for clean systems, growth is slowed down by an increasing temperature since thermal fluctuation tend to roughen the interfaces thus opposing the curvature driven mechanism. We estimate the T dependence of λ in Sect. 3.8.5.

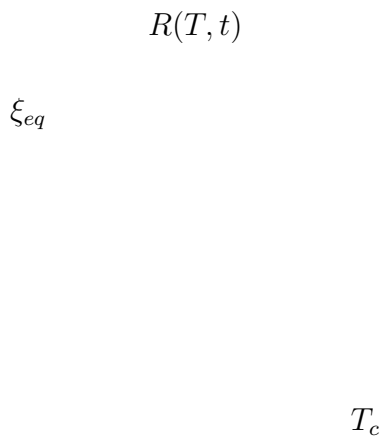


Figure 3.43: Sketch of the growth process in a second-order phase transition. The thick line is the equilibrium correlation length $\xi_{eq} \simeq |T - T_c|^{-\nu}$. The thin solid (red) arrows indicate the growing length R_c in the critical coarsening regime and the dashed (black) arrow the sub-critical growing length R in the coarsening regime.

In curvature driven Ising or Potts cases with non-conserved order parameter the domains are sharp and $z_d = 2$ with λ a weakly T-dependent coefficient.

3.8.4 $R(t)$ in conserved order parameter dynamics and the role of bulk diffusion

A different type of dynamics occurs in the case of phase separation (the water and oil mixture ignoring hydrodynamic interactions or a binary allow). In this case, the material is locally conserved, *i.e.* water does not transform into oil but they just separate. The main mechanism for the evolution is diffusion of material through the bulk of the opposite phase. After some discussion, it was established, as late as in the early 90s, that for scalar systems with **conserved order parameter** $z_d = 3$ [48].

3.8.5 Crossover between critical and sub-critical coarsening

Matching critical coarsening with sub-critical one allows one to find the T-dependent prefactor λ close to T_c [49]. The argument goes as follows. The out of equilibrium growth at criticality and in the ordered phase are given by

$$R(t) \sim \begin{cases} t^{1/z_{eq}} & \text{at} \quad T = T_c \,, \\ \lambda(T) t^{1/z_d} & \text{at} \quad T < T_c \,. \end{cases} \tag{3.34}$$

z_{eq} is the equilibrium dynamic critical exponent and z_d the out of equilibrium growth exponent. Close but below criticality one should have an interpolating expression of the kind

$$R(t) \sim \xi^{-a} t^{1/z_d} f\left(\frac{t}{\xi^{z_{eq}}}\right) \qquad \text{at} \qquad T = T_c - \epsilon \tag{3.35}$$

with ξ the T-dependent equilibrium correlation length, $\xi_{eq}(T) \sim (T_c - T)^{-\nu}$. The second factor tends to one, $f(x \to \infty) \to 1$, when $R(t) \gg \xi$, that is to say when the argument diverges and the system enters the sub-critical coarsening regime. See the sketch in Fig. 3.43. It is however non-trivial when $R(t) \sim \xi$, the argument is finite and critical coarsening must be described. In particular, we determine its behavior for $x = O(1)$ by requiring that eq. (3.35) matches the subcritical growing length which is achieved by (i) recovering the correct t dependence, (ii) cancelling the ξ factor. (i) implies

$$f(x) \sim x^{-1/z_d + 1/z_{eq}} \qquad \text{for} \qquad x = O(1) \,. \tag{3.36}$$

Then eq. (3.35) becomes

$$R(t) \sim \xi^{-a + z_{eq}/z_d - 1} \, t^{1/z_{eq}} \tag{3.37}$$

and to eliminate ξ we need

$$a = z_{eq}/z_d - 1 \,. \tag{3.38}$$

Comparing now the subcritical growing length and (3.35) in the very long times limit such that $R(t) \gg \xi$ and $f(x \to \infty) \to 1$:

$$\boxed{\lambda(T) \sim \xi^{-a} \sim (T_c - T)^{\nu(z_{eq} - z_d)/z_d}} \tag{3.39}$$

Note that quite generally one finds $z_{eq} > z_d$ and $\lambda(T)$ vanishes at T_c.

3.8.6 Role of weak disorder: thermal activation

The situation becomes much less clear when there is weak quenched disorder in the form of non-magnetic impurities in a magnetic sample, lattice dislocations,

residual stress, *etc.* These are assumed not to modify the nature of the equilibrium states with respect to the ones of the clean system. Qualitatively, the dynamics are expected to be slower than in the pure cases since disorder pins the interfaces. In general, based on an argument due to Larkin [50] (and in different form to Imry-Ma [51]) one expects that in $d < 4$ the late epochs and large scale evolution is no longer curvature driven but controlled by disorder. Indeed, within a phase space view disorder generates metastable states that trap the system and thus slow down the relaxation.

A hand-waving argument to estimate the growth law in dirty systems is the following. Take a system in one equilibrium state with a domain of linear size R of the opposite equilibrium state within it. This configuration could be the one of an excited state with respect to the fully ordered one with absolute minimum free-energy. Call $\Delta F(R)$ the free-energy barrier between the excited and equilibrium states. The thermal activation argument (see Sect. 2.4) yields the activation time scale for the decay of the excited state (*i.e.* erasing the domain wall)

$$t_A \sim \tau \; e^{\Delta F(R)/(k_B T)} \; . \tag{3.40}$$

For a barrier growing as a power of R, $\Delta F(R) \sim \Upsilon(T,J) R^{\psi}$ (where J represents the disorder) one inverts (3.40) to find the linear size of the domains still existing at time t, that is to say, the growth law

$$\boxed{R(t) \sim \left(\frac{k_B T}{\Upsilon(T,J)} \; \ln \frac{t}{\tau} \right)^{1/\psi} \; .} \tag{3.41}$$

All smaller fluctuation would have disappeared at t while typically one would find objects of this size. The exponent ψ is expected to depend on the dimensionality of space but neither on temperature nor on disorder strength. In 'normal' systems it is expected to be just $d-1$ – the surface of the domain – but in spin-glass problems, it might be smaller than $d-1$ due to the presumed fractal nature of the walls. The prefactor Υ is expected to be weakly temperature and disorder strength dependent.

One assumes that the same argument applies out of equilibrium to the reconformations of a portion of any domain wall or interface where R is the observation scale.

However, already for the (relatively easy) random ferromagnet there is no consensus about the actual growth law. In these problems there is a competition between the 'pure' part of the Hamiltonian, that tries to minimize the total $(d-1)$ dimensional area of the domain wall, and the 'impurity' part that makes the wall deviate from flatness and pass through the locations of lowest local energy (think of

$J_{ij} = J + \delta J_{ij}$ with J and δJ_{ij} contributing to the pure and impurity parts of the Hamiltonian, respectively). The activation argument in eq. (3.40) together with the power-law growth of barriers in $\Delta F(R) \sim \Upsilon(T, J) R^{\psi}$ imply a logarithmic growth of $R(t)$ [52]. Simulations, instead, suggest a power law with a temperature dependent exponent. Whether the latter is a pre-asymptotic result and the trully asymptotic one is hidden by the premature pinning of domain walls or it is a genuine behavior invalidating $\Delta F(R) \sim \Upsilon(T, J) R^{\psi}$ or even eq. (3.40) is still an open problem. See the discussion below for a plausible explanation of the numerical data that does not invalidate the theoretical expectations.

In the $3d$ RFIM the curvature-driven growth mechanism that leads to (3.33) is impeded by the random field roughening of the domain walls. The dependence on the parameters T and h has been estimated. In the early stages of growth, one expects the zero-field result to hold with a reduction in the amplitude $R(t) \sim (A - Bh^2)\, t^{1/2}$. The time-window over which this law is observed numerically decreases with increasing field strength. In the late time regime, where pinning is effective Villain deduced a logarithmic growth [53] $R(t) \sim (T/h^2) \ln t/t_0$ by estimating the maximum barrier height encountered by the domain wall and using the Arrhenius law to derive the associated time-scale.

In the case of spin-glasses, if the mean-field picture with a large number of equilibrium states is realized in finite dimensional models, the dynamics would be one in which all these states grow in competition. If, instead, the phenomenological droplet model applies, there would be two types of domains growing and $R(t) \sim (\ln t)^{1/\psi}$ with the exponent ψ satisfying $0 \leq \psi \leq d-1$ [54]. Some refined arguments that we will not discuss here indicate that the dimension of the bulk of these domains should be compact but their surface should be rough with fractal dimension $D_s > d-1$.

3.8.7 Temperature-dependent effective exponents

The fact that numerical simulations of dirty systems tend to indicate that the growing length is a power law with a T-dependent exponent can be explained as due to the effect of a T-dependent cross-over length L_T [55]. Indeed, if below $L_T \sim T^{\phi}$ the growth process is as in the clean limit while above L_T quenched disorder is felt and the dynamics is thermally activated:

$$R(t) \sim \begin{cases} t^{1/z_d} & \text{for} \quad R(t) \ll L_T\,, \\ (\ln t)^{1/\psi} & \text{for} \quad R(t) \gg L_T\,. \end{cases} \tag{3.42}$$

These growth-laws can be first inverted to get the time needed to grow a given

length and then combined into a single expression that interpolates between the two regimes:

$$t(R) \sim e^{(R/L_T)^\psi} R^{z_d} \tag{3.43}$$

where the relevant T-dependent length-scale L_T has been introduced.

Now, by simply setting $t(R) \sim R^{\overline{z}(T)}$ one finds $\overline{z}(T) \sim z_d + \frac{1}{\ln R(t)} \left(\frac{R^\psi(t)}{L_T^\psi} \right)$ that replacing $R \sim t^{1/\overline{z}(T)}$ becomes $\overline{z}(T) \sim z_d + \frac{\overline{z}(T)}{\ln t} \left(\frac{t^{\psi/\overline{z}(T)}}{L_T^\psi} \right)$. Using now $\overline{z}(T) \simeq z_d$ in the correction term and focusing on times such that $t^{\psi/z_d}/\ln t$ is almost constant and equal to c one finds $\overline{z}(T) - z_d \simeq \mathrm{c}\ z_d/L_T^\psi$. Similarly, by equating $t(R) \sim \exp(R^{\overline{\psi}(T)}/T)$ one finds that $\overline{\psi}(T)$ is a decreasing function of T approaching ψ at high T.

3.8.8 Logarithmic growth in clean systems

It is possible to slow down the growth of the characteristic length by introducing competing interactions in the Hamiltonian. One such model is the $2d$ Ising model with non-conserved order parameter dynamics and an additional antiferromagnetic next nearest-neighbour interaction where the growing length is logarithmic [56]. Another possibility is to add frustration, as in the case of vertex models on a square lattice with Monte Carlo single-spin flip dynamics: in coarsening in the ordered phases is anisotropic with different growing lengths in the two perpendicular directions [57].

3.9 Discrete variables: kinetic Ising model

If one chooses to work with discrete variables, of Ising, occupation number, or other kind but taking a finite number of values, analytic calculations can be pursued (up to a certain point) by writing down a **master equation** for the probability distribution to the configurations of the system at a given time knowing that the system was at a given configuration at the initial time. The form of the master equation, more precisely, of the transition probability factors in it, depends on the type of microscopic dynamics (local conserved or not order parameter, etc.). If these satisfy detailed balance, the dynamics eventually takes the system to its equilibrium distribution and the asymptotic solution to the master equation is the equilibrium probability distribution function. quite generally, the exact analysis of the master equation is not possible for systems in dimension larger than one but it is for the Ising chain with non-conserved order parameter dynamics [45] and to a certain extent in the conserved ordered parameter case as well [47]. The mean-field approximation can be applied in all cases and yields results that are summarized in [5].

Exercise 3.4 Write down the master equation for the evolution of the probability distribution function of the configuration of an Ising model with nearest-neighbour interactions, $\{s_i\}$, with $i = 1, \ldots, N$. Choose, for example, the transition probabilities

$$W(\{s_i\} \mapsto \{s_i'\}) = \frac{\lambda}{2}\left[1 - \tanh\left(\frac{\beta}{2}\Delta(H - hM)\right)\right] \tag{3.44}$$

where λ is a parameter that sets the time-scale, $\beta = 1/(k_B T)$ with T the temperature of the bath, H the energy of the system, h an applied external magnetic field and M the total magnetisation, and the variation Δ represents the difference between $H - hM$ evaluated at the final $\{s_i'\}$ and the departing $\{s_i\}$ configurations. Check whether the transition probabilities above satisfy detailed balance. Derive the evolution equation for the thermal average of a single spin, $\langle s_k \rangle$, in the sample by applying the mean-field approximation. Determine its stationary solution and compare to the equilibrium one under the same mean-field approximation. Derive a partial differential equation on the continuous limit of the local spin thermal average that takes the form of a **time-dependent Ginzburg-Landau equation**. Note that this equation acts on a thermal average and as such cannot capture thermal fluctuations. See [5] for details.

Exercise 3.5 Repeat the analysis in the previous exercise for the locally conserved order-parameter dynamics as realised by the Kawasaki exchange rule. Obtain the Cahn-Hilliard equation [] for the time-dependent evolution of the local order parameter. See [5] for details.

3.10 Field Theoretical approach

3.10.1 Statics: the Ginzburg-Landau framework

Equilibrium collective behaviour at second order phase transitions are largely independent of the microscopic details of the actual system and, as a consequence, also of the particular model used to describe it. Such **universality** naturally characterizes the physical behaviour close to a critical point, where the system undergoes a continuous phase transition.

The onset of collective behaviour is revealed by the correlation length ξ_{eq}, the typical distance over which the fluctuations of the microscopic variables are correlated. Far away from a critical point ξ_{eq} is of the order of the range of the microscopic interactions, whereas it diverges at the critical point. Accordingly, close enough to the

transition point, ξ_{eq} becomes mesoscopic and provides the only relevant length-scale of a critical system.

It is then possible to study the critical behaviour in terms of suitable mesoscopic field-theoretical models, in a formal development of the Landau approach to phase transitions. Indeed, as long as one is in mesoscopic length and time scales, an effective Hamiltonian functional of the field, which reflects the internal symmetries of the underlying microscopic system, can be used. Such Hamiltonian depends only on the order parameter (the field) and on a few other slow modes, whose actual nature is determined specifically by the system. For instance the order parameter can be identified with the magnetization in magnetic materials close to the Curie temperature, with the particle density in fluids etc.

By means of field-theoretical techniques it is possible to determine the non-analytic behaviour observed in various thermodynamic quantities and structure factors upon approaching the critical point. Such non-analyticities, parameterized by the standard critical exponents, some associated amplitude ratios and scaling functions turn out to be universal quantities. The values of universal quantities and scaling functions characterize the so-called universality class of the model.

3.10.2 Time-dependent Ginzburg-Landau description

Upon approaching a critical point the typical time scale of dynamics of the fluctuations around the equilibrium state diverges as $\xi_{eq}^{z_{eq}}$ (critical slowing down), where z_{eq} is the dynamic critical exponent. This provides the natural separation between the relevant slow evolution due to the developing collective behaviour and the fast one related to microscopic processes. This separation makes the mesoscopic description of the dynamics a particularly viable approach to the problem. Indeed it allows one to compute systematically the non-analytic behaviours observed in dynamical quantities, e.g., in the low-frequency limit of the dynamic structure factor. In turn the associated universal quantities define the **dynamic universality class**. One finds that each static universality class consists of several dynamic sub-universality classes which differ, e.g., by different conserved quantities, but nonetheless exhibit the same static universal properties.

The field theoretic approach can also be used away from the critical point to characterise the dynamics in the sub-critical phase.

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-

grained field,

$$\phi(\vec{x},t) \equiv \frac{1}{V}\sum_{i\in V_{\vec{x}}} s_i(t) \ , \tag{3.45}$$

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

$$F[\phi] = \int d^dx \ \left\{ \frac{c}{2}\left[\nabla\phi(\vec{x},t)\right]^2 + V[\phi(\vec{x},t)] \right\} \ . \tag{3.46}$$

The elastic constant c is usually re-absorbed with a series of re-definitions.

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 ϕ^4 form:

$$V(\phi) = a\phi^4 + b(g)\phi^2 \ . \tag{3.47}$$

The first term in eq. (3.46) 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 (3.46) 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 $f(m) = -Jm^2 - hm + k_BT\{(1+m)/2\ln[(1+m)/2] + (1-m)/2\ln[(1-m)/2]$ that close to the critical point where $m \simeq 0$ becomes $f(m) \simeq (k_BT - 2J)/2\ m^2 - hm + k_BT/12\ m^4$ demonstrating the passage from a harmonic form at $k_BT > k_BT_c = 2J$, to a quartic well at $T = T_c$, and finally to a double-well structure at $T < T_c$.

Exercise 3.6 Prove the above.

With a six-order potential one can mimic the situation in the right panel of Fig. 3.32. It suffices to take $V(\phi) = a + b\phi^2 + c\phi^4 + d\phi^6$. The sign of d, $d > 0$, is fixed by the condition that the potential be confining at large values of $|\phi|$. The potential has a local minimum at $\phi = 0$ for all $b > 0$. Next, we choose $c < 0$ to allow for the existence of two maxima and two minima at $\phi = \pm[(-c \pm \sqrt{c^2 - 3bd})/(3d)]^{1/2}$.

When discussing dynamics one should write down the stochastic evolution of the individual spins and compute time-dependent averaged quantities as the ones in (3.4). 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 **over-damped** (i.e. $t \gg t_r^{\dot{\phi}}$).

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

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = -\frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} \tag{3.48}$$

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

$$[\, \phi(\vec{x},0)\phi(\vec{x}',0)\,]_{ic} = \Delta \delta(\vec{x}-\vec{x}') \tag{3.49}$$

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, see *e.g.* eq. (3.23). The phase transition is controlled by the parameter b in the potential.

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

$$\frac{\partial \phi(\vec{x},t)}{\partial t} = -\frac{\delta F[\phi]}{\delta \phi(\vec{x},t)} + \xi(\vec{x},t)\ . \tag{3.50}$$

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. (3.46) with a potential form with fixed parameters (independent of T). ξ is a noise taken to be Gaussian distributed with zero mean and correlations

$$\langle \xi(\vec{x},t)\xi(\vec{x}',t')\rangle = 2k_B T \delta^d(\vec{x}-\vec{x}')\delta(t-t')\ . \tag{3.51}$$

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 ϕ 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 times such that the domain walls do not move with this approach.

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.

3.10.3 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 (3.48), 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 $\vec{k} = 2\pi/L \ (n_1, \ldots, n_d)$ and n_k integer, reads

$$\frac{\partial \phi(\vec{k},t)}{\partial t} = [-k^2 - V''(0)]\phi(\vec{k},t) + \xi(\vec{k},t) \ . \tag{3.52}$$

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 ϕ 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.

3.10.4 The domain walls

Our analytical understanding of domain growth problems is based on the dynamics of the interface between spatial regions that ordered in one or another of the equilibrium states.

The time-dependent Ginzburg-Landau model allows us to gain some insight on the mechanism driving the domain growth and the direct computation of the averaged domain length. In clean systems temperature does not play a very important role in the domain-growth process, it just adds some thermal fluctuations within the domains, as long as it is smaller than T_c. In dirty cases instead temperature triggers thermal activation.

We focus first on clean cases at $T = 0$ and only later we discuss thermal effects. Equation (3.48) for $T = 0$ is just a gradient descent in the energy landscape F. Two terms contribute to F: the bulk-energy term that is minimized by $\phi = \pm\phi_0$ and the elastic energy $(\nabla\phi)^2$ which is minimized by flat walls if present. As a consequence the minimization process implies that regions of constant field, $\phi(\vec{x}, t) = \pm\phi_0$, grow and they get separated by flatter and flatter walls.

Take the time-dependent Ginzburg-Landau equation and look for a static solution that minimises the free-energy density. Clearly, this is given by $\phi(\vec{x}, t) = \pm\phi_0$ with ϕ_0 the minima of the free-energy density.

But the time-dependent Ginzburg-Landau equation has another stationary solution, a **kink or flat interface**,

$$\phi_{K,A}(\vec{x}) = \phi_{K,A}(z) = \phi_0 \tanh\left(\pm\frac{z - z_0}{\sqrt{(}s)}\right) \tag{3.53}$$

with z some direction in space and z_0, the centre of the kink being arbitrary. This solution interpolates between $\phi_K(-\infty) = -\phi_0$ and $\phi_K(\infty) = \phi_0$ for the kink and $\phi_A(-\infty) = \phi_0$ and $\phi_A(\infty) = -\phi_0$ for the anti-kink. Both vary over a very small region of space around its centre, where the kink passes through zero (see below), and one identifies the kink width $\xi_K \simeq \sqrt{2}$ from this expression (the dimensional parameters have to be recovered).

The profile of a flat domain wall

Take a **flat domain wall** separating regions where the configuration is the one of the two equilibrium states, $\phi(\vec{x}, t) = \pm\phi_0 + \delta\phi(\vec{x}, t)$. Linearizing eq. (3.48) around $\pm\phi_0$ and looking for static configurations, *i.e.* $\delta\phi(\vec{x}, t) = \delta\phi(\vec{x}) = \delta\phi(n)$ where n is the distance from the wall along the normal direction one finds $d^2\delta\phi(n)/dn^2 = -V''(\phi_0)\delta\phi(n)$. This equation has the solution $\delta\phi(n) \sim e^{-\sqrt{V''(\phi_0)}n}$ where n is the perpendicular distance to the wall. The order parameter approaches $\pm\phi_0$ on both sides of the wall very rapidly. This means that the free-energy of a configuration with an interface (sum of the elastic and potential terms) is concentrated in a very narrow region close to it.

The excess free-energy a flat domain wall

The kink and anti-kink solutions have higher energy than the homogeneous one. By expressing the explicit different between the free-energies of the two solutions and using $\phi_K^2/2 - \phi_K^4/4 + 1/2\ (d\phi_K/dz)^2 = \text{cst} = \phi_0^2/2 - \phi_0^4/4$ that is obtained by

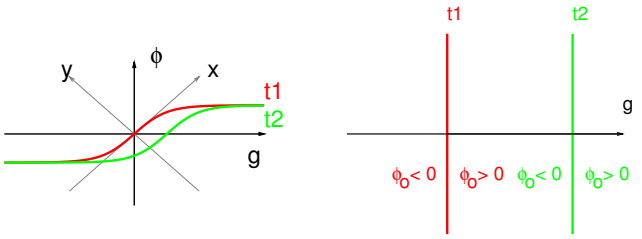


Figure 3.44: Left: domain wall profile. Right: view from the top. (g is n.)

multiplying the equation differential equation for the kink by $d\phi_K/dz$ and integrating it over z with the boundary conditions $\phi_K(\pm\infty) = \pm\phi_0$ and $\lim_{z\to\pm\infty} = d\phi_k/dz = 0$.

One computes the surface tension σ as

$$\sigma = \frac{\Delta F}{A} = \frac{1}{2}\int_{-\infty}^{\infty} dz \left(\frac{d\phi_K}{dz}\right)^2 = \frac{1}{2}\int_{-\infty}^{\infty} dz\ \mathrm{sech}^4\left(\frac{z}{\sqrt{2}}\right) = 2\sqrt{2}3 \tag{3.54}$$

with A the area perpendicular to the direction normal to the kink. We used adimensional variables here. One generalises the above to $\Delta F = \sigma \int d\vec{a}$ at the late stages of evolution when the domain walls are not completely flat.

3.10.5 Curvature driven dynamics in $d \geq 2$

Allen and Cahn showed that the local wall velocity is proportional to the local curvature working with the Ginzburg-Landau equation at $T = 0$. The proof goes as follows. Take the Ginzburg-Landau equation and transform the derivatives to apply in the direction normal to the wall that we call $\hat{n}$ in the direction of increasing ϕ:

$$\left.\frac{\partial\phi(\vec{x},t)}{\partial t}\right|_n = -\left.\frac{\partial\phi(\vec{x},t)}{\partial n}\right|_t \left.\frac{\partial n}{\partial t}\right|_\phi , \qquad \vec{\nabla}\phi(\vec{x},t) = \left.\frac{\partial\phi(\vec{x},t)}{\partial n}\right|_t \hat{n} ,$$
$$\nabla^2\phi(\vec{x},t) = \left.\frac{\partial^2\phi(\vec{x},t)}{\partial n^2}\right|_t + \left.\frac{\partial\phi(\vec{x},t)}{\partial n}\right|_t \vec{\nabla}\cdot\hat{n}$$

where the subscripts mean that the derivatives are taken at t, n or ϕ fixed. The GL equation reads

$$-\left.\frac{\partial\phi}{\partial n}\right|_t \left.\frac{\partial n}{\partial t}\right| = \left.\frac{\partial^2\phi}{\partial n^2}\right|_t + \left.\frac{\partial\phi}{\partial n}\right|_t \cdot\vec{\nabla}\hat{n} - V'(\phi) . \tag{3.55}$$

Assuming that for gently curving walls the wall profile is given by the condition

$$\frac{\partial^2\phi}{\partial n^2}|_t = V'(\phi) \tag{3.56}$$

(note that the derivative is taken at fixed t), one replaces it in the GL equation and one finds the Allen-Cahn result

$$\boxed{v \equiv \partial_t n|_\phi = -\vec{\nabla}\cdot\hat{n} \equiv -\kappa} \tag{3.57}$$

valid in all d with κ the geodesic curvature. v is the velocity of the wall in the direction of increasing ϕ. Therefore the local velocity points in the direction of the local centre of curvature. The effect is to reduce the wall roughness by rendering them smoother.

3.10.6 Consequences

Equation (3.57) allows one to get an intuition about the typical growth law in such processes. Take a spherical wall in any dimension. The local curvature is constant and $\kappa = (d-1)/R$ where R is the radius of the sphere within the hull. Equation (3.57) is recast as $dR/dt = -(d-1)/R$ that implies $R^2(t) = R^2(0) - 2(d-1)t$.

A closer look at the $2d$ equation allows one to go beyond and prove, in this case, that all areas enclosed by domain walls irrespective of their being other structures within (the so-called hull-enclosed areas) tend to diminish at constant rate $dA/dt = -\lambda$ [49]. This, of course, does not mean that all domains reduce their area since a domain can gain area from the disappearance of an internal domain of the opposite sign, for instance. The proof is simple and just uses the Gauss-Bonnet theorem: $\frac{dA}{dt} = \oint \vec{v}\wedge d\vec{\ell} = \oint v d\ell$. The local wall-velocity, $\vec{v}$, is proportional to the local geodesic curvature, κ, and the Gauss-Bonnet theorem implies $\oint \kappa d\ell = 2\pi$ for a planar $2d$ manifold with no holes. (This result cannot be extended to $d > 2$ since the topological constraint involves the Gaussian curvature as well.) Therefore, the hull-enclosed area decreases with constant velocity for any geometry.

3.10.7 The Porod tails

The correlation function in a system with linear length L and single kink mimicked by a step function is

$$C(x) = \frac{1}{L}\int_{-L/2}^{L/2} dy\ \mathrm{sgn}(y)\mathrm{sgn}(y+x) = 1 - \frac{2|x|}{L} \tag{3.58}$$

This function is non-analytic at $x = 0$. Extended to d dimensions, one needs to average this results over the $d-1$ perpendicular directions to the x one. One finds

$$C(r) \simeq 1 - \frac{2}{\sqrt{\pi}} \frac{\Gamma(d/2)}{\Gamma((d+1)/2} \frac{r}{L} \qquad \frac{r}{L} \to 0 \tag{3.59}$$

and, in the Fourier domain,

$$S(k) = L^d \frac{A_d}{(kL)^{d+1}} \qquad kL \to \infty \tag{3.60}$$

with $A_d = 2^{d+1}\pi^{d/2-1}\Gamma(d/2)$. This is the Porod law, found using scattering of two-phase systems [60]. See [5].

Exercise 3.7 Find the expression for A_d given above from Fourier transform of (3.59).

Another derivation of the short-distance behaviour of the space correlation goes as follows [**?**]. The product of the field at two points $\vec{x}$ and $\vec{x}+\vec{r}$ with $\xi \ll r \ll L$ is -1 if there is wall in between or 1 otherwise. At long times the probability of finding more than one wall is negligible. Then, $C(r,t) \simeq (-1)r/L + (1-r/L) = 1-2r/L$, for $r \ll L$, since r/L is the probability for a rod of length r to cut a wall. This expression is non-analytic at $\vec{r}/L = \vec{0}$. The structure factor scales as $S(k,t) \sim L^{-1}k^{-(d+1)}$, for $kL \gg 1$.

3.10.8 Scaling functions for subcritical coarsening

Even though the qualitative behavior of the solution to eq. (3.48) is easy to grasp, it is still too difficult to solve analytically and not much is known exactly on the scaling functions. A number of approximations have been developed but none of them is fully satisfactorily (see [4] for a critical review of this problem).

The **super-universality hypothesis** [4] states that in cases in which temperature and quenched disorder are 'irrelevant' in the sense that they do not modify the nature of the low-temperature phase (*i.e.* it remains ferromagnetic in the case of ferromagnetic Ising models) the scaling functions are not modified. Only the growing length changes from the, say, curvature driven $t^{1/2}$ law to a logarithmic one. Numerical evidence for the validity of this hypothesis in a number of two and three dimensional models including the RBIM and the RFIM was given in [67] but more recent numerical studies [68] claim that it does not hold, at least for the latter model. This issue is not settled.

3.10.9 Systems with several growth laws

Some special cases in which dynamic scaling with respect to a single growth law does not apply have also been exhibited. Their common feature is the existence of two (or more) growing lengths associated to different ordering mechanisms. An example is given by the one dimensional Heisenberg model with conserved order parameter at $T \to 0$ in which the two mechanisms are related to the vectorial ordering within domains separated by couples of parallel spins that annihilate in a way that is similar to domain-wall annihilation in the Ising chain [69].

3.11 The large $\mathcal{N}$ approximation

We would like to study, in full detail, the Langevin equation for the scalar field ϕ with Ginzburg-Landau free-energy

$$F = \int d^d x \left[\frac{1}{2} (\vec{\nabla}\phi)^2 - \frac{g}{2}\phi^2 + \frac{\lambda}{4}\phi^4 \right] , \tag{3.61}$$

As we will soon introduce a new vector and an another set of indices, let us recall here that space has d dimensions, the vector position is $\vec{x} = (x_1, \ldots, x_d)$ and the local contribution to the elastic term is proportional to

$$(\vec{\nabla}\phi)^2 = \vec{\nabla}\phi \cdot \vec{\nabla}\phi = \frac{\partial\phi}{\partial x_1}\frac{\partial\phi}{\partial x_1} + \ldots \frac{\partial\phi}{\partial x_d}\frac{\partial\phi}{\partial x_d} . \tag{3.62}$$

We used the standard notation for the parameters $g > 0$ and $\lambda > 0$ in the potential, and we chose the signs to have the double-well structure. The potential part has two minima at

$$\phi_0^2 = \frac{g}{\lambda} \tag{3.63}$$

and it can be rewritten in a convenient way

$$V(\phi) = \frac{\lambda}{4} \left[\left(\phi^2 - \phi_0^2\right)^2 - \phi_0^4 \right] \tag{3.64}$$

Without loss of generality we neglect the constant term $-\lambda\phi_0^4/4$. We therefore work with

$$V(\phi) = \frac{\lambda}{4} \left(\phi^2 - \phi_0^2\right)^2 . \tag{3.65}$$

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

$$\phi(\vec{x}, t) \to \vec{\phi}(\vec{x}, t) = (\phi_1(\vec{x}, t), \ldots, \phi_{\mathcal{N}}(\vec{x}, t)) , \tag{3.66}$$

and modify the free-energy

$$F = \int d^d x \left[\frac{1}{2} (\vec{\nabla}\vec{\phi})^2 + \frac{\mathcal{N}\lambda}{4} (\phi_0^2 - \mathcal{N}^{-1}\phi^2)^2 \right] , \tag{3.67}$$

with $\phi^2 = \sum_{\alpha=1}^{\mathcal{N}} \phi_\alpha^2$ and $\phi_0^2 > 0$ and finite. Note that the double-well structure of the potential is assumed from the start. The factors $\mathcal{N}$ and $\mathcal{N}^{-1}$ are added to ensure that each contribution to the free-energy F is of order $\mathcal{N}$ (note that ϕ^2 is expected to be order $\mathcal{N}$). The elastic contribution has now a double scalar product structure, in the $\mathcal{N}$-dimensional space and in the d-dimensional space. More precisely,

$$\begin{aligned} (\vec{\nabla}\vec{\phi})^2 &= \vec{\nabla}\phi_\alpha \cdot \vec{\nabla}\phi_\alpha = \frac{\partial \phi_\alpha}{\partial x_1}\frac{\phi_\alpha}{\partial x_1} + \cdots + \frac{\partial \phi_\alpha}{\partial x_d}\frac{\phi_\alpha}{\partial x_d} \\ &= \frac{\partial \phi_1}{\partial x_1}\frac{\phi_1}{\partial x_1} + \cdots \frac{\partial \phi_\mathcal{N}}{\partial x_1}\frac{\phi_\mathcal{N}}{\partial x_1} + \cdots + \frac{\partial \phi_1}{\partial x_d}\frac{\phi_1}{\partial x_d} + \cdots + \frac{\partial \phi_\mathcal{N}}{\partial x_d}\frac{\phi_\mathcal{N}}{\partial x_d} . \end{aligned} \tag{3.68}$$

This problem can be studied statically within the canonical formalism and a finite critical temperature $T_c(d, \phi_0)$ is found.

3.11.1 Statics

If the volume V is kept finite the system equilibrates in a finite time t_{eq} and the order parameter probability distribution reaches the Gibbs state [70]

$$P_{eq}[\vec{\phi}(\vec{k})] = \frac{1}{Z} \exp\left(-\frac{1}{2k_B T V} \sum_{\vec{k}} (k^2 + \xi_{eq}^{-2}) \vec{\phi}(\vec{k}) \cdot \vec{\phi}(-\vec{k}) \right) \tag{3.69}$$

where ξ_{eq} is the correlation length

$$\xi_{eq}^{-2} = -g + \frac{\lambda}{\mathcal{N}} \langle \vec{\phi}^2(\vec{x}) \rangle_{eq} \tag{3.70}$$

with $\langle \cdots \rangle_{eq}$ standing for the average taken with (3.69). (In this expression we have not distinguished one vector direction to signal the symmetry breaking [71] but we considered the symmetric measure in which one sums over all such states.) Note that this is a **Gaussian measure**.

In order to analyze the properties of $P_{eq}[\vec{\phi}(\vec{k})]$ it is necessary to extract from (3.70) the dependence of ξ_{eq}^{-2} on T, ϕ_0 and V. Evaluating the average, the above equation yields

$$\xi_{eq}^{-2} = -g + \frac{\lambda}{V} \sum_{\vec{k}} \frac{k_B T}{k^2 + \xi_{eq}^{-2}}. \tag{3.71}$$

The solution of this equation is well known[115] and here we summarize the main features, as presented in [70]. Separating the $\vec{k} = 0$ term under the sum, for very large volume we may rewrite

$$\xi_{eq}^{-2} = -g + \lambda k_B T B(\xi_{eq}^{-2}) + \frac{\lambda k_B T}{V \xi_{eq}^{-2}} \tag{3.72}$$

where

$$B(\xi_{eq}^{-2}) = \lim_{V\to\infty} \frac{1}{V} \sum_{\vec{k}} \frac{1}{k^2 + \xi_{eq}^{-2}} = \int \frac{d^d k}{(2\pi)^d} \frac{e^{-\frac{k^2}{\Lambda^2}}}{k^2 + \xi_{eq}^{-2}} \tag{3.73}$$

regularizing the integral by introducing the high momentum cutoff Λ. The function $B(x)$ is a non negative monotonically decreasing function with the maximum value at $x = 0$

$$B(0) = \int \frac{d^d k}{(2\pi)^d} \frac{e^{-\frac{k^2}{\Lambda^2}}}{k^2} = (4\pi)^{-\frac{d}{2}} \frac{2}{d-2} \Lambda^{d-2} \quad . \tag{3.74}$$

By graphical analysis one can easily show that (3.72) admits a finite solution for all $k_B T$. However, there exists the critical value of the temperature T_c defined by

$$-g + \lambda k_B T_c B(0) = 0 \tag{3.75}$$

such that for $T > T_c$ the solution is independent of the volume, while for $T \leq T_c$ it depends on the volume. Using

$$B(x) = (4\pi)^{-\frac{d}{2}} x^{\frac{d}{2}-1} e^{\frac{x}{\Lambda^2}} \Gamma\left(1 - \frac{d}{2}, \frac{x}{\Lambda^2}\right) \tag{3.76}$$

where $\Gamma(1 - \frac{d}{2}, \frac{x}{\Lambda^2})$ is the incomplete gamma function, for $0 < \frac{T-T_c}{T_c} \ll 1$ one finds $\xi_{eq} \sim (\frac{T-T_c}{T_c})^{-\nu}$, i.e. close but above T_c, where $\nu = 1/2$ for $d > 4$ and $\nu = 1/(d-2)$ in $d < 4$, with logarithmic corrections for $d = 4$. At T_c one has $\xi_{eq} \sim V^{\overline{\lambda}}$ with $\overline{\lambda} = 1/4$ for $d > 4$ and $\overline{\lambda} = 1/d$ for $d < 4$, again with logarithmic corrections in $d = 4$. Finally, below T_c one finds $\xi_{eq}^2 = \frac{M^2 V}{k_B T}$ where $M^2 = \phi_0^2 \left(\frac{T_c - T}{T_c}\right)$ and $\phi_0^2 = g/\lambda$.

Let us now see what are the implications for the equilibrium state. As Eq. (3.69) shows, the individual Fourier components are independent random variables, Gaussianly distributed with zero average. The variance is given by

$$\frac{1}{\mathcal{N}} \langle \vec{\phi}(\vec{k}) \cdot \vec{\phi}(-\vec{k}) \rangle_{eq} = V S(\vec{k}) \tag{3.77}$$

where

$$S(\vec{k}) = \frac{k_B T}{k^2 + \xi_{eq}^{-2}} \tag{3.78}$$

is the equilibrium structure factor. For $T > T_c$, all $\vec{k}$ modes behave in the same way, with the variance growing linearly with the volume. For $T \leq T_c$, instead, ξ_{eq}^{-2} is negligible with respect to k^2 except at $\vec{k} = 0$, yielding

$$S(\vec{k}) = \begin{cases} \frac{T_c}{k^2}(1 - \delta_{\vec{k},0}) + cV^{2\bar{\lambda}}\delta_{\vec{k},0} & \text{for } T = T_c \ , \\ \frac{T}{k^2}(1 - \delta_{\vec{k},0}) + M^2 V \delta_{\vec{k},0} & \text{for } T < T_c \ , \end{cases} \tag{3.79}$$

where c is a constant. This produces a volume dependence in the variance of the $\vec{k} = 0$ mode growing faster than linear. Therefore, for $T \leq T_c$ the $\vec{k} = 0$ mode behaves differently from all the other modes with $\vec{k} \neq 0$. For $T < T_c$ the probability distribution (3.69) takes the form

$$P_{eq}[\vec{\phi}(\vec{k})] = \frac{1}{Z} e^{-\frac{\vec{\phi}^2(0)}{2M^2V^2}} e^{-\frac{1}{2k_B TV}\sum_{\vec{k}} k^2 \vec{\phi}(\vec{k})\cdot\vec{\phi}(-\vec{k})} \quad . \tag{3.80}$$

Therefore, crossing T_c there is a transition from the usual disordered high temperature phase to a low temperature phase characterized by a macroscopic variance in the distribution of the $\vec{k} = 0$ mode. The distinction between this phase and the mixture of pure states, obtained below T_c when $\mathcal{N}$ is kept finite can be discussed but we will not discuss it here.

Although the effective Hamiltonian is 'almost' quadratic, the phase transition in the form of a Bose-Einstein-like condensation on the $\vec{k} = \vec{0}$ mode is due to the self-consistent constraint.

3.11.2 Dynamics

The (over-damped) Langevin equation then becomes

$$\partial_t \phi_\alpha(\vec{x}, t) = \nabla^2 \phi_\alpha(\vec{x}, t) + \phi_\alpha(\vec{x}, t)\left[\phi_0^2 - \mathcal{N}^{-1}\phi^2(\vec{x}, t)\right] + \xi_\alpha(\vec{x}, t) \ , \tag{3.81}$$

where the friction coefficient has been absorbed in a redefinition of time, the constant λ has been conveniently set to one, and the initial condition is taken from a Gaussian distribution with zero-mean and correlations

$$[\phi_\alpha(\vec{x}, 0)\phi_\beta(\vec{x}', 0)]_{ic} = \Delta\delta^d(\vec{x} - \vec{x}')\delta_{\alpha\beta} \ . \tag{3.82}$$

We take the noise to be delta correlated in space and time. It will turn out to be convenient (to avoid short distance divergencies) to introduce a short-distance cut-off:

$$\langle \xi_\alpha(\vec{x},t)\xi_\beta(\vec{x}',t')\rangle = 2k_BT\delta_{\alpha\beta}e^{-|\vec{x}-\vec{x}'|^2\Lambda^2/4}\ \delta(t-t')\ , \tag{3.83}$$

$$\langle \xi_\alpha(\vec{k},t)\xi_\beta(\vec{k}',t')\rangle = 2k_BT(2\pi)^d\delta_{\alpha\beta}e^{-k^2/\Lambda^2}\ \delta(\vec{k}+\vec{k}')\ \delta(t-t')\ . \tag{3.84}$$

In the limit $\mathcal{N}\to\infty$ while keeping the dimension of real space fixed to d, the factor that couples the different components in the cubic term in the right-hand-side can be replaced by

$$\mathcal{N}^{-1}\phi^2(\vec{x},t) \to \mathcal{N}^{-1}\ \langle [\,\phi^2(\vec{x},t)\,]_{ic}\rangle \equiv \tilde{a}(t) \tag{3.85}$$

since $\mathcal{N}^{-1}\phi^2(\vec{x},t)$ does not fluctuate, it is equal to its average over the initial conditions and temperature, 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 (3.85) 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):

$$\partial_t\phi(\vec{x},t) = [\nabla^2 + a(t)]\phi(\vec{x},t) + \xi(\vec{x},t)\ , \tag{3.86}$$

where the time-dependent harmonic constant

$$a(t) = \left[\phi_0^2 - \ \langle[\phi^2(\vec{x},t)]_{ic}\rangle\right] = \left[\phi_0^2 - \tilde{a}(t)\right] \tag{3.87}$$

has to be determined self-consistently. The factor $1/\mathcal{N}$ disappeared since we are now working with a single component of the $\mathcal{N}$-vector $\vec{\phi}$.

Consistently with the decoupling performed above, the dynamics is **isotropic** in the $\mathcal{N}$-dimensional space implying that all α components have the same self-correlation and that they are not correlated between themselves:

$$C_{\alpha\beta}(\vec{x},t;\vec{x}',t') = \delta_{\alpha\beta}C(\vec{x},t;\vec{x}',t')\ . \tag{3.88}$$

Equation (3.86) can be Fourier transformed

$$\partial_t\phi(\vec{k},t) = [-k^2 + a(t)]\phi(\vec{k},t) + \xi(\vec{k},t)\ , \tag{3.89}$$

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 $-k^2 + a(t)$ in the rhs. The solution is

$$\phi(\vec{k},t) = \phi(\vec{k},0)\ e^{-k^2 t + \int_0^t dt'\ a(t')} + \int_0^t dt'\ e^{-k^2(t-t') + \int_{t'}^t dt'' a(t'')}\ \xi(\vec{k},t') \tag{3.90}$$

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

$$a(t) = \phi_0^2 - \Delta\ e^{2\int_0^t dt' a(t')} \left(\frac{2\pi}{4t}\right)^{d/2} - k_B T \int_0^t dt' \left(\frac{2\pi}{4(t-t')}\right)^{d/2} e^{\int_{t'}^t dt'' a(t'')} \tag{3.91}$$

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 Δ. 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 $t \to t + 1/\Lambda^2$ with $\Lambda = 1/a$ the lattice spacing.

Without giving all the details of the calculation, eq. (3.91) can be solved at all temperatures [70]. One finds that there exists a finite $T_c(d)$, the same that is found with the equilibrium analysis of the static free-energy, and

Upper-critical quench

$$a(t) \to -\xi_{eq}^{-2} < 0 \tag{3.92}$$

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

Critical quench

The time-dependent contribution to the harmonic term vanishes asymptotically

$$a(t) \to -\frac{w}{2t} \quad \text{with} \quad w = 0 \ \text{ for } \ d > 4 \ \text{ and } \ w = (d-4)/2 \ \text{ for } \ d < 4\ . \tag{3.93}$$

The dynamics is trivial for $d \geq 4$ but there is critical coarsening in $d < 4$. z_{eq} equals 2 in agreement with the result from the ϵ expansion once evaluated at $\mathcal{N} \to \infty$. The averaged field is

$$\langle \phi(\vec{k},t) \rangle \simeq \phi(\vec{k},0)\ e^{-k^2 t}\ t^{(4-d)/4} \tag{3.94}$$

Zero-temperature sub-critical coarsening

The zero-T equation admits a simple solution. 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.*

$$a(t) \simeq \frac{d}{4t} \qquad \text{for} \qquad t \gg t_0 \tag{3.95}$$

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 exponentially both in critical and sub-critical quenches 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. The averaged field is

$$\langle \phi(\vec{k},t) \rangle \simeq \phi(\vec{k},0) e^{-k^2 t}\; t^{d/4} \tag{3.96}$$

We focus now on two interesting cases: quenches to $T = T_c$ and $T = 0$ (in this way the equilibrium relaxation is set to one in the correlation). We study the two space and two time correlation.

$$C(\vec{x},\vec{x}';t,t') \equiv [\,\langle \phi(\vec{x},t)\phi(\vec{x}',t') \rangle\,]_{ic} \tag{3.97}$$

This general correlation becomes the space-time one for $t = t'$ and the two-time one for $\vec{x} = \vec{x}'$.

Critical quench

The asymptotic behavior of the space-time correlation function is

$$[\,\langle \phi(\vec{x},t)\phi(\vec{x}',t') \rangle\,]_{ic} = \phi_0^2\, t'^{1-d/2} f(t/t')\;\exp\left[-\frac{(\vec{x}-\vec{x}')^2}{4(t+t')}\right]\,, \tag{3.98}$$

for a quench to T_c. We focus on $d < 4$. Note that ϕ_0 is still present

In critical quenches the two-time dependent pre-factor is of the form expected from dynamic scaling of $C(r,t)$ or $C(t,t')$ as discussed in eqs. (3.17) and (3.18) above.

The correlation 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. $d = 2$ is the lower critical dimension in this problem.

Sub-critical quench

The asymptotic behavior of the space-time correlation function after a quench to $T = 0$ is

$$[\,\phi(\vec{x},t)\phi(\vec{x}',t')\,]_{ic} = \phi_0^2 \left[\frac{4tt'}{(t+t')^2}\right]^{d/4} \exp\left[-\frac{(\vec{x}-\vec{x}')^2}{4(t+t')}\right] , \tag{3.99}$$

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

- The expression above has to be complemented with an additive contribution for quenches to finite temperature, $0 < T < T_c$. We are showing here the ageing contribution only. This stationary term will go from $1 - \phi_0^2$ to 0 for $t - t' \to \infty$.
- 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.
- 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 equilibrated regions 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 $\mathcal{N}$ $O(\mathcal{N})$ 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.
- For any finite and fixed $(\vec{x} - \vec{x}')$, in the long t' and t limit such that $t'/t \to 1$ the time dependence disappears and the correlation between two points converges to ϕ_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 will 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. We refer to the reviews in [118] for detailed accounts on the behavior of the linear response in critical dynamics.

3.12 The Ohta-Jasnow-Kawasaki approximation

An approximate analysis of the scalar stochastic field equation was given by Ohta-Jasnow-Kawasaki [61]. In a few words, the approximation amounts to writing the field as the sign (assumption of infinitely thin interfaces) of an auxiliary field that satisfies a diffusion equation. Details on how it is implemented can be found in [**?**, 5]. As a consequence, the correlation functions are non-trivial. Two importance successes of this approach are the fact that the correlation functions satisfy scaling with a growing length $t^{1/2}$ and that, better than the O(N) approximation, it has the correct Porod tail in the structure factor though with a different pre factor $A_{OJK} \neq A_d$ with respect to the one mentioned above [62].

Oono and Puri showed that a finite thickness of the interfaces has a non-trivial effect on the short-distance correlation function at finite time. The Porod law is recovered only at $t \to \infty$ [63].

Another approximation scheme, in which the field is given by another non-linear function of the auxiliary Gaussian field, was developed by Kawasaki, Yalabik and Gunton [64], gives the same correlation functions. The morphology of the network of defects (domain walls) given by this approximation is very different, though, from the one obtained from the numerical integration of the actual time-dependent Ginzburg-Landau equation.

In cases with vector order parameter and topological defects $n < d$, the Porod law is shown to be modified to $k^{-(d+n)}$ for $p = kL$. The KJG approximation has been extended to systems with vector order parameter by Bray and Puri [65] and Toyoki [66].

3.13 The $2d$ xy model

3.13.1 Statics

The classical xy, rotator or $O(2)$ model is a special case of the $O(N)$ model. This model is quite special in $d = 2$. Although there is no exact solution, contrary to the Ising case, several very convincing arguments and approximate calculations allowed one to reach a good understanding of its static behaviour. The model has a Kosterlitz-Thouless transition at $T_{\rm kt}$ that separates a disordered high-T from a critical low-T phase, both of them with vanishing order parameter, $m = 0$.[16] This

[16] N. D. Mermin and H. Wagner, *Absence of Ferromagnetism or Antiferromagnetism in One- or Two-Dimensional Isotropic Heisenberg Models*, Phys. Rev. Lett. **17**, 1133 - 1136 (1966).

phase transition is not accompanied by symmetry breaking. Topological defects proliferate in the disordered phase and they bind in pairs in the one with quasi long-range order and correlation functions that decay algebraically. Physical realisations are two-dimensional planar ferromagnets, superconducting films, Josephson-junction arrays, especially tailored nematic liquid crystals and toy models for two-dimensional turbulence. The $2d$ xy model is the paradigm in this class of *topological phase transitions*.

For any translational invariant two-body interaction $J_{ij} = J(i-j)$ and a site-dependent external field h_i, the Hamiltonian is

$$H = -\sum_{i\neq j} J_{ij}\vec{s}_i\cdot\vec{s}_j - \sum_i \vec{h}_i\cdot\vec{s}_i \tag{3.100}$$

$$= -\sum_{i\neq j} J_{ij}\cos(\theta_i-\theta_j) - \sum_i h_i\cos(\theta_i-\theta_{h_i}) \tag{3.101}$$

The model is fully solvable in the spin-wave approximation in which the field is supposed to vary smoothly in space and, hence, vortices are neglected. Indeed, at low temperature one can assume that the spins vary little from site to site the cos function can be expanded to second order and, in the absence of external fields, the Hamiltonian becomes

$$H \simeq -\sum_{i\neq j} J_{ij}\left[1-\frac{1}{2}(\theta_i-\theta_j)^2\right] . \tag{3.102}$$

In the continuum limit the two-component spin is parametrized as

$$\vec{s}(\vec{x}) = \cos\theta(\vec{x})\ e_x + \sin\theta(\vec{x})\ e_y \tag{3.103}$$

where the modulus $|\vec{s}(\vec{x})|$ has been fixed to one at all space points $\vec{x}$ and the angle $\theta\in(-\pi,\pi]$ is measured between the local spin and a chosen fixed axis. Taking now an homogeneous case, $J_{ij}=J$ for all ij pairs, the functional Ginzburg-Landau free-energy is proposed to be

$$F = \frac{J}{2}\int d^2x\ (\vec{\nabla}\theta(\vec{x}))^2 \tag{3.104}$$

where an irrelevant additive constant has been neglected. With the Fourier transform $\theta(\vec{x}) = (2\pi)^{-2}\int d^dk e^{i\vec{x}\cdot\vec{k}}\theta(\vec{k})$ one has

$$F = \frac{J}{2}\int \frac{d^2k}{(2\pi)^2}\ k^2|\theta(\vec{k})|^2 \tag{3.105}$$

and the modes are now manifestly decoupled. Within this approximation, there is no spontaneous magnetisation at any temperature in $d \leq 2$ as one easily shows that $\langle \vec{s} \rangle = 0$.

Within the same approximation, the spin-spin correlation function is [17]

$$C(r) = \langle \cos(\theta(r) - \theta(0)) \rangle = \frac{1}{2} \langle e^{i(\theta(r)-\theta(0))} \rangle + \frac{1}{2} \langle e^{-i(\theta(r)-\theta(0))} \rangle = e^{-\frac{1}{2}\langle (\Delta\theta)^2 \rangle} \quad (3.106)$$

where $\Delta\theta(r) = \theta(r) - \theta(0)$. The angle displacement function in equilibrium is $\langle (\Delta\theta(r))^2 \rangle = k_B T/(J a^{2-d})\ I(r)$ with

$$I(r) = \int \frac{d^d k}{(2\pi)^d} \frac{1 - e^{i\vec{k}\cdot\vec{r}}}{k^2} \ , \quad (3.107)$$

where the integral over each $\vec{k}$ component runs from π/L to π/a with L the size of the system and a a microscopic length scale (that can be associated to the lattice spacing). $I(r)$ behaves asymptotically, for $r \to \infty$, as

$$I(r) \simeq \begin{cases} \frac{\Omega_d}{d-2} \left(\frac{\pi}{L}\right)^{d-2} & d > 2 \\ \frac{1}{2\pi} \ln(r/L) & d = 2 \\ r & d = 1 \end{cases}$$

Therefore,

$$\langle (\Delta\theta(r))^2 \rangle \simeq \begin{cases} c\ T & d > 2 \\ \frac{k_B T}{\pi J} \ln \frac{r}{L} & d = 2 \\ k_B T/(Ja)\ r & d = 1 \end{cases}$$

We see from these expressions that for $d > 2$ correlations persist, with $C(r)$ approaching a constant asymptotically. For $d = 1$ the correlation decays to zero exponentially. While $d = 2$ is a special case and

$$C(r) = \left(\frac{a}{r}\right)^{k_B T/(2\pi J)} = \left(\frac{a}{r}\right)^{\eta(T)} \quad (3.108)$$

a power-law decay typical of a critical point, though in this model this decay applies to all temperatures, with a temperature dependent exponent $\eta(T)$. Spin-waves are non-local and extensive excitations.

The high-temperature series analysis of the partition function of the original XY spin model shows that the correlation function decays exponentially in this limit,

[17] We used here $\langle e^z \rangle = e^{\langle z^2 \rangle/2}$ valid for a Gaussian variable, in this case $z = \pm i \Delta\theta(r)$.

$C(r) \simeq e^{-r/\xi_{eq}}$, with a correlation length $\xi_{eq}(T) \propto a/\ln(k_B T/J)$ that tends to zero only at $T \to \infty$ and diverges at $T \to 0$.

The different decays found at low and high T imply that there should be a phase transition in between. When the effect of vortices is included this finite temperature phase transition is found. Vortices cannot be eliminated by simple perturbations but they annihilate when a vortex and an anti-vortex encounter. The correct treatment of vortices by Kosterlitz and Thouless[18] shows that the model has a phase transition at $k_B T_{KT} = \pi J/2$. The power-law scaling of correlation functions survives in the low T phase with $\eta(T)$ continuously varying from 0 at $T = 0$ to 1/4 at $T = T_{KT}$.

3.13.2 Dynamics

One *assumes* that the angle θ is governed by an over-damped Langevin equation,

$$\partial_t \theta(\vec{x}, t) = \nabla^2 \theta(\vec{x}, t) + \xi(\vec{x}, t) \ , \tag{3.109}$$

where a white-noise scalar noise is proposed to act additively on the angle θ and the friction coefficient has been set to one. This equation can be readily solved in Fourier space

$$\theta(\vec{k}, t) = \theta(\vec{k}, 0) e^{-k^2 t} + \int_0^t dt' \ e^{-k^2 (t-t')} \ \xi(\vec{k}, t') \ . \tag{3.110}$$

The noise-noise correlation is usually taken to be delta-correlated in space and time. As for the large $\mathcal{N}$ field it is convenient to use a microscopic short-distance cut-off, a, inherited from the lattice spacing that translates into a large k cut-off Λ and will help regularise the behaviour of correlation functions at equal times:

$$\langle \xi(\vec{k}, t) \xi(\vec{k}', t') \rangle = (2\pi)^d \ 2 k_B T \ e^{-k^2/\Lambda^2} \delta(\vec{k} + \vec{k}') \delta(t - t') \ . \tag{3.111}$$

The angle $\theta(\vec{k}, t)$ in Fourier space is a Gaussian variable with zero mean. Going back to real space, $\theta(\vec{x}, t)$ remains a Gaussian variable with zero mean.

The space-time spin correlation function is

$$C(r, t) = \langle \vec{s}(\vec{x}, t) \cdot \vec{s}(\vec{0}, t) \rangle = \langle \cos[\theta(\vec{x}, t) - \theta(\vec{0}, t)] \rangle = e^{-\frac{1}{2} \langle (\Delta\theta(\vec{x}, t))^2 \rangle} \tag{3.112}$$

The average in the exponential is

$$\begin{aligned} \langle (\Delta\theta(\vec{x}, t))^2 \rangle &= \langle \left[\int \frac{d^d k}{(2\pi)^d} \ e^{i\vec{k}\cdot\vec{x}} \ \theta(\vec{k}, t) - \int \frac{d^d k}{(2\pi)^d} \ \theta(\vec{k}, t) \right]^2 \rangle \\ &= \int \frac{d^d k}{(2\pi)^d} \left[e^{i\vec{k}\cdot\vec{x}} - 1 \right] \ \int \frac{d^d k'}{(2\pi)^d} \left[e^{i\vec{k}'\cdot\vec{x}} - 1 \right] \ \langle \theta(\vec{k}, t) \theta(\vec{k}', t) \rangle \end{aligned} \tag{3.113}$$

[18] J. M. Kosterlitz and D. J. Thouless, *Ordering, metastability and phase transitions in 2 dimensional systems* J. Phys. C. - Solid State Physics **6**, 1181 (1973).

Uniform initial conditions.

For simplicity, let us take $\theta(\vec{x},0)=0$ for all $\vec{x}$. This implies $\theta(\vec{k},0)=0$. The average above then becomes

$$\langle(\Delta\theta(\vec{x},t))^2\rangle = 2(2k_BT)\int\frac{d^dk}{(2\pi)^d}\left[e^{i\vec{k}\cdot\vec{x}}-1\right]\int_0^t dt'\; e^{-2k^2[t-t'+1/(2\Lambda^2)]} \tag{3.114}$$

After some calculations one finds that the spin-spin correlation function takes the scaling form predicted [72]:

$$C(r,t)\simeq r^{2-d-\eta}\; f(r/R_c(t)) \qquad \text{with} \qquad f(y)=\int_0^{y^2/8}\frac{dz}{z}(1-e^{-z}) \tag{3.115}$$

and $R_c(t)\simeq t^{1/z_{eq}}$, with $z_{eq}=2$.

The global correlation and linear response, $C(t,t')=V^{-1}\int d^2x\;\langle\vec{s}(\vec{x},t)\cdot\vec{s}(\vec{x},t')\rangle$ and $R(t,t')=V^{-1}\int d^2r\;\left.\frac{\delta\langle\vec{s}(\vec{x},t)\rangle}{\delta\vec{h}(\vec{x},t')}\right|_{\vec{h}=0}$ take the following scaling forms in the limit $t-t'\gg\Lambda^{-2}$:

$$C(t,t') \;\sim\; \frac{1}{(t-t')^{\eta(T)/2}}\;\Phi_C\left(\frac{R_c(t)}{R_c(t')}\right) \tag{3.116}$$

$$R(t,t') \;\sim\; \frac{1}{4\pi\rho(T)(t-t')^{1+\eta(T)/2}}\;\Phi_R\left(\frac{R_c(t)}{R_c(t')}\right) \tag{3.117}$$

with Φ_C and Φ_R two scaling functions and $R_c(t)$ the growing correlation length (that should not be confused with the linear response). The first remarkable property of these functions is that they are both decomposed in the product of a function of the time-difference $t-t'$ and a function of the ratio $\lambda\equiv R_c(t')/R_c(t)$, like in the general critical coarsening case. When $t-t'\ll[d\ln R_c(t')/dt']^{-1}$, the argument of the scaling functions gets close to one, $\lambda\sim 1$, and the decay is stationary

$$C(t,t')\sim(t-t')^{-\eta(T)/2}\;, \qquad R(t,t')\sim(t-t')^{-1-\eta(T)/2}$$

and the fdr equals one. This limit defines a quasi-equilibrium regime. When the time difference increases and λ becomes larger than one the relaxation enters an aging regime in which the decay of the correlation and response depends on the waiting-time t'. The behavior in the aging regime depends on the initial conditions as discussed below.

The uniform initial condition contains no free vortices and none are generated by thermal fluctuations at any $T < T_{\rm kt}$. The evolution is well captured by the simple spin-wave approximation and after a simple calculation one finds

$$\Phi_C\left(\frac{R_c(t)}{R_c(t')}\right) = \left[\frac{(1+\lambda)}{4\lambda}\right]^{\eta(T)/4} , \qquad R_c(t) = t^{1/2} . \tag{3.118}$$

Beyond the crossover time $t - t' \sim t'$, when $C(2t', t') \sim t'^{-\eta(T)/2}$ and λ becomes smaller than one, the correlation and response decay to zero as power laws of the waiting-time t'. There is no clear-cut separation of time-scales characterised by the correlation reaching a constant value independently of the waiting-times but only a t' dependent pseudo-plateau where the behavior of the two-time correlation changes. This is to be confronted to the behavior of ferromagnetic coarsening systems quenched to the low-temperature phase for which the crossover occurs at $C(2t', t') = m_{eq}^2$. Above this plateau, the relaxation corresponds to the equilibrium fluctuations of short wave-length while below the plateau the decorrelation is due to the domain-wall motion that manifests into a scaling in terms of $\lambda = t'/t$ only. In the 2d xy case the order parameter vanishes and there is no plateau at any finite value of C.

In the aging regime the fluctuation – dissipation ratio is larger than one. This *a priori* surprising result can be understood when interpreted in terms of the effective – temperature. The completely order configuration is the equilibrium state at zero temperature. The evolution of this initial state at finite temperature can be thought of as representing a sudden inverse quench of the system from $T = 0$ to $T > 0$. If the fdr is related to a remembrance of the temperature of the initial condition, in this case this is lower than the working temperature T and thus, the effective temperature also turns out to be lower than T.

Random initial conditions.

When random initial conditions with only short-ranged spatial correlations are considered, free vortices and antivortices are present initially. The relaxation occurs via the annihilation of vortex-antivortex pairs and this coarsening process is much slower than the relaxation of spin-waves. The simple Gaussian theory is no more suited to describe this dynamics and a full analytic treatment is too hard to implement. With scaling and numeric analysis the dynamic correlation length has been estimated to be [4]

$$\boxed{R_c(t) \sim (t/\ln t)^{1/2} .}$$

The numerical simulations of Berthier, Holdsworth and Sellitto [73] have proven that the two-time correlation and response are correctly described by the scaling form (3.116) and (3.117) with this length scale and the full decay looks like the one shown in the sketch above. The fdr is rather different from the one following the evolution of a uniform initial condition. The non-equilibrium susceptibility is now smaller than the equilibrium value, and in terms of the effective temperature this means that the fluctuations of the wave-lengths longer than $R_c(t)$ occur at a $T_{\rm eff} > T$ and hence keep a memory of the initial temperature $T = \infty$. The effective temperature will be discussed later.

3.14 Annealing: crossover from critical to subcritical coarsening

There has been recent interest in understanding how a finite rate cooling affects the defect density found right after the quench. A scaling form involving equilibrium critical exponents was proposed by Zurek [74] following work by Kibble [75]. The interest is triggered by the similarity with the problem of quantum quenches in atomic gases, for instance. An interplay between critical coarsening (the dynamics that occurs close in the critical region) that is usually ignored (!) and sub-critical coarsening (once the critical region is left) is the mechanism determining the density of defects right after the end of the cooling procedure.

The usual protocol is such that the control parameter is tuned linearly in time with a convention such that at time zero the system crossed the critical point. In this way, at negative times the system is in the disordered phase while at positive times it enters the ordered one. In short,

$$T(t) = T_c \left(1 - \frac{t}{\tau_Q} \right) \ , \tag{3.119}$$

with τ_Q the annealing time.

We assume that, for positive time t, the dynamic growing length that, for infinite rapid quenches, is a function of time and the control parameter, $R(t,T)$, becomes, for very slow quenches a function of time in the form $R(t,T(t))$. Then it is natural to propose a new scaling behaviour for the growing length [76]

$$\begin{aligned} R(t,\epsilon(t)) &\sim \epsilon^{-\nu}(t)\ f[t\epsilon^{z_{eq}\nu}(t)] \qquad\qquad \epsilon(t) = |T(t) - T_c|/T_c \\ &\sim \xi_{eq}(T(t))\ f\left[\frac{t}{\xi_{eq}^{z_{eq}}(T(t))}\right] \end{aligned} \tag{3.120}$$

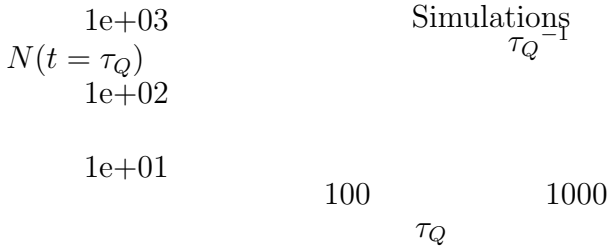


Figure 3.45: The number of interfaces after an annealing (quench at finite rate) as defined in (3.119) through the critical point, measured at time $t = \tau_Q$, *i.e.* at $T = 0$, in a $2d$IM.

with the limiting values

$$f(x) \;\to\; \begin{cases} \text{ct} & x \ll -1 \qquad \text{Equilibrium at high } T \\ x^{1/z_d} & x \gg 1 \qquad \text{Coarsening at low } T \end{cases}$$

t is measured from the instant when the critical point is crossed and $x \in (-1, 1)$ is the critical region.

Dynamic scaling allows one to relate the growing length to the number of defects, $n_d(t, \tau_Q) \simeq R^{-d}(t, \tau_Q)$ and one finds

$$n_d(t, \tau_Q) \simeq \tau_Q^{d\nu(z_{eq}-z_d)/z_d}\; t^{-d[1+\nu(z_{eq}-z_d)]/z_d} \tag{3.121}$$

that is to say a function of both t and τ_Q. In particular, for $t \simeq \tau_Q$ one has

$$N_d(t \simeq \tau_Q, \tau_Q) \simeq n_d(t \simeq \tau_Q, \tau_Q) L^2 \simeq \tau_Q^{-1} \tag{3.122}$$

which is very different from the behaviour found assuming there is no more dynamics after the system falls out of equilibrium in the disordered phase ($N_{KZ} \simeq \tau_Q^{-\nu/(1+\nu z_{eq})} \simeq \tau_Q^{-0.31}$). In particular, $N_d \ll N_{KZ}$.

A careful analysis of this problem can be found in [76] and the extension to the Kosterlitz-Thouless transition [77].

3.15 Summary

In the table below we summarize the results describe above.

In short, critical and sub-critical coarsening occurs in models with conventional second order phase transitions (or for systems with first order phase transitions

	g_c	$g < g_c$
Order param.	0	$\neq 0$
Growing length	$R_c(t) \simeq \begin{array}{ll} t^{1/z_{eq}} & \text{clean} \\ \frac{t^{\frac{1}{2}}}{\ln^{\frac{1}{2}} \frac{t}{t_0}} & 2d \text{ xy} \\ ? & \text{disordered} \end{array}$	$R(t) \simeq \begin{array}{ll} t^{1/2} & \text{sc. NCOP} \\ t^{1/3} & \text{sc. COP} \\ \left(\ln \frac{t}{t_0}\right)^{\frac{1}{\psi}} & \text{dis.} \end{array}$
$V \simeq R^{D_F^V}(t)$	$D_F^V < d$	$D_F^V = d$
$S \simeq R^{D_F^S}(t)$	$D_F^S < d-1$	$D_F^S = d-1$
$C(r,t)$	$r^{2-d-\eta}\ f\left(\frac{r}{R_c(t)}\right)$	$C_{st}(r) + \ C_{ag}\left(\frac{r}{R_c(t)}\right)$
$C(t,t')$	$R_c^{2-d-\eta}(t-t')\ g\left(\frac{R_c(t')}{R_c(t)}\right)$	$C_{st}(t-t') + C_{ag}\left(\frac{R_c(t')}{R_c(t)}\right)$

Table 1: This table summarizes the behavior of growing structures and correlation functions in critical and sub-critical quenches. V and S are the volume and surface of the equilibrium growing structures (FK clusters and geometric domains in critical and sub-critical quenches respectively). D_F^V and D_F^S are their fractal dimension. Interesting information is also contained in the behavior of the linear response function but we will discuss it later.

when one quenches well below the region of metastability). Close to the critical point the dynamics is characterized by **critical slowing down** with the relaxation time diverging as a power law of the distance to criticality. Growth of order is characterized by a growing length that depends on time as a power law at criticality and with a different power below the transition (in the absence of disorder). The dynamic mechanisms are well understood but quantitative results are hard to obtain since the equation to solve are highly non-linear and there is no small parameter to expand around.

In structural glasses the slowing down is not of power law type so such a simple coarsening description seems to be excluded for these systems.

For spin-glasses this modeling has been pushed by Bray, Moore, Fisher and Huse. It is not clear whether it is correct as no clearcut experimental evidence for the coarsening type of scaling has been presented yet.

3.16 Nucleation and growth

In a **first-order** phase transition the equilibrium state of the system changes abruptly. Right at the transition the free-energies of the two states involved are identical and the transition is driven by lowering the free-energy as the new phase forms, see Fig. 3.32. The original phase remains meta-stable close to the transition. The nucleation of a sufficiently large bubble of the truly stable phase into the metastable one needs to be thermally activated to trigger the growth process [3]. The rate of the process can be very low or very fast depending on the height of the free-energy barrier between the two states and the ambient temperature.

Two types of nucleation are usually distinguished: **homogeneous** (occurring at the bulk of the meta-stable phase) and **heterogeneous** (driven by impurities or at the surface). The more intuitive examples of the former, on which we focus here, are the condensation of liquid droplets from vapor and the crystallization of a solid from the melt.

The **classical theory of nucleation** applies to cases in which the identification of the nucleus is easy. It is based on a number of assumptions that we now list. First, one associates a number of particles to the nucleus (although in some interesting cases this is not possible and a different approach is needed). Second, one assumes that there is no memory for the evolution of the number densities of clusters of a given size in time (concretely, a Markov master equation is used). Third, one assumes that clusters grow or shrink by attachment or loss of a single particle, that is to say, coalescence and fission of clusters are neglected. Thus, the length-scale over which the slow part of the dynamics takes place is the one of the critical

droplet size, the first one to nucleate. Fourth, the transition rates satisfy detail balance and are independent of the droplet form. They just depend on the free-energy of the droplet with two terms: a contribution proportional to the droplet volume and the chemical potential difference between the stable and the metastable states, Δf, and a contribution proportional to the bubble surface that is equal to the surface area times the surface tension, σ, that is assumed to be the one of coexisting states in equilibrium - that is to say the energy of a flat domain wall induced by twisted boundary conditions. Fifth, the bubble is taken to be spherical-like and thus dependent of a single parameter, the radius. Thus

$$\Delta F[R] = \sigma\ \Omega_{d-1}\ R^{d-1} - |\Delta f|\ \Omega_d\ R^d \tag{3.123}$$

for $d > 1$. Ω_d is the volume of the unit sphere in d dimensions. For small radii the surface term dominates and it is preferable to make the droplet disappear. In contrast, for large radii the bulk term dominates and the growth of the bubble is favored by a decreasing free-energy. Thus the free-energy difference has a maximum at

$$\boxed{R^* = \frac{(d-1)\ \Omega_{d-1}\ \sigma}{d\ \Omega_d\ |\Delta f|} \propto \sigma |\Delta f|^{-1}} \tag{3.124}$$

and the system has to thermally surmount the barrier $\Delta F^* \equiv \Delta F[R^*]$. The Kramers escape theory, see Sect. 2.4, implies that the nucleation rate or the average number of nucleations per unit of volume and time is suppressed by the Arrhenius factor

$$\boxed{r_A = t_A^{-1} \sim e^{-\beta \Delta F^*} \qquad \text{with} \qquad \Delta F^* = \frac{(d-1)^{d-1}}{d^d}\ \frac{\Omega_{d-1}^d}{\Omega_d^{d-1}}\ \frac{\sigma^d}{|\Delta f|^{d-1}}} \tag{3.125}$$

As expected, ΔF^* increases with increasing σ and/or $|\Delta f|^{-1}$ and r^{-1} vanishes for $T \to 0$ when thermal agitation is switched off. The implicit assumption is that the time to create randomly the critical droplet is much longer than the time involved in the subsequent growth. The relaxation of the entire system is thus expected to be given by the inverse probability of escape from the metastable well. The determination of the pre-factor [that is ignored in eq. (3.125)] is a hard task.

3.17 Elastic manifold dynamics

An **interface** is a frontier separating two regions of space with two phases. It could be the border between water and oil in a liquid mixture, the border between

regions with positive and negative magnetization in a magnet, the limit of a fluid invading porous media, *etc.* The static and dynamic properties of interfaces have many points in common with the ones of (sometimes directed) manifolds with d internal dimensions embedded in $N+d$ dimensional spaces with N the dimension of the transverse space. In this way, one includes cases such as directed lines ($d = 1$) that mimic vortex lines in $N+d = 3$ dimensional high-T_c superconductors, polymers in ($N + d = 2$ or 3-dimensional) random media, *etc.* [16]

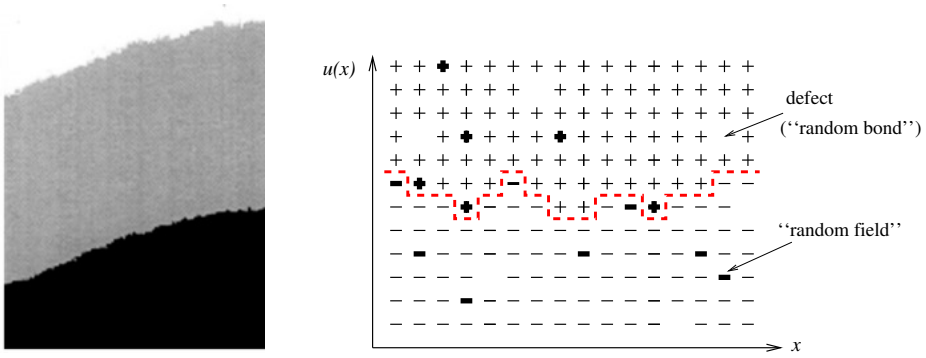


Figure 3.46: Left: an experimental view of a domain wall. Right: a sketch of a domain wall in a $2d$ Ising magnet.

A slightly different situation is the one of **growth** phenomena, as for instance, the burning front in a forrest, the advance of a crack in a rock, fluid invasion in porous media, the growth of a surface on a substrate due to material deposition combined (or not) with transverse diffusion of the material that reaches the surface, or even the growth of bacterial colony. The surface is usually defined by a height field $h(\vec{x}, t)$ defined with respect to an origin level 'zero' on the d-dimensional substrate. We will assume that h is a single-valued function of $\vec{x}$. $N = 1$ in the parametrization described above.

As a physicist one would like to characterize the static and dynamic properties of these interfaces and surfaces. The analysis os the static properties of domain walls and interfaces corresponds, typically, to determining their equilibrium conformations (geometric properties, numbers, degeneracies, *etc.*) The study of the dynamic properties of domain walls and interfaces includes the analysis of their relaxation to equilibrium, response to external driving forces, creep motion and depinning transition.

Domain growth and interface growth in the presence of quenched disorder is sometimes considered to be a 'baby' spin-glass problem due to the presence of frustration given by the competition between the elastic energy that tends to reduce the deformations and quenched disorder that tends to distort the structure.

3.17.1 Scale invariance

In general, the morphology of an interface depends on the length scale of observation: the Alps look rough on Earth but they look smooth seen from the Moon. However, a number of surfaces called *self-similar* do not depend on the scale of observation; they are characterized by the absence of a characteristic scale. Such scale-invariance is ubiquitous in nature, with the classical example of critical phenomena, and it is characterized by the existence of power laws that characterize many quantities over many orders of magnitude.

Figure 3.47: Schematic evolution of a pinned object on well separated time scales. On scale $t(\ell_1)$, the object reconforms by flipping a small portion of size ℓ_1 from one favourable configuration to another (a $\rightarrow$ b). On a much longer time scale $t(\ell_2) \gg t(\ell_1)$, the conformation on scale ℓ_2 (dotted lines) has evolved (b $\rightarrow$ c). The dynamics of the short wavelengths happens on a time scale such that long wavelengths are effectively frozen.

3.17.2 Solid-on-solid models of surface growth

These models are discrete and microscopic; they represent a truly experimental situation, such as atom deposition as in film growth by molecular beam epitaxy, and they are also advantageous to do numerical simulations.

A substrate d dimensional surface of size L^d is divided into cells that can be occupied by columns of falling particles. Particles fall on this substrate and stick to it according to different rules that define different models. The height of the surface is a discrete variable h_i where i labels the cell on the substrate. In *restricted* SOS models the height is also constrained to satisfy $|h_i - h_j| \leq 1$ with i and j nearest-neighboring cells on the substrate.

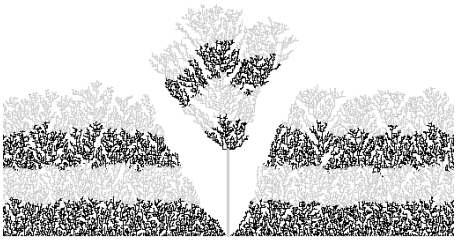


Figure 3.48: Balistic deposition

Figure 3.49: Snow fall

In *ballistic deposition* particles are released from a randomly chosen position above the surface, they follow a vertical trajectory, and they simply stick to the nearest or next-nearest neighbor encountered, see Figs. 3.48 and 3.49.

In *random deposition* the particle falls vertically until reaching the top of its column.

In *random deposition with surface relaxation*, after reaching the top of its column the particle further diffuses along the surface until it finds the position with the lowest height.

3.17.3 Continuous models

Continuous models often describe the surfaces at larger length-scales. A coarsening process is employed in such a way that the surface can be described by a continuous function.

The Edwards-Wilkinson model

The simplest model for the growth and rearrangement of a surface is due to Edwards and Wilkinson who showed that the continuum limit of the process of sedimentation of granular particles under gravity on an initial flat substrate and their further diffusion on the surface leads to [78]

$$\frac{\partial h(\vec{x},t)}{\partial t} = \nu \nabla^2 h(\vec{x},t) + \xi(\vec{x},t) \ , \tag{3.1}$$

where $\vec{x}$ is a d-dimensional spatial vector denoting position on the substrate, t is time and h is a scalar function taking real values and measuring the height with respect to its average value. The last term is a thermal noise, typically chosen to have a Gaussian probability distribution a zero average and correlations

$$\langle\, \xi(\vec{x},t)\xi(\vec{x}',t')\,\rangle = 2T\delta(\vec{x}-\vec{x}')\delta(t-t')\ . \tag{3.2}$$

Equation (3.3) is a stochastic field equation. The first term on the rhs of eqn (3.3) penalizes rapid variations of the surface in space and ν is then a measure of the surface tension. The noise term describes the randomness in the deposition process. Note that the Edwards-Wilkinson equation can in fact be seen as describing the equilibrium fluctuations of an interface (for example liquid vapor), with the noise term describing the thermal fluctuations. The stochastic equation (3.3) is linear and can be easily solved using a Fourier transform of the space coordinate $\vec{x}$.

The Kardar-Parisi-Zhang model

More generally, one can expect that the deterministic 'force' acting on the surface may depend on other kinds of local terms, such as H itself, $\vec{\nabla}h$, and higher power of this and $\nabla^2 h$. Fortunately, the use of symmetries and conservation laws allows one to reduce the number of allowed terms to just a few ones.

For example, one expects the dynamics to be translational invariant, meaning that a symmetry breaking term such as ch, with c a constant, or any other term depending directly on h, is not allowed. The next term one can consider is one proportional to the local slope. Now, by symmetry, one expects that positive and negative slopes should lead to the same result. Thus, this term should appear squared: $[\nabla h(\vec{x},t)]^2$. Indeed, the effect of this term has a simple geometric interpretation sketched in Fig. 3.50. One can then assume that higher order derivatives $\nabla^n h$ are less relevant that the first two ones, $n = 1, 2$, and neglect them all (one can actually prove that they do not change the scaling properties at long times and large length scales). This leads to the well-studied *Kardar-Parisi-Zhang equation* [79]

$$\frac{\partial h(\vec{x},t)}{\partial t} = \nu\nabla^2 h(\vec{x},t) + \lambda[\vec{\nabla}h]^2 + \xi(\vec{x},t)\ , \tag{3.3}$$

that seems to describe most of the random growth problems encountered in nature. The new term is proportional to the slope of the surface and pushes it to grow in the directions of large slope (see Fig. 3.50).

3.17.4 Dynamic scaling at work

Figure 3.50: Sketch of the KPZ growth

For concreteness let us use the continuous notation. The following definitions carry through to the discrete case with minor modifications.

A simple quantity that describes whether the surface is actually growing is the averaged height

$$\langle\, h(\vec{x},t)\,\rangle = \frac{1}{L^d}\int_0^L d^d x\, h(\vec{x},t)\ . \tag{3.4}$$

Here and in what follows the angular brackets represent a spatial average over the substrate coordinates or else an average over thermal noise or random initial conditions.

The kinetics of the surface is characterized by its width, defined as the mean-squared displacement of the total height

$$W(L,t) \equiv \langle\, (h(\vec{x},t) - \langle\, h(\vec{x},t)\,\rangle)^2\,\rangle^{1/2}\ . \tag{3.5}$$

The surface is said to be *rough* when $W(L,t)$ diverges with the system size L. In rough surfaces the height is uncorrelated over long distances while in smooth ones the height is correlated.

In the rough case, asymptotically $W(L,t)$ has the **Family-Vicsek** scaling limit given by [80]

$$W(L,t) = L^{\alpha}\mathcal{F}(tL^z)\ , \tag{3.6}$$

where the roughness exponent α, the dynamical exponent z and the scaling function $\mathcal{F}$ are defined by the above equation in the large L limit. The scaling function $\mathcal{F}$ is such that

$$W(L,t) \sim \begin{cases} t^{1/2}\ , & \text{for short times} \\ t^{\alpha/z}\ , & \text{for intermediate times} \\ L^{\alpha}\ , & \text{for very long times} \end{cases} \tag{3.7}$$

The dynamic exponent describes the evolution of correlated regions with time; initially, different 'sites' on the substrate are not correlated but correlation develop over time with correlated regions growing as $R(t) \sim t^{1/z}$. In each correlated region the width of the surface grows as the observation scale raised to the roughness exponent α. $R(t)$ is *time-dependent correlation length*. In the literature one finds the name β associated to α/z.

The above definition leads to what can be called a "global" characterization of the roughness of the interface, averaged over the whole surface. Another, more local, characterization of the roughness of the surface, is defined as

$$W^2(\vec{x},\vec{x}',t,t') \equiv \langle\, (h(\vec{x},t) - h(\vec{x}',t')\,)^2 \rangle = |\vec{x}-\vec{x}'|^\alpha\, \mathcal{F}\,(|t-t'||\vec{x}-\vec{x}'|^z)\ , \qquad (3.8)$$

where we are now looking at the limit $\Lambda^{-1} \ll |\vec{x}-\vec{x}'| \ll L$. Often, the exponents and the scaling function defined globally over the whole surface [as in eq. (3.6)] coincide with their local counterpart, but this is not always the case. Note that in (3.8) one measures at two different times t and t'.

Scale invariance

The Family-Vicsek scaling is a manifestation of the scale invariance of the growth process. Indeed, if one assumes that in the very long time limit $t \to \infty$ under the rescaling of space

$$\vec{x} \to b\vec{x}\ , \qquad (3.9)$$

the field changes in such a way that

$$h(\vec{x}, t\to\infty) \sim b^{-\alpha} h(b\vec{x}, t\to\infty) \qquad (3.10)$$

one has

$$\begin{aligned} W^2(L,t\to\infty) &\equiv L^{-d}\int d^dx h^2(\vec{x},t\to\infty) \sim L^{-d}\int d^dx b^{-2\alpha} h^2(b\vec{x},t\to\infty) \\ &= b^{-2\alpha} W^2(bL,t\to\infty)\ . \end{aligned} \qquad (3.11)$$

Now, taking $b = L^{-1}$ in such a way that the last factor is just a numerical constant, one has

$$W^2(L,t\to\infty) \sim L^{2\alpha} \qquad (3.12)$$

and the roughness exponent is related to the scale invariant properties of the stationary surface, see eq. (3.10). Note that one transforms differently the longitudinal ($\vec{x}$) and transverse (h) directions.

Moreover, the Family-Vicsek scaling means that the statistical properties of the roughness are invariant under the changes

$$\vec{x} \to b\vec{x}\ , \qquad t \to b^z t\ , \qquad h \to b^\alpha h\ . \qquad (3.13)$$

b is a dilation parameter.

Universality classes

It has been proposed to use the exponents α and β to classify growing surfaces in universality classes. Although the microscopic processes leading to the interface morphology can be very different, one finds that indeed they group in classes, determined by the symmetry properties of the continuous stochastic equations defining different growth processes.. This is so since the asymptotic (long times, large scales) morphologies depend only on mesoscopic aspects such as the diffusion process, the random character of the process, the presence of non-linear terms, *etc.* Let us give a few examples below.

A simple random deposition process is characterised by $\partial h = \eta$, which is the random walk Langevin equation (h is here just a function of time). The roughness W is here the mean square displacement of the walk and, consequently, $\beta = 1/2$ and α and z are not defined independently.

An Edwards-Wilkinson surface has

$$\alpha = (2-d)/2 \ , \qquad \beta = (2-d)/4 \ , \qquad z = \alpha/\beta = 2 \ , \qquad d - \text{dim EW} \tag{3.14}$$

($z = 2$ shows the the diffusive character of the process in all dimensions) The EW equation is invariant under

$$\begin{array}{ll} \vec{x} \to \vec{x} + \vec{\Delta} x \ , & t \to t + \Delta t \ , \\ h \to h + \Delta h \ , & \vec{x} \to -\vec{x} \ , \\ h \to -h \ , & \end{array} \tag{3.15}$$

Note the similarity between this problem and the one of the fluctuations of the global magnetization in the critical $2d$ XY model that we discussed in Sect. . Indeed, the two problems are intimately connected since the dynamics of the $2d$ XY model in the spin-wave approximation is given by eq. (3.3).

The d-dimensional KPZ surface has

$$\begin{array}{llll} \alpha = 1/2 \ , & \beta = 1/3 \ , & z = 3/2 \ , & d = 1 \ , \\ \alpha = 0.38 \ , & \beta = 0.24 \ , & z = 1.58 \ , & d = 2 \ , \end{array} \tag{3.16}$$

note that $z = \alpha/\beta$. The KPZ exponents in generic d are known numerically. Note that the KPZ suface does not evolve through normal diffusion $z < 2$). Moreover, the height reversal invariance, $h \to -h$, is not preserved by the KPZ equation, reflecting the fact that growing surfaces in which atoms fall from above should not have this symmetry.

At nonzero temperature an equilibrium domain wall in a pure system – as imposed, for example, by twisting boundary conditions – is rough for $d \leq 3$ because

Figure 3.51: Family-Vicsek scaling.

of thermal fluctuations. In the presence of weak-disorder, RG arguments suggest that disorder becomes relevant in $d > 5/3$. In a random ferromagnet in $d = 2$ one has $\alpha = 4/3$ (through a connection with the continuum model and then the KPZ-equation, see below), while in $d > 2$ $\alpha = 0.416(4 - d)$.

Recently, there has been growing interest in characterizing the complete dynamic probability distribution $P_L(W^2, t)$ since it has been suggested that it might be used to define universality classes for non-equilibrium steady states *via* the scaling function:

$$\langle W^2 \rangle_{L\to\infty} P_L(W^2, t) = \Phi\left(\frac{W^2}{\langle W^2 \rangle_{L\to\infty}}\right) .$$

3.17.5 Non-equilibrium relaxation

The analysis of the out of equilibrium relaxation of a one-dimensional EW elastic line with finite length L that from an initial condition in equilibrium at a temperature T_0 is, at time called $t = 0$, instantaneously quenched to another temperature T, can be performed exactly [81]. The out of equilibrium dynamics in this, and other finite dimensional elastic lines, appear as a dynamic crossover. There is an equilibration time $t_r(L)$ such that for longer times the line attains equilibrium. For waiting times that are shorter than $t_r(L)$ one has to distinguish time delays that are closer than $t_r(L)$ and show aging from those that go beyond this characteristic time and show saturation.

3.17.6 Roughening transition

It is a transition between a smooth and a rough phase. It is usually accompanied by a diverging correlation length in the d-dimensional substrate space. In the smooth phase the surface is typically rough over this (finite) length-scale while it is smooth at longer length-scales.

Transitions between phases with different roughness properties are also possible, especially when adding quenched disordered potential. One observes a high-temperature phase where disorder is irrelevant and the roughness properties are those of the clean limit – *e.g.* the EW thermal exponent appears – and a low-

temperature phase where the surface is rougher and its roughness is characterized by a disorder-controlled exponent that takes a large value than the thermal one.

3.18 Driven systems

In the Introduction we mentioned a number of systems of interest that are driven out of equilibrium by external forces. There is a large variety of phenomenological nonequilibrium phase transitions in nature, ranging from morphological transitions of growing surfaces to traffic jams. The universality classes of nonequilibrium critical phenomena are expected to be very diverse as they are governed by various symmetry properties of the evolution dynamics. On the other hand, the experimental evidence for universality of nonequilibrium phase transitions is still very poor, calling for intensified experimental efforts.

Let us mention here one some examples and how it is modelled along the lines described in this chapter.

Lattice gases [82, 83, 84, 85] are models of indistinguishable classical particles moving on a d dimensional hypercubic lattice. Hard-core constraints inhibit the double occupancy of sites. The dynamics consists in particle exchange over nearest-neighbor sites (Kawasaki rule). The total number of particles is therefore conserved. Stochastic dynamics satisfying detailed balance at temperature T ensure the approach to equilibrium characterized by an anergy function that is the one of the Ising model after the usual spin - occupancy change of variables.

A uniform force in space and time force can be added to drive the system if periodic boundary conditions are used. Particle current wrapping around the system is thus enforced by choosing this force, say $\vec{E} = E\hat{x}$, to point along one of the axes of the lattice. A non-equilibrium steady state establishes. A continuous phase transition $T_c(E)$ has been found numerically, with $T_c(E)$ an increasing function of E that saturates at a finite value for $E \to \infty$. The nature of the phase transition has been, though, a much debated issue. The difficulty in characterising it resides in the much peculiar behaviour of the space and time-delayed correlation functions, and its anisotropic effects, on the numerical side. On the theoretical side, the problem is that it has not been possible to derive the field theory in the vanishing lattice size limit. Instead, it has been postulated in the form of a Langevin dynamics for the order parameter that respects all the symmetries of the microscopic lattice model, and several proposal exist in the market. Moreover, for such essentially non-equilibrium critical phenomena the meaning of universality is still not clear and how small changes in the theory may affect the ultimate behaviour remains to be better

understood.

Particle hopping models and reaction-diffusion models under different external forces are also very interesting in this respect. The dynamic properties of a reaction-diffusion model on a lattice are fully specified by its master equation but these are only rarely solvable. Progress in one dimensional cases has been achieved from the formal mapping to quantum spin models, allowing exact methods of many-body quantum mechanics such as the Bethe ansatz and free-fermion techniques to be applied in nonequilibrium physics.

In the context of coarsening problems, such forces can be shearing ones, that can, for instance, impose a given length in one direction and let the system coarsen in the orthogonal one. Note that a shear is a force that does not derive from a potential.

Another external effect of interest is the one induced by a gravitational force that may act differently on different species in the problem provoking phase separation in the vertical direction.

Intriguing coarsening effects, in the form of phase separation, also exist in other areas of science. Ecology is one of them. Phase separation exists in models à la Lotka-Volterra of different species in interaction in a given space. Interactions can be of predator-prey type and the effect of the environment is taken into account via some reaction rates. Sociology is another one where, for instance, models with discrete variables taking three values $(\pm, 0)$, the so-called Blume-Capel model, is used to mimic neighbour segregation in towns.

3.19 Phase separation

The phase diagram is shown in Fig. 3.52 and snapshots obtained after different running times from a random initial conditions in Fig. 3.53. One should distinguish between shallow quenches (just below the coexistence curve) and deep quenches (far below the coexistence curve). For shallow quenches, in the region between the coexistence and the spinodal lines the homogeneous system is metastable and decomposes by the nucleation and growth of droplets. For deep quenches, into the region below the spinodal lines, the homogeneous system spontaneously decomposes into A-rich and B-rich regions, a process referred to as spinodal decomposition. However, there is no sharp physical distinction between the nucleation and growth and spinodal decomposition regions of the phase diagram.

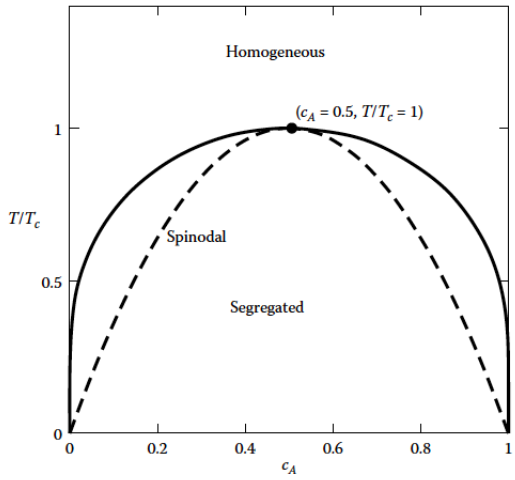


Figure 3.52: Phase diagram of a binary (AB) mixture. The system parameters are the concentration of the A species ($c_A = 1 - c_B$) and the temperature (T). The point ($c_A = 0.5, T/T_c = 1$) corresponds to a second-order critical point. Above the coexistence curve (solid line), the system is in a homogeneous or disordered state. Below the coexistence curve, the system is in a segregated or phase-separated state, characterized by A-rich and B-rich regions. The dashed lines denote spinodal curves. The homogeneous system is metastable between the coexistence and spinodal curves and unstable below the spinodal lines. From [5].

The Porod law and short-distance behaviour of correlation functions are the same as in the case of non-conserved order parameter but the growth law, as already stated, becomes $t^{1/3}$. The conservation law constraints $\int d^d r\, C(r,t) = 0$ or $S(0,t) = 0$ and the small wave vector behaviour of the structure factor as $\simeq p^4$.

The closure techniques à la OJK, KYG, etc. have not given good results under the conservation of the order parameter condition though, surprisingly, they work better for vector order parameter than for the scalar case.

3.20 Concluding remarks

From a mathematical point of view coarsening dynamics are gradient flow dynamics described (at zero temperature) with partial differential equations acting on a field. Properties of the solutions to these equations have been analysed with

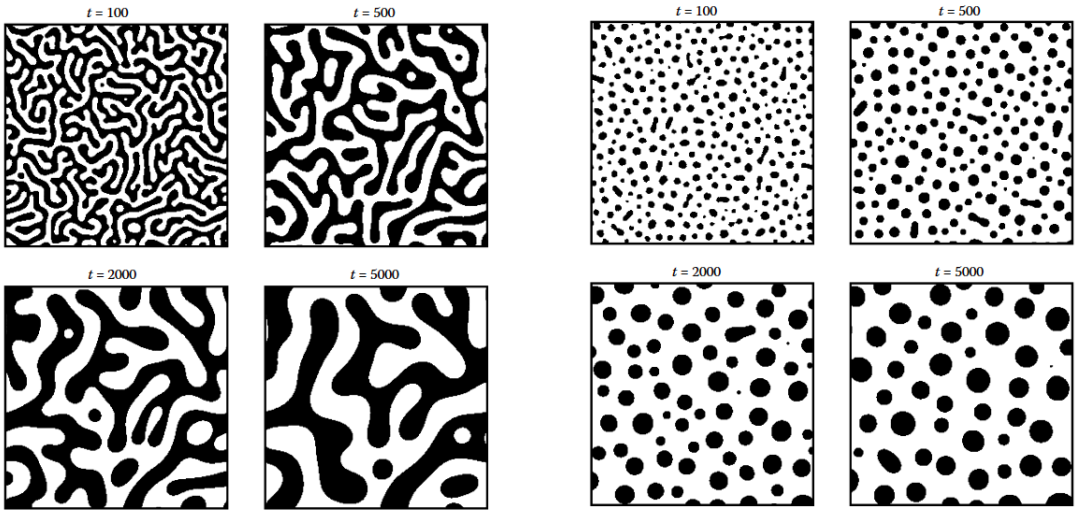


Figure 3.53: Left: Evolution of a homogeneous binary (AB) mixture, which is quenched below the coexistence curve at time $t = 0$. Numerical solution to the field equation with discretization mesh sizes were $\Delta t = 0.01$ and $\Delta x = 1$, and lattice size $N = 2562$. The random initial condition consisted of small-amplitude fluctuations about $\phi = 0$, corresponding with a mixture with equal amounts of A and B (critical composition). Regions with $\phi > 0$ (A-rich) and $\phi < 0$ (B-rich) are marked in black and white, respectively. Right: Off-critical binary mixture. The initial condition consisted of small-amplitude fluctuations about $\phi = 0.4$, corresponding to a mixture with 30% A and 70% B.

formal mathematical methods.

4 Dynamic generating functional and symmetries

Until here we used the Langevin equation and, in white noise cases, the corresponding Fokker-Planck equation to analyze stochastic processes. Yet, within the study of Markov but also non-Markov stochastic processes there exists also the possibility of approaching the problem via the path integral formulation of generating functionals [86]. The use of generating functionals is an elegant and powerful method to derive generic properties of dynamical systems. A path-integral is handy for computing moments, probability distribution functions, transition probabilities and responses. It is also particularly well suited when it comes to perturbation theory and renormalization group analysis, as one can easily set up a diagrammatic expansion.

In this Section we introduce the classical path integral formalism for stochastic processes governed by the Langevin equation [87, 88, 89, 90]. We limit ourselves to one degree of freedom, the generalization to several degrees of freedom or fields being immediate. We discuss some of the subtleties appearing in processes with multiplicative white noise [90, 91, 92, 93]. The symmetry arguments follow closely the discussion in [94].

4.1 The generating functional

In Sect. 2.4 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.

The thermal and/or initial condition averages of observables which are functions of the solution to the Langevin equation can also be computed by using a dynamic generating functional. As usual when one constructs a functional integral for a generating functional (as in quantum mechanics) time should be discretized: $t_k = t_0 + k(\mathcal{T}-t_0)/\mathcal{N}$ with $k = 0, \ldots, \mathcal{N}$ and $\mathcal{N} \to \infty$ while $(\mathcal{T}-t_0)$ is kept finite. The time-step is then $\epsilon = (\mathcal{T}-t_0)/\mathcal{N}$ and t_k varies between t_0 and $\mathcal{T}$.

The generating functional reads [87]

$$Z_{\rm d}[\eta] \equiv {\rm N}^{-1} \int \mathcal{D}\xi \; dP(t_0) \; e^{-\frac{1}{2k_BT}\sum_{k=0}^{\mathcal{N}}\sum_{l=0}^{\mathcal{N}}\xi(t_k)\Gamma^{-1}(t_k-t_l)\xi(t_l)+\sum_{k=0}^{\mathcal{N}}\eta(t_k)x_\xi(t_k)} \; .$$

The Gaussian factor is proportional to $P[\xi]$ the functional probability measure of the noise

$$P[\xi] = \mathrm{N}^{-1} \int \mathcal{D}\xi \; e^{-\frac{1}{2k_B T} \sum_{k=0}^{\mathcal{N}} \sum_{l=0}^{\mathcal{N}} \xi(t_k) \Gamma^{-1}(t_k - t_l) \xi(t_l)} \tag{4.1}$$

with N^{-1} a factor that depends upon the kernel Γ and $k_B T$ and ensures normalization $\int \mathcal{D}\xi \; P[\xi] = 1$. The measure is $\mathcal{D}\xi \equiv \prod_{k=0}^{\mathcal{N}} d\xi(t_k)$. The inverse kernel Γ^{-1} is defined within the interval $[t_0, \mathcal{T}]$: $\sum_{l=0}^{\mathcal{N}} \Gamma(t_k - t_l)\Gamma^{-1}(t_l - t_m) = \delta_{t_k,t_m} = \delta_{km}$. $x_\xi(t_k)$ 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, $dP(t_0) \equiv dx_0 d\dot{x}_0 \, P_{\mathrm{i}}[x_0, \dot{x}_0]$. The integral symbol involves an integral over the initial values as well.

The Langevin equation is a stochastic differential equation and one can give a rigorous meaning to it by specifying a particular discretization scheme for the time derivatives

$$\dot{x}(t) \;\; \to \;\; [x(t_{k+1}) - x(t_k)]/\epsilon \; , \tag{4.2}$$

$$\ddot{x}(t) \;\; \to \;\; [x(t_{k+2}) - 2x(t_{k+1}) + x(t_k)]/\epsilon^2 \; , \tag{4.3}$$

and the evaluation of the products of functions of the stochastic variable x and the noise, ξ:

$$g(x)\xi \to g(\overline{x}_k)\xi(t_k) \qquad \text{with} \qquad \overline{x}_k \equiv \alpha x(t_{k+1}) + (1-\alpha)x(t_k) \; . \tag{4.4}$$

α is a real parameter, $\alpha \in [0, 1]$. $\alpha = 0$ is called the Itô prescription and $\alpha = 1/2$ the Stratonovich one. As explained in Sec. the Stratonovich calculus is the one with the usual rules (for instance, the chain rule is $d_t V = \partial_x V \dot{x}$) while all other calculii have unusual rules (the chain rule has to be modified). For this reason, analytic calculations are more conveniently done with the Stratonovich prescription (while Itô is preferred for numerical simulations).

4.1.1 Additive generic noise

We focus here on the additive noise case, as the construction of a generating functional for Langevin processes with multiplicative noise is slightly more involved [91] and we will discuss it separately.

With an abuse of notation in which the continuum time limit is implicitly taken without further details that will be given below, one has

$$Z_{\mathrm{d}}[\eta] \equiv \int \mathcal{D}\xi \; P[\xi] \; dP(t_0) \; e^{\int_{t_0}^{\mathcal{T}} dt' \, \eta(t') x_\xi(t')}$$

and the inverse is $\int_{t_0}^{\mathcal{T}} dt''\ \Gamma(t-t'')\Gamma^{-1}(t''-t') = \delta(t-t')$. In the following we adopt the continuous time notation and we come back to the discrete one when necessary.

A very useful expression for $Z_{\rm d}[\eta]$, usually called the Martin-Siggia-Rose generating functional (actually derived by Janssen [88]), is obtained by introducing the identity

$$\mathrm{Eq}[x(t)] \equiv m\ddot{x}(t) + \int_{t_0}^{\mathcal{T}} dt'\ \gamma(t-t')\dot{x}(t') + V'[x(t)] - \xi(t) = 0 \tag{4.5}$$

valid at each time t, with the functional delta function (to be interpreted as the product of ordinary delta functions on each discrete time)

$$1 = \int \mathcal{D}x\ \ \delta\left(\mathrm{Eq}[x(t)]\right)\ \left|\det \frac{\delta \mathrm{Eq}[x(t)]}{\delta x(t')}\right|\ , \tag{4.6}$$

with $\mathcal{D}x \equiv \prod_{k=1}^{\mathcal{N}} dx(t_k)$. The factor $|\det \dots|$ is the determinant of the operator $\{m\partial_t^2 + V''[x(t)]\}\delta(t-t') + \gamma(t-t')\partial_{t'}$ and ensures that the integral equals one.[19] As we will be interested in the forward (causal) solution to the Langevin equation for each noise realization, one can forget the modulus in this expression as it only involves a sign that will go into the normalization. The delta function can be exponentiated with an auxiliary time-dependent variable $\hat{x}(t)$ (using the Fourier representation of the δ-function[20]). $\mathcal{D}\hat{x} = \prod_{k=1}^{\mathcal{N}} d\hat{x}(t_k)$.

The determinant can be exponentiated with time-dependent anticommunting variables – opening the way to the use of super-symmetry [96, 92], a subject that we will not touch in these notes. The expression of the Jacobian using these variables is given in App. .

A formal manipulation of the Jacobian goes as follows. We distinguish the under-damped dynamics ($m \neq 0$) from the over-damped limit (no inertia), and the white from the colored thermal noises.

Over-damped dynamics with white noise

In this case

$$\frac{\delta \mathrm{Eq}[x(t)]}{\delta x(t')} = \gamma_0 \frac{d}{dt}\delta(t-t') + \frac{\delta V'[x(t)]}{\delta x(t')} = \left(\gamma_0 \frac{d}{dt} + V''[x(t)]\right)\delta(t-t')\ . \tag{4.7}$$

[19] 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: $\int dx\ \delta[g(x)]\ |g'(x)| = 1$.

[20] $\delta(x) = (2\pi)^{-1}\int_{-\infty}^{\infty} dk\ e^{ikx}$.

The idea is to factorize this operator as product of two in such as way that

$$\mathcal{O}(t,t') = \int dt''\ \mathcal{O}_1(t,t'')\mathcal{O}_2(t'',t') \tag{4.8}$$

$$\det \mathcal{O}(t,t') = \det \mathcal{O}_1(t,t'') \det \mathcal{O}_2(t'',t') \tag{4.9}$$

For the operator in (4.7) the factorization is

$$\frac{\delta \mathrm{Eq}[x(t)]}{\delta x(t')} = \int dt''\ \gamma_0 \delta(t-t'') \frac{d}{dt''} \left[\delta(t''-t') + \gamma_0^{-1}\theta(t''-t')V''[x(t')]\right] \tag{4.10}$$

therefore

$$\mathcal{J} = \det \frac{\delta \mathrm{Eq}[x(t)]}{\delta x(t')} = \det \left[\gamma_0 \delta(t-t') \frac{d}{dt'}\right]\ \det \left[\delta(t-t') + \gamma_0^{-1}\theta(t-t')V''[x(t)]\right]\ .$$

The second factor is of the form $\det(1+B) = \exp \mathrm{Tr} \ln(1+B) = \exp \mathrm{Tr} \sum_{n=1}^{\infty} B^n = \exp \mathrm{Tr} B$ as $\mathrm{Tr} B^n = 0$ for all $n \geq 2$ (since $\int dt'\ \theta(t-t')\theta(t'-t) = 0$). Then

$$\mathcal{J} = \det \left[\gamma_0 \delta(t-t') \frac{d}{dt'}\right]\ \exp\{\gamma_0^{-1}\theta(0) \int_{t_0}^{\mathcal{T}} dt'\ V''[x(t')]\}\ . \tag{4.11}$$

The first factor is just an (infinite) irrelevant constant. There is some ambiguity in the second factor, linked to the value of the theta-function at zero, say $\theta(0) = \alpha$. One can show that this is related to the discrete meaning given to the product of functions of the stochastic variable x and the noise, Eq. (4.4). It can also be related to the choice of operator-ordering in an equivalent 'quantum-mechanical' formalism that one can use to express the equivalent Fokker-Planck equation [90].

Under-damped dynamics with white noise

A similar expansion of the Jacobian leads to

$$\mathcal{J} = \det \left[(m\partial_t^2 + \gamma_0 \partial_t)\delta(t-t')\right]\ \det \left[\delta(t-t') + G(t-t') \frac{\delta V'[x(t)]}{\delta x(t')}\right] \tag{4.12}$$

with $G(t-t')$ the retarded Green function of the operator $(m\partial_t^2 + \gamma_0 \partial_t)\delta(t-t')$ that is given by

$$G(t-t') = \gamma_0^{-1}[1 - e^{-\gamma_0 (t-t')/m}]\theta(t-t')\ . \tag{4.13}$$

The same expansion of the second factor as above yields now no contribution, as $G(0) = 0$ (because of $m \neq 0$). Therefore,

$$\mathcal{J} = \det[(m\partial_t^2 + \gamma_0 \partial_t)\delta(t-t')] \tag{4.14}$$

and is independent of x.

Coloured noise

In this case one cannot give a simple expression for the Jacobian as done in the white noise limit. See the Appendices for a representation using Grassman variables.

Accordingly, $Z_{\rm d}$ reads

$$\begin{aligned} Z_{\rm d}[\eta,\hat\eta] \equiv \int \mathcal{D}\xi\mathcal{D}x\mathcal{D}\hat x\; dP(t_0)\; P[\xi]\; e^{\ln \mathcal{J}} \\ \times\; e^{-\int_{t_0}^{\mathcal{T}} dt'\, i\hat x(t')\left[m\ddot x(t')+\int_{t_0}^{\mathcal{T}} dt''\;\gamma(t'-t'')\dot x(t'')+V'[x(t')]-\xi(t')\right]} \\ \times\; e^{\int_{t_0}^{\mathcal{T}} dt'\,[\eta(t')x(t')+\hat\eta(t')i\hat x(t')]} \end{aligned}$$

where we have introduced a new source $\hat\eta(t)$, coupled to the auxiliary field $i\hat x(t)$. Note that the sign in the exponential in the second line is irrelevant since one can change $i\hat x \mapsto -i\hat x$ at no cost. The integration over the noise $\xi(t)$ is Gaussian and it can be readily done; it yields

$$\exp\left\{\frac{k_BT}{2}\int_{t_0}^{\mathcal{T}} dt' \int_{t_0}^{\mathcal{T}} dt''\; i\hat x(t')\,\Gamma(t'-t'')\,i\hat x(t'')\right\} \tag{4.15}$$

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

$$\begin{aligned} \mathcal{Z}_{\rm d}[\eta,\hat\eta] &\equiv \int \mathcal{D}x\mathcal{D}\hat x\; dP(t_0)\; e^{S[x,i\hat x,\eta,\hat\eta]} \\ S[x,i\hat x,\eta,\hat\eta] &= -\int dt'\, i\hat x(t')\left\{m\ddot x(t') + \int dt''\;\gamma(t'-t'')\dot x(t'') + V'[x(t')]\right\} \\ &+\frac{k_BT}{2}\int dt'\int dt''\, i\hat x(t')\Gamma(t'-t'')i\hat x(t'') + \ln\mathcal{J} + \text{sources}\;. \end{aligned} \tag{4.16}$$

All integrals run over $[t_0,\mathcal{T}]$. Causality in the integral over t'' in the second line is ensured by the fact that γ is proportional to θ.

The MSRJD action has two kinds of contributions: the ones that depend on the characteristics of the bath (through Γ) and the ones that do not. The latter also exist in a functional representation of Newton dynamics and we call them $S_{\rm det}+S_{\rm jac}$ (for

deterministic and Jacobian) while the former contain all information about thermal fluctuations and dissipation and we call it $S_{\rm diss}$ (for dissipation):

$$S[x, i\hat{x}, \eta, i\hat{\eta}] = S_{\rm diss}[x, i\hat{x}; \Gamma] + S_{\rm det}[x, i\hat{x}, \eta, i\hat{\eta}] + S_{\rm jac}[x] \ . \tag{4.17}$$

If the distribution of the initial condition were to be included in the action as an additional term, $\ln P_{\rm i}[x_0, i\hat{x}_0]$, it would be part of $S_{\rm det}$.

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

$$\mathcal{Z}_{\rm d}[\eta = 0, \hat{\eta} = 0] = 1 \tag{4.18}$$

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 utilised in disordered systems to render the dynamic calculations relatively easier than the static ones.

One can extract from the construction above the probability distribution of the stochastic variable x

$$P[x] \propto \int \mathcal{D}\hat{x} \ P_{\rm i}(x_0, \dot{x}_0) \ e^{S[x, {\rm i}\hat{x}]} \tag{4.19}$$

where $S[x, {\rm i}\hat{x}] = S[x, {\rm i}\hat{x}, 0, 0]$.

4.1.2 Multiplicative white noise

We start from the Langevin equation

$$\boxed{d_t x(t) = f(x) + g(x)\xi(t)} \tag{4.20}$$

with multiplicative white noise, $\langle \xi(t) \rangle = 0$ and $\langle \xi(t)\xi(t') \rangle = 2D\delta(t - t')$. Using the Fokker-Planck formalism we have proven that this equation takes to the Gibbs-Boltzmann measure independently of α and $g(x)$ if the force is chosen as

$$\boxed{f(x) = -g^2(x)V'(x) + 2D \ (1 - \alpha) \ g(x)g'(x)} \ . \tag{4.21}$$

In the construction below we keep the force f generic.

The probability distribution for a given trajectory of x ruled by Eq. (4.20) is

$$P[x] \propto \langle \, |\mathcal{J}| \ \delta \left({\rm Eq}[x, \xi] \right) \rangle \propto \langle \, |\mathcal{J}| \int \mathcal{D}\hat{x} \ e^{-\int dt \ i\hat{x} \, {\rm Eq}[x,\xi]} \, \rangle \tag{4.22}$$

where we introduced the auxiliary field $i\hat{x}$ to exponentiate the δ-function, and the Jacobian $\mathcal{J}$ is given by

$$\mathcal{J} \equiv \det\left[\frac{\delta \mathrm{Eq}[x(t),\xi(t)]}{\delta x(t')}\right] . \tag{4.23}$$

where

$$\mathrm{Eq}[x(t),\xi(t)] \equiv d_t x - f(x) - g(x)\xi(t) = 0 , \tag{4.24}$$

and we made explicit the dependence on the noise ξ since this will be important. The explicit calculation of the operator yields

$$\mathcal{J} \equiv \det\left[d_t\delta(t-t') + A(x,\xi)\delta(t-t')\right] \tag{4.25}$$

with $A(x,\xi) \equiv -f'(x) - g'(x)\xi(t)$, $f'(x) = d_x f(x)$ and $g'(x) = d_x g(x)$. Note that if $g(x) \neq \mathrm{ct}$ the noise appears explicitly in the functional under $\det_{tt'}$. After some simple algebra, $\mathcal{J}$ can be factorized as

$$\mathcal{J} \equiv \det_{tt'}\left[d_t\delta(t-t')\right] \det_{tt'}\left[\delta(t-t') + \theta(t-t')A(x,\xi)\right] , \tag{4.26}$$

and the first factor can be discarded in the normalization. We can now re-write the second factor with the help of the identity $\det(1+C_\xi) = \exp \mathrm{Tr}\ln(1+C_\xi)$ with the causal function $C_\xi(x,t,t') = \theta(t-t')A(x,\xi)$, where we highlighted the dependence of C_ξ on the noise by adding a subscript ξ to C. The $\ln(1+C_\xi)$ can now be expanded in Taylor series. In the additive noise case C_ξ is independent of the noise and its causal structure truncates the series at first order in C. However, in this explicitly noise dependent case one needs to be careful and also keep the quadratic order [95]:

$$\begin{aligned}\mathcal{J} &\propto \exp \mathrm{Tr}_{tt'}\left[\theta(t-t')A(x,\xi) - \frac{1}{2}C_\xi^2(x,t,t')\right] \\ &= \exp\int \mathrm{d}t\left[\theta(0)A(x,\xi) - \frac{1}{2}C_\xi^2(x,t,t)\right]\end{aligned} \tag{4.27}$$

where $C_\xi^2(x,t,t') \equiv \int dt''\ \theta(t-t'')A(x(t),\xi(t))\,\theta(t''-t')A(x(t''),\xi(t''))$. Using now $\theta(0) = \alpha$, and simplifying notations such as $\dot{x} = d_t x$, $g'(x(t)) = g'$, $C_\xi^2(x,t,t') = C_\xi^2$ and $\int dt = \int$, $P[x]$ reads (where again we lift the modulus)

$$P[x] \propto \int \mathcal{D}\xi\mathcal{D}\hat{x}\ e^{\alpha\int A(x,\xi) - \frac{1}{2}\mathrm{Tr}_{tt'}C_\xi^2 - \int i\hat{x}[\dot{x}-f-g\xi] - \frac{1}{4D}\int\xi^2} . \tag{4.28}$$

Before performing the integration over ξ that involves

$$\int \mathcal{D}\xi \; e^{-\frac{1}{4D}\int \xi^2 - \int(-i\hat{x}g+\alpha g')\xi - \frac{1}{2}\mathrm{Tr}_{tt'}C^2_\xi} \; , \tag{4.29}$$

we translate the noise by a function of the variables x and $i\hat{x}$, $\xi \mapsto \xi - 2D\,(-i\hat{x}g + \alpha g')$, in the functional integral. [Notice that $\xi \in \mathbb{R}$ but $i\hat{x} \in i\mathbb{R}$. In principle we can restore the original integration domain using the analyticity of the exponential that is zero on the boundary thanks to the term $-(4D)^{-1}\int \xi^2$.] The functional integral in (4.29) transforms into a new path integral

$$e^{D\int(-i\hat{x}g+\alpha g')^2} \int \mathcal{D}\xi \; e^{-\frac{1}{4D}\int \xi^2 - \frac{1}{2}\mathrm{Tr}_{tt'}C^2_{\xi-2D(-i\hat{x}g+\alpha g')}} \; . \tag{4.30}$$

Keeping the terms in $C^2_{\xi-2D(-i\hat{x}g+\alpha g')}$ that are quadratic in the noise and yield a $\delta(t-t')$ contribution within the $\mathrm{Tr}_{tt'}$ under the noise average, and using the notation $\langle \dots \rangle = \int \mathcal{D}[\xi] \; e^{-(4D)^{-1}\int \xi^2} \dots$ one has

$$\begin{aligned} \langle e^{-\frac{1}{2}\mathrm{Tr}_{tt'}C^2_{\xi-2D(-i\hat{x}g+\alpha g')}} \rangle &= e^{-\frac{1}{2}\langle \mathrm{Tr}_{tt'}C^2_{\xi-2D(-i\hat{x}g+\alpha g')}\rangle} \\ &= e^{-\frac{1}{2}\int dt\theta(t-t')\theta(t'-t)g'(x(t))g'(x(t'))\langle\xi(t)\xi(t')\rangle} = e^{-D\alpha^2\int g'^2} \; . \end{aligned}$$

Altogether we obtain

$$P[x] \propto \int \mathcal{D}\hat{x} \; e^{S[x,i\hat{x}]} \tag{4.31}$$

with the action [90, 91]

$$\begin{aligned} S[x,i\hat{x}] &\equiv \int \left[D\,(-i\hat{x}g + \alpha g')^2 - \alpha f' - i\hat{x}(\dot{x} - f) - D\alpha^2 g'^2 \right] + \ln P_{\mathrm{i}} \\ &= \int \left[-i\hat{x}(\dot{x} - f + 2D\alpha g' g) + D(i\hat{x})^2 g^2 - \alpha f' \right] + \ln P_{\mathrm{i}} \; . \end{aligned} \tag{4.32}$$

where we used the short-hand notation $\int$ for the time integrals to make the expressions shorter.

After replacing f by $-g^2V' + 2D(1-\alpha)gg'$, the action reads

$$\begin{aligned} S[x,i\hat{x}] = \int \big\{ & -i\hat{x}[\dot{x} + g^2V' - 2D(1-2\alpha)gg'] + D(i\hat{x})^2 g^2 \\ & -\alpha\partial_x[-g^2V' + 2D(1-\alpha)gg'] \big\} + \ln P_{\mathrm{i}} \; . \end{aligned} \tag{4.33}$$

Let us rewrite the action as

$$S[x, i\hat{x}] = S_{\rm det}[x, i\hat{x}] + S_{\rm diss}[x, i\hat{x}] + S_{\rm jac}[x] \tag{4.34}$$

with

$$\begin{aligned} S_{\rm det}[x, i\hat{x}] &= \int -i\hat{x} g_t^2 V_t' + \ln P_i \\ S_{\rm diss}[x, i\hat{x}] &= \int [-i\hat{x}_t (d_t x_t - 2D(1-2\alpha) g_t g_t') + D(i\hat{x}_t)^2 g_t^2] \\ S_{\rm jac}[x] &= -\alpha \int \partial_x [-g_t^2 V_t' + 2D(1-\alpha) g_t g_t'] \end{aligned} \tag{4.35}$$

4.2 Generic correlation and response.

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

$$\langle A(t) \rangle = \int \mathcal{D}x \mathcal{D}\hat{x}\ dP(t_0)\ A[x(t)]\ e^{S[x, i\hat{x}]}\ , \tag{4.36}$$

where $S[x, i\hat{x}]$ is a short-hand notation for $S[x, i\hat{x}, \eta = 0, \hat{\eta} = 0]$. The average we compute in this way is the average over thermal histories (noise and initial conditions) but we use the probability weight give by e^S to do the calculation. The self-correlation of x is given by

$$C(t, t') = \langle x(t) x(t') \rangle = \frac{1}{Z_{\rm d}[\eta, \hat{\eta}]}\ \frac{\delta^2 Z_{\rm d}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\eta(t')}\bigg|_{\eta=\hat{\eta}=0} = \frac{\delta^2 Z_{\rm d}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\eta(t')}\bigg|_{\eta=\hat{\eta}=0} \tag{4.37}$$

We insist upon the fact that no normalization is needed in the last member as the zero-source generating functional is identical to one. Similarly, we define the two-time correlation between two generic observables A and B,

$$C_{AB}(t, t') \equiv \int \mathcal{D}x \mathcal{D}\hat{x}\ dP(t_0)\, A[x(t)] B[x(t')]\, e^{S[x, i\hat{x}]} = \langle A[x(t)] B[x(t')] \rangle \tag{4.38}$$

The simplest linear response is defined and given by

$$\begin{aligned} R(t, t') &= \frac{\delta \langle x(t) \rangle}{\delta h(t')}\bigg|_{h=0} = \langle x(t) \frac{\delta S[x, i\hat{x}; h]}{\delta h(t')} \rangle|_{h=0} = \langle x(t) i\hat{x}(t') \rangle \\ &= \frac{1}{Z_{\rm d}[\eta, \hat{\eta}]}\ \frac{\delta^2 Z_{\rm d}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\hat{\eta}(t')}\bigg|_{\eta=\hat{\eta}=0} = \frac{\delta^2 Z_{\rm d}[\eta, \hat{\eta}]}{\delta\eta(t)\delta\hat{\eta}(t')}\bigg|_{\eta=\hat{\eta}=0} \end{aligned} \tag{4.39}$$

with $h(t')$ a small field applied at time t' that modifies the potential energy according to $V \to V - h(t')x(t')$. 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.

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

$$R_{AB}(t,t') \equiv \left.\frac{\delta\langle A[x(t)]\rangle_{f_B}}{\delta f_B(t')}\right|_{f_B=0}, \tag{4.40}$$

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 $t \to -t$). By plugging eq. (4.36) in this definition we get the **classical Kubo formula** for generic observables:

$$R_{AB}(t,t') = \langle A[x(t)]\,\frac{\delta S[x,i\hat{x};f_B]}{\delta f_B(t')}\rangle\Big|_{f_B=0} = \langle A[x(t)]i\hat{x}(t')B'[x(t')]\rangle \tag{4.41}$$

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 $i\hat{x}$.

For a multiplicative noise process the linear response is also defined as

$$R(t,t') = \left.\frac{\delta\langle x(t)\rangle_h}{\delta h(t')}\right|_{h=0} = \langle x(t)\left.\frac{\delta S_h[x,i\hat{x}]}{\delta h(t')}\right|_{h=0}\rangle \tag{4.42}$$

where the action has been modified as

$$S_h[x,i\hat{x}] = S[x,i\hat{x}] - \int \left[-i\hat{x}_t g_t^2 h_t + \alpha\partial_x(g_t^2 h_t)\right] \tag{4.43}$$

and, as the perturbing field is independent of x,

$$S_h[x,i\hat{x}] = S[x,i\hat{x}] - \int h_t\left[-i\hat{x}_t g_t^2 + 2\alpha g_t g_t'\right]. \tag{4.44}$$

With this, we find that the linear response is given by

$$\boxed{R(t,t') = -\langle x_t[-i\hat{x}_{t'} g_{t'}^2 + 2\alpha g_{t'} g_{t'}']\rangle} \tag{4.45}$$

where the average has to be taken with the functional integral and the measure given by the unperturbed action.

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 [89]. The normalization factors $1/Z_{\rm d}[\eta,\hat{\eta}]$ in (4.37) and (4.39) have to be evaluated at zero external sources in which they are trivially independent of the random interactions. Hence, it is sufficient to average $Z_{\rm d}[\eta,\hat{\eta}]$ 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 $[\langle A\rangle]=[1/Z\sum_{\rm conf}A\exp(-\beta H)]$, 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** [117] 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 dyamics 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.

4.2.1 The linear response as a variable-noise correlation

Additive noise

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

$$\int dt''dt'''\ \lambda(t'',t''')\,x(t'')\xi(t''') \tag{4.46}$$

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

$$\text{Linear terms} = \frac{k_B T}{2} \int dt_1 dt_2 dt_3 dt_4 \ [\lambda(t_1,t_2) x(t_1) \Gamma(t_2,t_3) i\hat{x}(t_4) \delta(t_4 - t_3) + i\hat{x}(t_1)\delta(t_1 - t_2)\Gamma(t_2,t_3)\lambda(t_4,t_3)x(t_4)] \ . \tag{4.47}$$

The variation with respect to $\lambda(t,t')$ yields $(k_B T)/2 \int dt'' \ [\Gamma(t',t'') + \Gamma(t'',t')]$ $\langle x(t) i\hat{x}(t'')\rangle$ and the searched result

$$k_B T \int dt'' \ \Gamma(t',t'') \langle x(t) i\hat{x}(t'')\rangle = k_B T \int dt'' \ \Gamma(t',t'') R(t,t'') = \langle x(t)\xi(t')\rangle \tag{4.48}$$

or, equivalently,

$$\boxed{R(t,t') = (k_B T)^{-1} \int dt'' \ \Gamma^{-1}(t,t'') \langle x(t'')\xi(t')\rangle} \tag{4.49}$$

In the white noise limit this relation becomes $2k_B T\gamma_0 \langle x(t) i\hat{x}(t')\rangle = 2k_B T \gamma_0 R(t,t') = \langle x(t)\xi(t')\rangle$.[21]

4.3 Onsager-Machlup

The probability density in the space of paths is obtained by integrating away the auxiliary function $i\hat{x}(t)$, a calculation that can be carried out since the functional integral is Gaussian. In the additive white noise case the Onsager-Machlup action reads ($\gamma_0 = 1$)

$$S_{\rm OM} = \ln P_{\rm i} + \int_t \left\{ -\frac{1}{4k_B T} \left(m\ddot{x}_t + \gamma_0 \dot{x}_t + V'(x_t) \right)^2 + \alpha V''[x_t] \right\} \ . \tag{4.50}$$

In the additive colored noise

$$S_{\rm OM} = \ln P_{\rm i} - \frac{1}{2k_B T} \int_t \int_{t'} \left\{ \left(m\ddot{x}_t + \int_{t''} \gamma_{tt''} \dot{x}_{t''} + V'(x_t) \right) \Gamma^{-1}_{tt'} \times \left(m\ddot{x}_{t'} + \int_{t'''} \gamma_{t't'''} \dot{x}_{t'''} + V''(x_{t'}) \right) \right\} + \ln \mathcal{J} \ . \tag{4.51}$$

[21] This result can be easily checked in the random walk case. The calculation of R from its definition as the variation of $\langle x(t)\rangle$ with respect to $h(t')$ yields $R(t,t') = \gamma_0^{-1}\theta(t-t')$ while the correlation between position and noise is $\langle x(t)\xi(t')\rangle = 2k_B T\theta(t-t')$.

In the multiplicative white noise case

$$S_{\rm OM} = \ln P_{\rm i} - \frac{1}{4k_BT}\int_t \left\{ \frac{1}{g_t^2}\left(\dot{x}_t - f_t + 2D\alpha g_t g_t'\right)^2\right) - \alpha f_t' \right\} \ . \tag{4.52}$$

4.4 Fluctuations

The stochastic nature of the dynamics is responsible for fluctuations of the field (here x_t) and more generally of all the possible physical observables that depend on this field [*i.e.*, any $A(x)$]. Amongst the few universal results that apply to these dynamics, there is a class of exact relations between the path probabilities that are very precious since they lead to strong relations between observables. In a functional formalism, these relations can be proven by 1) making use of physical symmetries or broken symmetries of the system or its dynamics, 2) exploiting the invariance of the generating functional under a dummy linear change of integration variables. In this Subsection, we shall discuss these relations in the context of stochastic Markov processes with multiplicative white noise as defined in Eq. (2.215).

4.4.1 Relation between path probabilities

Let us consider the cases in which the force f depends on a set of externally controlled, possibly time-dependent, parameters λ_t. The stochastic process is characterised by the path integral that expresses the joint probability distribution, $P[x, \mathrm{i}\hat{x}; \alpha, \lambda]$, of the time series $\{x_t,\ \mathrm{i}\hat{x}_t\}$ of the physical and the auxiliary fields, in the α-prescription, and under the set of parameters λ_t. Following Crooks [109], we ask how does $P[x, \mathrm{i}\hat{x}; \alpha, \lambda]$ compare to the probability distribution of the transformed time-dependent variables $\{\mathcal{T}x_t, \mathcal{T}\mathrm{i}\hat{x}_t\}$ in another discretisation prescription, $\overline{\alpha}$, and, possibly, under a transformed set of parameters, $\overline{\lambda}_t$. By choosing adequately the transformation rules $\mathcal{T}x$, $\mathcal{T}\mathrm{i}\hat{x}$, $\overline{\alpha}$ and $\overline{\lambda}$ we will obtain relations of the type

$$\frac{P[\mathcal{T}x, \mathcal{T}\mathrm{i}\hat{x}; \overline{\alpha}, \overline{\lambda}]}{P[x, \mathrm{i}\hat{x}; \alpha, \lambda]} = \mathrm{e}^{\Delta S[x, \mathrm{i}\hat{x}; \alpha, \lambda]} \ . \tag{4.53}$$

We have distinguished the notation for the transformation of the dynamical fields, $\mathcal{T}x, \mathcal{T}\mathrm{i}\hat{x}$, from the changes in the discretisation parameter, $\overline{\alpha}$, and the external time-dependent parameter, $\overline{\lambda}_t$.

The relation (4.53) implies, for the average of a generic function A of the physical and auxiliary fields (but, for simplicity, not of their time-derivatives)

$$\begin{aligned}\int \mathcal{D}[x,\hat{x}]\ A[x,\mathrm{i}\hat{x}]\ P[x,\mathrm{i}\hat{x};\overline{\alpha},\overline{\lambda}]&\\ = \int \mathcal{D}[\mathcal{T}x,\mathcal{T}\hat{x}]\ A[\mathcal{T}x,\mathcal{T}\mathrm{i}\hat{x}]\ P[\mathcal{T}x,\mathcal{T}\mathrm{i}\hat{x};\overline{\alpha},\overline{\lambda}]&\\ = \int \mathcal{D}[\mathcal{T}x,\mathcal{T}\hat{x}]\ A[\mathcal{T}x,\mathcal{T}\mathrm{i}\hat{x}]\ P[x,\mathrm{i}\hat{x};\alpha,\lambda]\ \mathrm{e}^{\Delta S[x,\mathrm{i}\hat{x};\alpha,\lambda]}\ .&\end{aligned} \tag{4.54}$$

Moreover, if the measure over the transformed fields can be related to the one over the original ones with a unit Jacobian, and if the domain of integration at each time slice, here the real axis, is unchanged or can be taken back to the real axis, then the relation above becomes

$$\begin{aligned}\int \mathcal{D}[x,\hat{x}]\ A[x,\mathrm{i}\hat{x}]\ P[x,\mathrm{i}\hat{x};\overline{\alpha},\overline{\lambda}]&\\ = \int \mathcal{D}[x,\hat{x}]\ A[\mathcal{T}x,\mathcal{T}\mathrm{i}\hat{x}]\ \mathrm{e}^{\Delta S[x,\mathrm{i}\hat{x};\alpha,\lambda]}\ P[x,\mathrm{i}\hat{x},\alpha,\lambda]\ .&\end{aligned} \tag{4.55}$$

Writing $A[\mathcal{T}x,\mathcal{T}\mathrm{i}\hat{x}]$ as a new function of the original fields x and $\mathrm{i}\hat{x}$, say $B[x,\mathrm{i}\hat{x}] \equiv A[\mathcal{T}x,\mathcal{T}\mathrm{i}\hat{x}]$, one has a generic relation between averages of different functions:

$$\begin{aligned}\int \mathcal{D}[x,\hat{x}]\ A[x,\mathrm{i}\hat{x}]\ P[x,\mathrm{i}\hat{x};\overline{\alpha},\overline{\lambda}]&\\ = \int \mathcal{D}[x,\hat{x}]\ B[x,\mathrm{i}\hat{x}]\ \mathrm{e}^{\Delta S[x,\mathrm{i}\hat{x};\alpha,\lambda]}\ P[x,\mathrm{i}\hat{x};\alpha,\lambda]\ .&\end{aligned} \tag{4.56}$$

With different choices of the function A, and their associated B, one can derive various relation. In particular, choosing $A = 1$,

$$1 = \langle \mathrm{e}^{\Delta S[x,\mathrm{i}\hat{x};\alpha,\lambda]} \rangle\ . \tag{4.57}$$

We will identify the transformation $\mathcal{T}_{\mathrm{eq}}$, associated with the time-reversal invariance of equilibrium dynamics, that leaves the probability density invariant ($\Delta S = 0$) whenever the system is subject to equilibrium conditions, meaning initial conditions drawn from the Gibbs-Boltzmann distribution $P_{\mathrm{GB}} \propto \mathrm{e}^{-V/D}$ and dynamics given by the Langevin equation Eq. (2.215), with a drift force deriving from the same potential V, and in contact with a thermal bath at the same temperature such that $k_B T = D$. We later use this invariance to derive generic properties of equilibrium

dynamics, such as the fluctuation-dissipation theorem. Out of equilibrium, $\Delta S \neq 0$, and we will derive various fluctuation relations that have been extensively studied in recent years [97, 98, 99, 100, 101, 102, 103].

4.5 An equilibrium symmetry

For convenience, we symmetrize the time-interval of integration. We call $-\mathcal{T}$ the initial time and $\mathcal{T}$ the final time.

4.5.1 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

$$A_{\rm r}([x],t) \equiv A([\bar{x}],-t). \tag{4.58}$$

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 $A_{\rm r}[x(t)] = -\partial_t x(-t)$. As an example for non-local observables, the time-reversed Langevin equation reads

$$\mathrm{Eq}_{\rm r}([x],t) \;\; = \;\; m\ddot{x}(t) - F_{\rm r}([x],t) - \int_{-\mathcal{T}}^{\mathcal{T}} du\; \gamma(u-t)\dot{x}(u)\;. \tag{4.59}$$

where all forces, deterministic and stochastic, have been collected in $F_{\rm r}$. Notice the change of sign in front of the friction term that is no longer dissipative in this new equation.

4.5.2 The transformation in the additive noise case

If the initial time t_0 is set to $t_0 = -\mathcal{T}$ and the system is in equilibrium at this instant, $P_{-\mathcal{T}}$ is given by the Maxwell-Boltzmann measure. One can then check that the zero-source action, $S[x, i\hat{x}]$, is fully invariant under the transformation $\mathcal{T}_c$:

$$\mathcal{T}_c \equiv \left\{ \begin{array}{rcl} x_u & \mapsto & x_{-u}\;, \\ i\hat{x}_u & \mapsto & i\hat{x}_{-u} + \beta d_u x_{-u}\;. \end{array} \right.$$

We introduced $x_t = x(t)$ so as to make the notation more compact. Note that $d_u x_{-u} = -d_{-u}x_{-u}$. This transformation does not involve the kernel Γ and it includes a time-reversal. The invariance is achieved independently by the deterministic ($S_{\rm det}$) and dissipative ($S_{\rm diss}$) terms in the action. The former includes the contribution from

the initial condition, $\ln P_{-\mathcal{T}}$. Moreover, the path-integral measure is invariant since the Jacobian associated to this transformation is also block triangular with ones on the diagonal. The proof goes as follows. (In the over-damped white noise limit we use the Stratonovich convention; for the generalization to other rules of calculus see the discussion of the multiplicative noise case.)

Invariance of the measure

The Jacobian $\mathcal{J}_{\rm eq}$ of the transformation $\mathcal{T}_{\rm eq}$ is the determinant of a triangular matrix:

$$\mathcal{J}_{\rm eq} \equiv \det \frac{\delta(x, i\hat{x})}{\delta(\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}i\hat{x})} = \det{}^{-1}_{uv} \begin{bmatrix} \frac{\delta x_{-u}}{\delta x_v} & 0 \\ \frac{\delta i\hat{x}_{-u}}{\delta x_v} & \frac{\delta i\hat{x}_{-u}}{\delta i\hat{x}_v} \end{bmatrix} = \left(\det{}^{-1}_{uv}\left[\delta_{u+v}\right]\right)^2 = 1$$

and it is thus identical to one.

Invariance of the integration domain

Before and after the transformation, the functional integration on the field x_t is performed for values of x_t on the real axis. However, the new domain of integration for the field $\hat{x}$ is complex. For all times, $\hat{x}_t$ is now integrated over the complex line with a constant imaginary part $-i\beta\partial_t x_t$. One can return to an integration over the real axis by closing the contour at both infinities. Indeed the integrand, e^S, goes to zero sufficiently fast at $x_t \to \pm\infty$ for neglecting the vertical ends of the contour thanks to the term $\beta^{-1}\gamma_0(i\hat{x}_t)^2$ in the white noise limit (or the correspondong ones in colored noise cases) in the action. Furthermore the new field is also integrated with the boundary conditions $\hat{x}(-\mathcal{T}) = \hat{x}(\mathcal{T}) = 0$.

Invariance of the action functional

The deterministic contribution satisfies

$$\begin{aligned} S_{\rm det}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}i\hat{x}] &= \ln P_{\rm i}(x_{\mathcal{T}}, \dot{x}_{\mathcal{T}}) - \int_u \left[i\hat{x}_{-u} + \beta\partial_u x_{-u}\right]\left[m\partial_u^2 x_{-u} + V'(x_{-u})\right] \\ &= \ln P_{\rm i}(x_{\mathcal{T}}, \dot{x}_{\mathcal{T}}) - \int_u i\hat{x}_u\left[m\ddot{x}_u + V'(x_u)\right] + \beta\int_u \dot{x}_u\left[m\ddot{x}_u + V'(x_u)\right] \\ &= \ln P_{\rm i}(x_{\mathcal{T}}, \dot{x}_{\mathcal{T}}) - \int_u i\hat{x}_u\left[m\ddot{x}_u + V'(x_u)\right] + \beta\int_u \partial_u \ln P_{\rm i}(x_u, \dot{x}_u) \\ &= S_{\rm det}[x, i\hat{x}]\ , \end{aligned}$$

where we used the initial equilibrium measure $\ln P_{\rm i}(x, \dot{x}) = -\beta\left(\frac{1}{2}m\dot{x}^2 + V(x)\right) - \ln \mathcal{Z}$. In the first line we just applied the transformation; in the second line we

made the substitution $u \mapsto -u$; in the third line we wrote the last integrand as a total derivative, the integral of which cancels the first term and recreates the initial measure at $-\mathcal{T}$. Note that in this last step we assumed that we are using the Stratonovich convention ($\alpha = 1/2$) since we used the usual rules of calculus.

Secondly, we show that the dissipative contribution is also invariant under $\mathcal{T}_{\rm eq}$. We have

$$\begin{aligned} S_{\rm diss}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}i\hat{x}] &= \int_u [i\hat{x}_{-u} + \beta\partial_u x_{-u}] \int_v \beta^{-1}\,\gamma_{u-v}\, i\hat{x}_{-v} \\ &= \int_u [i\hat{x}_u - \beta\dot{x}_u] \int_v \gamma_{v-u}\beta^{-1} i\hat{x}_v \\ &= S_{\rm diss}[x, i\hat{x}]\ . \end{aligned}$$

In the first line we just applied the transformation, in the second line we made the substitution $u \mapsto -u$ and $v \mapsto -v$ and in the last step we exchanged u and v.

Invariance of the Jacobian (Grassmann variables)

Finally we show that the Jacobian term in the action is invariant once it is expressed in terms of a Gaussian integral over conjugate Grassmann fields (c and c^*) and provided that the transformation $\mathcal{T}_{\rm eq}$ is extended to act on these as follows[22]

$$\mathcal{T}_{\rm eq} \equiv \left\{ \begin{array}{lcllcl} x_u & \mapsto & x_{-u}\ , & \qquad c_u & \mapsto & c^*_{-u}\ , \\ i\hat{x}_u & \mapsto & i\hat{x}_{-u} + \beta\partial_u x_{-u}\ , & \qquad c^*_u & \mapsto & -c_{-u}\ . \end{array} \right. \tag{4.60}$$

We start from

$$S_{\rm det}[c, c^*, x] = \int_u \int_v c^*_u \left[m\partial_u^2\delta_{u-v} + \partial_u\gamma_{u-v}\right] c_v + \int_u c^*_u V''(x_u) c_u \tag{4.61}$$

and we have

$$\begin{aligned} &S_{\rm det}(\mathcal{T}_{\rm eq}c, \mathcal{T}_{\rm eq}c^*, \mathcal{T}_{\rm eq}x) \\ &\quad = -\int_u \int_v c_{-u} \left[m\partial_u^2\delta_{u-v} + \partial_u\gamma_{u-v}\right] c^*_{-v} + \int_u c_{-u}\left[-V''(x_{-u})\right] c^*_{-u} \\ &\quad = \int_u \int_v c^*_v \left[m\partial_u^2\delta_{v-u} - \partial_u\gamma_{v-u}\right] c_u + \int_u c^*_u V''(x_u) c_u \\ &\quad = S_{\rm jac}(c, c^*, x)\ . \end{aligned}$$

[22] More generally, the transformation on c and c^* is $c_u \mapsto \alpha\, c^*_{-u}$ and $c^*_u \mapsto -\alpha^{-1}\, c_{-u}$ with $\alpha \in C^*$.

In the first line we just applied the transformation, in the second line we exchanged the anti-commuting Grassmann variables and made the substitutions $u \mapsto -u$ and $v \mapsto -v$, finally in the last step we used $\partial_v \gamma_{v-u} = -\partial_v \gamma_{u-v}$ and we exchanged u and v. Finally the set of boundary conditions $[c(-\mathcal{T}) = \dot{c}(-\mathcal{T}) = c^*(\mathcal{T}) = \dot{c}^*(\mathcal{T})]$ is left invariant.

4.5.3 The transformation in the multiplicative white noise case

This part follows article [**?**]. We still have to make the $i\hat{x}$ sign notation homogeoeus; here it is the one in [**?**]

We look for the invariance of the generating functional that corresponds to the time-reversal invariance of the equilibrium dynamics. Although the action functional in Eq. (4.33) is relatively cumbersome, the identification of the correct field transformation that leaves it invariant can be simplified by the fact that one expects the time-reversal invariance to hold for the system and its environment separately. In other words, we expect the terms in the action that have their origin in the coupling to the bath to transform independently from the rest of the action. We collect them in

$$S_{\text{diss}}[x, \mathrm{i}\hat{x}] \equiv \int -\mathrm{i}\hat{x}_t[-D\mathrm{i}\hat{x}_t g_t^2 - \mathrm{d}_t^{(\alpha)} x_t] \tag{4.62}$$

where, to simplify notations, we defined

$$\mathrm{d}_t^{(\alpha)} x_t \equiv \mathrm{d}_t x_t - 2D(1-2\alpha) g_t g_t' \tag{4.63}$$

and, we recall, $D = k_B T = \beta^{-1}$. For a field x_t corresponding to a physical quantity x that is even under time-reversal transformation (such as the particle's position), the transformation of the physical field must naturally be $x_t \mapsto x_{-t}$. The expression of S_{diss} in Eq. (4.62) suggests that we look for a transformation such that $\mathrm{d}_t^{(\alpha)} x_t$ behaves as a usual time derivative under time reversal, *i.e.*

$$\mathrm{d}_t^{(\alpha)} x_t \mapsto -\mathrm{d}_{-t}^{(\alpha)} x_{-t} \,. \tag{4.64}$$

This is only true if we simultaneously transform the discretisation parameter $\alpha \mapsto 1-\alpha$. Altogether, we are led to propose the following transformation of the dynamical field x_t and its associated auxiliary field $\mathrm{i}\hat{x}_t$

$$\mathcal{T}_{\text{eq}} = \left\{ \begin{array}{rcl} x_t & \mapsto & x_{-t} \,, \\ \mathrm{i}\hat{x}_t & \mapsto & \mathrm{i}\hat{x}_{-t} + D^{-1} g_{-t}^{-2} \mathrm{d}_{-t}^{(\alpha)} x_{-t} \,, \end{array} \right. \tag{4.65}$$

complemented with the transformation of the discretisation parameter

$$\alpha \mapsto \overline{\alpha} \equiv 1 - \alpha \, . \tag{4.66}$$

It is easy to check that $S_{\rm diss}$ is indeed invariant under this transformation: Have to correct signs below to make them be the same as in the additive noise case

$$\begin{aligned} S_{\rm diss}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}\mathrm{i}\hat{x}; \overline{\alpha}] &= \int \Big\{ [\mathrm{i}\hat{x}_{-t} - D^{-1} g_{-t}^{-2} \mathrm{d}_{-t}^{(\alpha)} x_{-t}] \\ &\qquad \times [\mathrm{d}_{-t}^{(\alpha)} x_{-t} + D\ g_{-t}^2 \mathrm{i}\hat{x}_{-t} - D g_{-t}^2 \beta g_{-t}^{-2} \mathrm{d}_{-t}^{(\alpha)} x_{-t}] \Big\} \\ &= \int \Big\{ [\mathrm{i}\hat{x}_{-t} - D^{-1} g_{-t}^{-2} \mathrm{d}_{-t}^{(\alpha)} x_{-t}]\ D\ g_{-t}^2 \mathrm{i}\hat{x}_{-t} \Big\} \\ &= \int \Big\{ [D\ g_t^2 \mathrm{i}\hat{x}_t - \mathrm{d}_t^{(\alpha)} x_t]\ \mathrm{i}\hat{x}_t \Big\} = S_{\rm diss}[x, \mathrm{i}\hat{x}; \alpha] \, . \end{aligned} \tag{4.67}$$

We now have to check that the remaining terms in the action functional are also invariant under the proposed transformation. In the potential case with no time-dependent parameter ($\lambda_t = \mathrm{ct}$) and a drift force ensuring the convergence to the usual Gibbs-Boltzmann equilibrium measure, the remaining terms are gathered into

$$S_{\rm det+jac}[x, \mathrm{i}\hat{x}; \alpha] = \ln P_{\rm i}(x_{-\mathcal{T}}) - \int \mathrm{i}\hat{x} g_t^2 V_t' - \alpha \int \partial_x [-g_t^2 V_t' + 2D(1-\alpha) g_t g_t']$$

and they transform as

$$\begin{aligned} & S_{\rm det+jac}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}\mathrm{i}\hat{x}; \overline{\alpha}] \\ &= \ln P_{\rm i}(x_{\mathcal{T}}) + \int \Big[(-\mathrm{i}\hat{x}_{-t} + D^{-1} g_{-t}^{-2} \mathrm{d}_{-t}^{(\alpha)} x_{-t}) g_{-t}^2 V_{-t}' + (1-\alpha) \partial_{x_{-t}} (g_{-t}^2 V_{-t}') \Big] \\ &\qquad -2D\alpha(1-\alpha) \int \partial_x (g_{-t} g_{-t}') \\ &= \ln P_{\rm i}(x_{\mathcal{T}}) + \int \Big[-\mathrm{i}\hat{x}_t g_t^2 V_t' + D^{-1} \mathrm{d}_t^{(\alpha)} x_t V_t' + (1-\alpha) \partial_{x_t} (g_t^2 V_t') \Big] \\ &\qquad -2D\alpha(1-\alpha) \int \partial_x (g_t g_t') \, . \end{aligned} \tag{4.68}$$

We recognise that the first boundary term, $\ln P_{\rm i}(x_{\mathcal{T}})$, needs to be taken back to the initial time, $-\mathcal{T}$, if one wants to recover the original $S_{\rm det+jac}[\mathrm{i}\hat{x}, x; \alpha]$; the second and last terms are already part of $S_{\rm det+jac}[\mathrm{i}\hat{x}, x; \alpha]$; rewriting $1 - \alpha = \alpha + (1 - 2\alpha)$,

the fourth term produces the last piece needed to fully reconstruct the original $S_{\rm det+jac}[{\rm i}\hat{x}, x; \alpha]$. All in all, we have

$$S_{\rm det+jac}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}{\rm i}\hat{x}; \overline{\alpha}] = \; S_{\rm det+jac}[x, {\rm i}\hat{x}, \alpha] + D^{-1}\int {\rm d}_t^{(\alpha)}x_t \; V_t' \\ + (1-2\alpha)\int \partial_{x_t}(g_t^2 V_t') + \ln P_{\rm i}(x_{\mathcal{T}}) - \ln P_{\rm i}(x_{-\mathcal{T}}) \; . \tag{4.69}$$

Using the explicit form of ${\rm d}_t^{(\alpha)}x_t$ in Eq. (4.63), we can simplify this expression as follows

$$S_{\rm det+jac}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}{\rm i}\hat{x}; \overline{\alpha}] = S_{\rm det+jac}[x, {\rm i}\hat{x}; \alpha] + D^{-1}\int {\rm d}_t x_t \; V_t' \\ + (1-2\alpha)\int g_t^2 \; V_t'' + \ln P_{\rm i}(x_{\mathcal{T}}) - \ln P_{\rm i}(x_{-\mathcal{T}}) \; . \tag{4.70}$$

Replacing the term in ${\rm d}_t x_t \; V_t'$ above by using the chain-rule of stochastic calculus,

$${\rm d}_t V_t = {\rm d}_t x_t \; V_t' + (1-2\alpha) D g_t^2 \; V_t'', \tag{4.71}$$

we obtain

$$S_{\rm det+jac}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}{\rm i}\hat{x}; \overline{\alpha}] = S_{\rm det+jac}[x, {\rm i}\hat{x}; \alpha] \\ + D^{-1}\int {\rm d}_t V_t + \ln P_{\rm i}(x_{\mathcal{T}}) - \ln P_{\rm i}(x_{-\mathcal{T}}) \; . \tag{4.72}$$

Finally, with initial conditions drawn from the Gibbs-Boltzmann distribution

$$P_{\rm i}(x_{-\mathcal{T}}) = Z^{-1} \; {\rm e}^{-D^{-1}V(x_{-\mathcal{T}})} \, , \tag{4.73}$$

we end the proof of the full invariance of the equilibrium action functional in Eq. (4.33) under the transformation $\mathcal{T}_{\rm eq}$ given in Eq. (4.65):

$$S[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}{\rm i}\hat{x}; \overline{\alpha}] = S[x, {\rm i}\hat{x}; \alpha] \tag{4.74}$$

and $\Delta S = 0$. Note that to achieve this invariance, there was a subtle interplay between the contributions coming from the deterministic part of the action and the ones coming from the α-dependent Jacobian.

This invariance of the action functional yields the following relation between path probabilities

$$P[x, {\rm i}\hat{x}; \alpha] \; \mathcal{D}[x, \hat{x}] = P[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}{\rm i}\hat{x}; \overline{\alpha}] \; \mathcal{D}[\mathcal{T}_{\rm eq}x, \mathcal{T}_{\rm eq}{\rm i}\hat{x}] \; . \tag{4.75}$$

After the transformation $\mathcal{T}_{\rm eq}$, the domain of integration of $\hat{x}_t$ at each time slice of the generating functional is shifted from the real axis to the complex line with a constant imaginary part $\mathrm{i}D^{-1}\mathrm{d}_t x_t$. Using the analyticity of $\exp S[x;\mathrm{i}\hat{x};\alpha]$, one can return to an integration over the real axis by closing the contour at both infinities and by dropping the contributions of the vertical ends that vanish owing to the term $D(\mathrm{i}\hat{x}_t)^2$. Note also that the Jacobian associated to the change of variables $\{x,\mathrm{i}\hat{x}\}\mapsto\{\mathcal{T}_{\rm eq}x,\mathcal{T}_{\rm eq}\mathrm{i}\hat{x}\}$ is unity. Finally, $\mathcal{D}[x,\hat{x}]=\mathcal{D}[\mathcal{T}_{\rm eq}x,\mathcal{T}_{\rm eq}\mathrm{i}\hat{x}]$ and we obtain the following relation between the forward and backward path probabilities

$$\frac{P_{\rm B}[x,\mathrm{i}\hat{x}]}{P_{\rm F}[x,\mathrm{i}\hat{x}]}=1\ , \tag{4.76}$$

where we defined

$$P_{\rm F}[x,\mathrm{i}\hat{x}]\equiv P[x,\mathrm{i}\hat{x},\alpha]\ ,\qquad\qquad P_{\rm B}[x,\mathrm{i}\hat{x}]\equiv P[\mathcal{T}_{\rm eq}x,\mathcal{T}_{\rm eq}\mathrm{i}\hat{x},\bar{\alpha}]\ . \tag{4.77}$$

The relation (4.76) is valid whenever the system is in thermal equilibrium.

4.6 Consequences of the transformation

We now use the transformation $\mathcal{T}_{\rm eq}$ to derive a number of exact results: the equilibrium fluctuation-dissipation theorem and the out of equilibrium fluctuation theorems.

The equilibrium **fluctuation-dissipation theorem** is a model independent relation between induced and spontaneous fluctuations characterized by the linear response function to an infinitesimal perturbation and the correlation function. It applies to systems in equilibrium with a probability measure given by the Gibbs-Boltzmann form.

The out of equilibrium **fluctuation theorems** are exact and model independent relations linking the probability distribution of the positive and negative measurement of a quantity such as the entropy production rate, the work done by some external non-potential force, etc. Quite generally, either the positive or negative value is given by a rare event. These take negligible values when the observation are done on macroscopic length and/or time scales. However, microscopic scales are becoming accessible in different areas of physics and biology where these relations may be relevant.

A fluctuation theorem first appeared in a simulation of sheared fluids by Evans et al. [97]. Shortly afterwards, Gallavotti and Cohen [98] proved rigorously a closely related FT for deterministic dynamics and Jarzynski [99] showed how to relate

non-equilibrium properties to equilibrium quantities. These results were proven for deterministic dynamics and under some restrictive conditions on it. Later, a fluctuation theorem was proven for the single-particle stochastic Langevin dynamics [100] and an extension to fairly general Markov processes [101]. Several reviews of the theoretical foundations of this topic have been published [102, 103, 104].

Experimental tests of fluctuation theorems have faced many technical difficulties. Asymptotic theorems need the measurements of fluctuations over very long times, a limit in which rare events become less and less probable; the evaluation of transient theorems are confronted to the difficulty of identifying thermodynamic quantities such as work or heat. Some of the experiments done to test or use these relations used:
- a thermal conductors with the extremes connected to two heat reservoirs at different temperature;
- an electrical conductor maintained at constant temperature by an external bath and connected to a voltage drop [105];
- colloidal particles in time-dependent traps [105];
- single molecule manipulation such as pulling molecules with optical tweezers or atomic force microscopes [106];
- tracers immersed in granular gases [107].

4.6.1 The fluctuation-dissipation theorem

Additive noise

This symmetry implies

$$\begin{aligned} \langle x_t i\hat{x}_{t'}\rangle_{S[x,i\hat{x}]} &= \langle \mathcal{T}_c x_t \mathcal{T}_c i\hat{x}_{t'}\rangle_{S[\mathcal{T}_c x,\mathcal{T}_c i\hat{x}]} \\ &= \langle x_{-t} i\hat{x}_{-t'}\rangle_{S[x,i\hat{x}]} + \beta\langle x_{-t} d_{t'} x_{-t'}\rangle_{S[x,i\hat{x}]} \end{aligned} \tag{4.78}$$

that, using time-translational invariance and $\tau \equiv t - t'$, becomes

$$R(\tau) - R(-\tau) = -\beta d_\tau C(-\tau) = -\beta d_\tau C(\tau) \; . \tag{4.79}$$

For generic observables one can similarly apply the $\mathcal{T}_c$ transformation to expression (4.41) of the linear response

$$R_{AB}(\tau) - R_{A_r B_r}(-\tau) = -\beta d_\tau C_{AB}(-\tau) = -\beta d_\tau C_{AB}(\tau) \; . \tag{4.80}$$

where we defined A_r and B_r as

$$A_r([x],t) \equiv A([\bar{x}],-t) \; . \tag{4.81}$$

Take for instance a function $A[x(t),t] = \int du f(x(u))\delta(u-t) + \int du f(\dot{x}(u))\delta(u-t) + \int du f(\ddot{x}(u))\delta(u-t) + \dots$ then $A_r[x(t),t] = A[x(-t),-t] = \int du f(x(-u))\delta(u+t) + \int du f(\dot{x}(-u))\delta(u+t) + \int du f(\ddot{x}(-u))\delta(u+t) + \dots$.

Relations between higher order correlation functions evaluated at different times $t_1, t_2, \dots t_n$ are easy to obtain within this formalism.

Multiplicative noise

The fluctuation-dissipation theorem is a model-independent relation between the linear response and the correlation of spontaneous equilibrium fluctuations of a given observable. The linear response of x with respect to a previous perturbation is defined as

$$R_\alpha(t,t') = \left.\frac{\delta\langle x(t)\rangle_h}{\delta h(t')}\right|_{h=0} , \tag{4.82}$$

where the infinitesimal perturbation h couples linearly to the field x in such a way that the potential $V \to V_h = V - hx$ and, therefore, $V' \to V'_h = V' - h$. In the path-integral formulation, the linear response is given by

$$R_\alpha(t,t') = \int \mathcal{D}[x,\mathrm{i}\hat{x}]\; x_t \left.\frac{\delta S_h[x,\mathrm{i}\hat{x};\alpha]}{\delta h_{t'}}\right|_{h=0} \mathrm{e}^{S[x,\mathrm{i}\hat{x};\alpha]} \tag{4.83}$$

where the action has been modified as

$$S_h[x,\mathrm{i}\hat{x};\alpha] = S[x,\mathrm{i}\hat{x};\alpha] + \int h_t \left[\mathrm{i}\hat{x}_t g_t^2 - 2\alpha g_t g_t'\right] . \tag{4.84}$$

Therefore, the linear response is expressed as a correlation function reading

$$R_\alpha(t,t') = \langle x_t[\mathrm{i}\hat{x}_{t'} g_{t'}^2 - 2\alpha g_{t'} g_{t'}']\rangle_{S[x,\mathrm{i}\hat{x};\alpha]} \tag{4.85}$$

where the average has to be taken with the measure given by the unperturbed action $S[x,\mathrm{i}\hat{x};\alpha]$. The subindex α expresses the fact that the stochastic process is defined with a discretisation parameter α. Exchanging momentarily α by $1-\alpha$ one has

$$R_{1-\alpha}(t,t') = \langle x_t[\mathrm{i}\hat{x}_{t'} g_{t'}^2 - 2(1-\alpha) g_{t'} g_{t'}']\rangle_{S[x,\mathrm{i}\hat{x};1-\alpha]} . \tag{4.86}$$

Take now the expression in Eq. (4.86) and perform the change variables in the path integral from $\{x_t, \mathrm{i}\hat{x}_t\}$ to $\{\mathcal{T}_{\mathrm{eq}} x_t, \mathcal{T}_{\mathrm{eq}} \mathrm{i}\hat{x}_t\}$:

$$R_{1-\alpha}(t,t') = \langle \mathcal{T}_c x_t[\mathcal{T}_{\mathrm{eq}} \mathrm{i}\hat{x}_{t'} \mathcal{T}_{\mathrm{eq}} g_{t'}^2 - 2(1-\alpha)\mathcal{T}_{\mathrm{eq}} g_{t'} \mathcal{T}_{\mathrm{eq}} g_{t'}']\rangle_{S[\mathcal{T}_{\mathrm{eq}} x, \mathcal{T}_{\mathrm{eq}}\mathrm{i}\hat{x};1-\alpha]} \tag{4.87}$$

where $\mathcal{T}_{\rm eq} g = g(\mathcal{T}_{\rm eq} x_t)$ and similarly for $\mathcal{T}_{\rm eq} g'$. Using that $S[\mathcal{T}_{\rm eq} x, \mathcal{T}_{\rm eq} \mathrm{i}\hat{x}; 1-\alpha] = S[x, \mathrm{i}\hat{x}; \alpha]$, and applying the transformation $\mathcal{T}_{\rm eq}$ to the function of x_t and $\mathrm{i}\hat{x}_{t'}$ to be averaged, one has

$$\begin{aligned} R_{1-\alpha}(t,t') &= \langle x_{-t} \Big\{ [\mathrm{i}\hat{x}_{-t'} - D^{-1} g_{-t'}^{-2} \mathrm{d}_{-t'}^{(\alpha)} x_{-t'}] g_{-t'}^2 \\ &\qquad -2(1-\alpha) g_{-t'} g'_{-t'}] \Big\} \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} \\ &= \langle x_{-t} [\mathrm{i}\hat{x}_{-t'} g_{-t'}^2 - 2(1-\alpha) g_{-t'} g'_{-t'} \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} \\ &\quad -D^{-1} \langle x_{-t} \mathrm{d}_{-t'}^{(\alpha)} x_{-t'}] \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} \\ &= \langle x_{-t} [\mathrm{i}\hat{x}_{-t'} g_{-t'}^2 - 2\alpha g_{-t'} g'_{-t'} \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} \\ &\quad -\langle x_{-t} 2(1-2\alpha) g_{-t'} g'_{-t'} \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} - D^{-1} \langle x_{-t} \mathrm{d}_{-t'}^{(\alpha)} x_{-t'}] \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} \end{aligned}$$

Identifying $R_\alpha(-t,-t')$ in the first term in the rhs and using now $\mathrm{d}_{-t}^{(\alpha)} x_{-t} = \mathrm{d}_{-t} x_{-t} - 2D(1-2\alpha) g_{-t} g'_{-t}$,

$$R_{1-\alpha}(t,t') = R_\alpha(-t,-t') + D^{-1} \langle x_{-t} \mathrm{d}_{t'} x_{-t'} \rangle_{S[\mathrm{i}\hat{x},x;\alpha]} \,. \tag{4.88}$$

Using the fact that the physics cannot depend on the discretisation parameter [see the discussion below the drifted Fokker-Planck Eq. (2.213)], we can drop the irrelevant index α (or $1-\alpha$) in the linear response and the correlation function and

$$R(t,t') = R(-t,-t') + D^{-1} \partial_{t'} C(-t,-t') \,. \tag{4.89}$$

We apply the transformation $\mathcal{T}_{\rm eq}$ once again on the correlation function in the rhs to show $C(-t,-t') = C(t,t')$. Owing to the time-translational invariance of equilibrium dynamics, $C(t,t') = C(\tau)$ and $R(t,t') = R(\tau)$ where $\tau \equiv t - t'$, and to the causality of the response $R(\tau) = 0$ for $\tau < 0$, we obtain the celebrated fluctuation-dissipation theorem (FDT)

$$R(\tau) = -D^{-1} \theta(\tau) \mathrm{d}_\tau C(\tau) = -\beta \theta(\tau) \mathrm{d}_\tau C(\tau) \,. \tag{4.90}$$

Here $\theta(\tau)$ is the Heaviside step function.

4.6.2 Fluctuation theorems

Let us assume that the system is initially prepared in thermal equilibrium with respect to the potential $V(x, \lambda_{-\mathcal{T}})$[23]. The expression for the deterministic part of

[23] This is in fact a restriction on the initial velocities, $\dot{x}_{-\mathcal{T}}$, that are to be taken from the Maxwell distribution with temperature β^{-1}, independently of the positions $x_{-\mathcal{T}}$. These latter can be chosen from a generic distribution since the initial potential can be tailored at will through the λ dependence of V.

the MSRJD action functional is

$$\begin{aligned} S_{\rm det}[x,\hat{x};\lambda,\mathrm{f}] &= -\beta\mathcal{H}([x_{-\mathcal{T}}],\lambda_{-\mathcal{T}}) - \ln\mathcal{Z}(\lambda_{-\mathcal{T}}) \\ &\quad - \int_u i\hat{x}_u\left[m\ddot{x}_u + V'(x_u,\lambda_u) - \mathrm{f}_u[x]\right] \ , \end{aligned}$$

where $\mathcal{H}([x_t],\lambda_t) \equiv \frac{1}{2}m\dot{x}_t^2 + V(x_t,\lambda_t)$ and f is a non-conservative force applied on the system. The external work done on the system along a given trajectory between times $-\mathcal{T}$ and $\mathcal{T}$ is given by

$$W[x;\lambda,\mathrm{f}] \equiv \int_A^B dE = \int_t \partial_t\lambda_t\ \partial_\lambda V(x_t,\lambda_t) + \int_t \dot{x}_t f[x_t,t] \tag{4.91}$$

where we take into account the time variation of the parameter λ.

Fluctuation Theorem 1.

The transformation $\mathcal{T}_{\rm eq}$ does not leave $S_{\rm det}$ invariant but yields

$$S_{\rm det}[x,\hat{x};\lambda,\mathrm{f}] \overset{\mathcal{T}_{\rm c}}{\longmapsto} S_{\rm det}[x,\hat{x};\bar{\lambda},\mathrm{f_r}] - \beta\Delta\mathcal{F} - \beta W[x;\bar{\lambda},\mathrm{f_r}] \tag{4.92}$$

where $S_{\rm det}[x,\hat{x};\bar{\lambda},\mathrm{f_r}]$ is the MSRJD action of the system that is prepared (in equilibrium) and evolves under the time-reversed protocol ($\bar{\lambda}(u) \equiv \lambda(-u)$) and external forces ($\mathrm{f_r}([x],u) \equiv \mathrm{f}([\bar{x}],-u)$). $\Delta\mathcal{F}$ is the change in free energy: $\beta\Delta\mathcal{F} = \ln\mathcal{Z}(\lambda(-\mathcal{T})) - \ln\mathcal{Z}(\lambda(\mathcal{T}))$ between the initial and the final 'virtual' equilibrium states. W is defined above. The dissipative part of the action, $S_{\rm diss}$ does not involve λ and it is still invariant under $\mathcal{T}_{\rm eq}$. This means that, contrary to the external forces, the interaction with the bath is not time-reversed: the friction is still dissipative after the transformation. This immediately yields

$$\langle A[x,\hat{x}]\rangle_{S_{\rm c}[x,\hat{x};\lambda,\mathrm{f}]} = e^{-\beta\Delta\mathcal{F}}\langle A[\mathcal{T}_{\rm eq}x,\mathcal{T}_{\rm eq}\hat{x}]e^{-\beta W[x;\bar{\lambda},\mathrm{f_r}]}\rangle_{S_{\rm c}[x,\hat{x};\bar{\lambda},\mathrm{f_r}]} \tag{4.93}$$

for any functional A of x and $\hat{x}$. In particular for a local functional of the field, $A[x(t)]$, it leads to the Crooks relation [108]

$$\langle A[x(t)]\rangle_{S_{\rm c}[x,\hat{x};\lambda,\mathrm{f}]} = e^{-\beta\Delta\mathcal{F}}\langle A_{\rm r}[x(-t)]e^{-\beta W[x;\bar{\lambda},\mathrm{f_r}]}\rangle_{S_{\rm c}[x,\hat{x};\bar{\lambda},\mathrm{f_r}]} \ , \tag{4.94}$$

or also

$$\begin{aligned} &\langle A[x(t)]B[x(t')]\rangle_{S_{\rm c}[x,\hat{x};\lambda,\mathrm{f}]} \\ &\qquad = e^{-\beta\Delta\mathcal{F}}\langle A_{\rm r}[x(-t)]B_{\rm r}[x(-t')]e^{-\beta W[x;\bar{\lambda},\mathrm{f_r}]}\rangle_{S_{\rm c}[x,\hat{x};\bar{\lambda},\mathrm{f_r}]}. \end{aligned} \tag{4.95}$$

Setting $A[x,\hat{x}]=1$, we obtain the Jarzynski equality [99]

$$1 = e^{\beta\Delta\mathcal{F}}\langle e^{-\beta W[x;\lambda,\mathrm{f}]}\rangle_{S_\mathrm{c}[x,\hat{x};\lambda,\mathrm{f}]} \ . \tag{4.96}$$

Setting $A[x,\hat{x}]=\delta(W-W[x;\lambda,\mathrm{f}])$ we obtain the transient fluctuation theorem

$$P(W) = P_\mathrm{r}(-W)\ e^{\beta(W-\Delta\mathcal{F})} \ , \tag{4.97}$$

where $P(W)$ is the probability for the external work done between $-\mathcal{T}$ and $\mathcal{T}$ to be W given the protocol $\lambda(t)$ and the non-conservative force $\mathrm{f}([x],t)$. $P_\mathrm{r}(W)$ is the same probability, given the time-reversed protocol $\bar{\lambda}$ and time-reversed force f_r.

Fluctuation Theorem 2.

The result we prove in the following lines is not restricted to Langevin processes with an equilibrium dissipative bath. It applies to generic classical equations of motion, with or without stochastic noise. In short, the proof consists in applying time-reversal on the system and yields an equality between observables and their time-reversed counterparts in a so-called backward (B) process in which the system is prepared in equilibrium with respect to the final conditions of the forward process and is evolved according to the time-reversed equations of motions and protocol. Let us rewrite the action as

$$\begin{aligned} S_\mathrm{c}[x,\hat{x},\lambda] \ &= \ -\beta\mathcal{H}(x_{-\mathcal{T}},\dot{x}_{-\mathcal{T}},\lambda_{-\mathcal{T}}) - \int_u i\hat{x}_u\ \mathrm{Eq}([x_u],\lambda_u) \\ &\quad + \frac{1}{2}\int_u\int_v i\hat{x}_u\ \beta^{-1}\Gamma_{uv}\ i\hat{x}_v - \ln\mathcal{Z}(\lambda_{-\mathcal{T}}) \ , \end{aligned}$$

and apply the following time-reversal of the fields

$$\mathcal{T}_\mathrm{tr} \equiv \left\{ \begin{array}{rcl} x_u & \mapsto & x_{-u} \ , \\ i\hat{x}_u & \mapsto & i\hat{x}_{-u} \ . \end{array} \right. \tag{4.98}$$

This yields

$$\begin{aligned} S_\mathrm{c}[x,\hat{x},\lambda] \ &\mapsto \ -\beta\mathcal{H}([x_\mathcal{T}],\bar{\lambda}_\mathcal{T}) - \int_u i\hat{x}_u\mathrm{Eq}_\mathrm{r}([x_u],\bar{\lambda}_u) \\ &\quad + \frac{1}{2}\int_u\int_v i\hat{x}_u\ \beta^{-1}\Gamma_{uv}\ i\hat{x}_v - \ln\mathcal{Z}(\lambda_{-\mathcal{T}}) \end{aligned}$$

or, by introducing zeroes:

$$\begin{aligned} &-\beta W_\mathrm{r} - \beta\mathcal{H}([x_{-\mathcal{T}}],\bar{\lambda}_{-\mathcal{T}}) - \int_u i\hat{x}_u\mathrm{Eq}_\mathrm{r}([x_u],\bar{\lambda}_u) \\ &\quad + \frac{1}{2}\int_u\int_v i\hat{x}_u\ \beta^{-1}\Gamma_{uv}\ i\hat{x}_v - \beta\Delta\mathcal{F} - \ln\mathcal{Z}(\bar{\lambda}_{-\mathcal{T}}) \ , \end{aligned} \tag{4.99}$$

where $\Delta\mathcal{F} \equiv \mathcal{F}(\lambda_\mathcal{T}) - \mathcal{F}(\lambda_{-\mathcal{T}})$ is the free-energy difference between the two 'virtual' equilibrium states corresponding to $\lambda_\mathcal{T}$ and $\lambda_{-\mathcal{T}}$. $W_\mathrm{r} \equiv \mathcal{H}([x_\mathcal{T}], \bar{\lambda}_\mathcal{T}) - \mathcal{H}([x_{-\mathcal{T}}], \bar{\lambda}_{-\mathcal{T}})$ is the work applied on the system that evolves with the time-reversed equation of motion $\mathrm{Eq_r}$ and under the time-reversed protocol $\bar{\lambda}$. In particular and contrary to the previous paragraph, the friction is no longer dissipative after the transformation. This defines the backward (B) process. Finally, for any observable $A[x, \hat{x}]$ we get the relation

$$\langle A[x, \hat{x}] \rangle_F = e^{-\beta\Delta\mathcal{F}} \langle A[\bar{x}, \overline{\hat{x}}] e^{-\beta W_\mathrm{r}} \rangle_B \ . \tag{4.100}$$

In particular, for two-time correlations, it reads

$$\langle A[x(t)] B[x(t')] \rangle_F = e^{-\beta\Delta\mathcal{F}} \langle A_\mathrm{r}[x(-t)] B_\mathrm{r}[x(-t')] e^{-\beta W_\mathrm{r}} \rangle_B \ . \tag{4.101}$$

Setting $A[x, \hat{x}] = \delta(W - W[x; \lambda, f])$ we obtain the transient fluctuation theorem

$$P_F(W) = P_B(-W) \ e^{\beta(W - \Delta\mathcal{F})} \ , \tag{4.102}$$

where $P_F(W)$ is the probability for the external work done between $-\mathcal{T}$ and $\mathcal{T}$ to be W in the forward process. $P_B(W)$ is the same probability in the backward process.

4.7 Equations on correlations and linear responses

Take any Langevin process in the MSRJD path-integral formalism. From the following four identities

$$\left\langle \frac{\delta i\hat{x}(t)}{\delta i\hat{x}(t')} \right\rangle = \left\langle \frac{\delta x(t)}{\delta x(t')} \right\rangle = \delta(t - t') \ , \qquad \left\langle \frac{\delta x(t)}{\delta i\hat{x}(t')} \right\rangle = \left\langle \frac{\delta i\hat{x}(t)}{\delta x(t')} \right\rangle = 0 \ , \tag{4.103}$$

where the angular brackets indicate an average with the MSRJD weight, after an integration by parts, one derives four equations

$$\left\langle x(t) \frac{\delta S}{\delta x(t')} \right\rangle = -\delta(t - t') \ , \qquad \left\langle i\hat{x}(t) \frac{\delta S}{\delta i\hat{x}(t')} \right\rangle = -\delta(t - t') \ , \tag{4.104}$$

$$\left\langle x(t) \frac{\delta S}{\delta i\hat{x}(t')} \right\rangle = 0 \ , \qquad \left\langle i\hat{x}(t) \frac{\delta S}{\delta x(t')} \right\rangle = 0 \ . \tag{4.105}$$

The second and third one read

$$\left\langle i\hat{x}(t)\left\{m\ddot{x}(t')+\int dt''\ \gamma(t'-t'')\ \dot{x}(t'')+V'[x(t')]\right\}\right\rangle$$
$$+k_BT\int dt''\ \Gamma(t'-t'')\ \langle i\hat{x}(t)i\hat{x}(t'')\rangle=\delta(t-t')\ ,$$
$$\left\langle x(t)\left\{m\ddot{x}(t')+\int dt''\ \gamma(t'-t'')\ \dot{x}(t'')+V'[x(t')]\right\}\right\rangle$$
$$+k_BT\int dt''\ \Gamma(t'-t'')\ \langle x(t)i\hat{x}(t'')\rangle=0\ , \tag{4.106}$$

while the other ones, once causality is used (basically $\langle x(t')i\hat{x}(t)\rangle = 0$ for $t > t'$ and $\langle i\hat{x}(t)i\hat{x}(t')\rangle = 0$) do not yield further information. All terms are easily identified with the four types of two-time correlations apart from the ones that involve the potential and are not necessarily quadratic in the fields. The linear terms in two-time functions can be put together after identifying the **free-operator**

$$G_0^{-1}(t',t'')=\delta(t'-t'')m\frac{d^2}{dt''^2}+\gamma(t'-t'')\frac{\partial}{\partial t''} \tag{4.107}$$

The non-linear terms can be approximated in a number of ways: perturbation theory in a small parameter, Gaussian approximation of the MSRJD action, self-consistent approximations, etc. The choice should be dictated by some knowledge on the system's behavior one wishes to reproduce. In short then

$$0=\int dt''G_0^{-1}(t',t'')C(t'',t)+\langle x(t)V'[x(t')]\rangle+k_BT\int dt''\Gamma(t'-t'')R(t,t'')\ ,$$
$$\delta(t-t')=\int dt''G_0^{-1}(t',t'')R(t'',t)+\langle i\hat{x}(t)V'[x(t')]\rangle\ . \tag{4.108}$$

4.8 The instanton calculation

The path-integral formalism yields an alternative calculation of the Kramers escape time, the Arrhenius exponential law and its prefactor that, in principle, is easier to generalize to multidimensional cases. For the sake of simplicity let us focus on the over-damped limit in which we neglect inertia. We first rederive the Arrhenius exponential using a simplified saddle-point argument, and then show how Kramers calculation can be recovered by correctly computing the fluctuations around this

saddle point. We start from the following representation of the probability to reach the top of the barrier from the potential well:

$$P(x_{\max}, t|x_{\min}) = \left\langle \int_{x(0)=x_{\min}}^{x(t)=x_{\max}} \mathcal{D}x\ \delta(\xi - \mathrm{Eq}[x])\ \left|\det\left(\frac{\delta \mathrm{Eq}[x](t)}{\delta x(t')}\right)\right| \right\rangle_{\xi} .$$

then, for a Gaussian white noise ξ, we integrate over the noise and the auxiliary variable $i\hat{x}$ to find [111, 112]:

$$P(x_{\max}, t|x_{\min}) = \int_{x(0)=x_{\min}}^{x(t)=x_{\max}} \mathcal{D}x\ e^{-\frac{1}{4k_BT}\int_0^t dt'(\dot{x}+V'(x))^2 + \frac{1}{2}\int_0^t dt' V"(x)}$$

the Onsager-Machlup form, in the Stratonovich convention. In the low T limit the term coming from the determinant is negligible. Expanding the square, we find a total derivative contribution to the integral equal to

$$\text{1st contribution} = 2[V(x_{\max}) - V(x_{\min})] \tag{4.109}$$

plus the sum of two squares: $\int_0^t dt'\ [\dot{x}^2 + (V'(x))^2]$, i.e a positive definite term. For small T, the path, x^*, contributing the most to the transition probability is such that this integral is minimized. Using standard rules of functional derivation one finds

$$\frac{d^2x^*}{dt'^2} = V'(x^*)V''(x^*) \quad \Rightarrow \quad \dot{x}^* = \pm V'(x^*) .$$

The result is found by multiplying the equation by $\dot{x}$ in such as way that one constructs

$$\frac{d\dot{x}^2}{dt} = \frac{d[V'(x)]^2}{dt} , \tag{4.110}$$

and setting $\dot{x}(t) = 0$ and $V'(x^*(t)) = 0$ at the maximum of the barrier, i.e. at time t, to eliminate the constant of integration. Moreover, in order to be compatible with the boundary conditions $x^*(0) = x_{\min}$ and $x(t) = x_{\max}$, the + solution must be chosen,

$$\dot{x}^* = V'(x) \tag{4.111}$$

for which both terms are positive in the relevant region of variation of x. This trajectory corresponds to an equivalent mechanical problem in which one has overdamped zero-temperature motion in the inverted potential $-V(x)$. The 'action' of this trajectory is

$$\int_0^t dt' \left[\dot{x}^{*2} + (V'(x^*))^2\right] = 2\int_0^t dt' \dot{x}^* V'(x^*) = 2[V(x_{\max}) - V(x_{\min})] ,$$

where in each term we replaced one factor using the equation of motion for the solution x^*, that doubles the contribution of the total derivative above. Hence,

$$P(x_{\max}, t|x_{\min}) \approx e^{-\beta[V(x_{\max})-V(x_{\min})]},$$

independently of t, as in eq. (2.173).

The Gaussian fluctuations around this saddle-point calculation yield an estimate for the prefactor.

This type of calculation can be readily extended to cases in which the noise ξ has temporal correlations, or non Gaussian tails, and to see how these effects change the Arrhenius result. The calculation of the attempt frequency is done using the standard dilute gas instanton approximation developed by several authors but we will not discuss it here.

The path-integral that we have just computed is a sum over the subset of noise trajectories that lead from the initial condition to a particular final condition that we imposed. Imposing a boundary condition in the future destroys the causal character of the theory.

In a one dimensional problem as the one treated in this Section there is only one possible 'reaction path'. In a multidimensional problem, instead, a system can transit from one state to another following different paths that go through different saddle-points. The lowest saddle-point might not be the most convenient way to go and which is the most favorable path is, in general, difficult to establish.

A Conventions

A.1 Fourier transform

The convention for the Fourier transform is

$$f(\tau) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, e^{-i\omega\tau}\, f(\omega)\,, \tag{A.1}$$

$$f(\omega) = \int_{-\infty}^{\infty} d\tau\, e^{+i\omega\tau}\, f(\tau)\,. \tag{A.2}$$

The Fourier transform of the theta function reads

$$\theta(\omega) = i\mathrm{vp}\frac{1}{\omega} + \pi\delta(\omega)\,. \tag{A.3}$$

The convolution is

$$[f\cdot g](\omega) = f\otimes g(\omega) \equiv \int \frac{d\omega'}{2\pi} f(\omega')g(\omega-\omega')\,. \tag{A.4}$$

A.2 Discretized delta function

Let us discretize time $t_k = \epsilon k$ with k an integer and ϵ the time-step. A discrete representation of the Dirac delta function is

$$\delta_\epsilon(t) = \begin{cases} 1/(\epsilon) & -\epsilon/2 < t < \epsilon/2 \\ 0 & \text{otherwise} \end{cases} \tag{A.5}$$

One easily checks that $\lim_{\epsilon\to 0}\delta_\epsilon(t) = \infty$ for $t\to 0$ and $\lim_{\epsilon\to 0}\delta_\epsilon(t) = 0$ otherwise, and $\int_{-\infty}^{\infty} dt'\delta_\epsilon(t') = 1$.

B Additive noise: Stratonovich prescription

The Langevin equation is a stochastic differential equation and one can give a rigorous meaning to it by specifying a particular discretization scheme. We adopt

here the Stratonovitch prescription where the rules of conventional differential calculus can be used. This corresponds to a mid-point discretization scheme and is coherent with the convention $\theta(0) = 1/2$ in the continuum limit. The presentation is taken from [94].

Let us divide the time interval $[-\mathcal{T}, \mathcal{T}]$ into $N+1$ infinitesimal slices of width $\epsilon \equiv 2\mathcal{T}/(N+1)$. The discretized times are $t_k = -\mathcal{T} + k\epsilon$ with $k = 0, ..., N+1$. The discretized version of $x(t)$ is $x_k \equiv x(t_k)$. The continuum limit is achieved by sending N to infinity and keeping $(N+1)\epsilon = 2\mathcal{T}$ constant. Given some initial conditions $x_{\rm i}$ and $\dot{x}_{\rm i}$, we set $x_1 = x_{\rm i}$ and $x_0 = x_{\rm i} - \epsilon \dot{x}_{\rm i}$ meaning that the first two times (t_0 and t_1) are reserved for the integration over the initial conditions whereas the N following ones correspond to the stochastic dynamics given by the discretized Langevin equation:

$$\begin{aligned} {\rm Eq}_k \equiv\ & m\frac{x_{k+2} - 2x_{k+1} + x_k}{\epsilon^2} - F_{k+2}(x_{k+2}, x_{k+1}, ...) \\ & + \sum_{l=1}^{k} \gamma_{kl}(x_{l+2} - x_{l+1}) = \xi_{k+1} \ , \end{aligned} \tag{B.1}$$

defined for $k = 0, ..., N-1$. The notation γ_{kl} stands for $\gamma_{kl} \equiv \epsilon^{-1} \int_{0^-}^{\epsilon} du \gamma(t_k - t_l + u)$ The ξ_k $(k = 1, ..., N)$ are independent Gaussian random variables with variance $\langle \xi_k \xi_l \rangle = \beta^{-1} \Gamma_{kl}$ where $\Gamma_{kl} \equiv \gamma_{kl} + \gamma_{lk}$. Inspecting the equation above, we notice that the value of x_k depends on the realization of the previous noise realisation ξ_{k-1} so that there is no need to specify ξ_0 and ξ_N. In the Markovian limit, one has $\gamma_{kl} = \epsilon^{-1}\gamma_0 \delta_{kl}$, $\langle \xi_k \xi_l \rangle = 2\gamma_0 \beta^{-1} \epsilon^{-1} \delta_{kl}$ where δ is the Kronecker delta, and

$$\begin{aligned} {\rm Eq}_k \equiv\ & m\frac{x_{k+2} - 2x_{k+1} + x_k}{\epsilon^2} - \overline{F_{k+2}}(x_{k+2}, x_{k+1}, ...) \\ & + \gamma_0 \frac{x_{k+2} - x_{k+1}}{\epsilon} = \xi_{k+1} \ . \end{aligned} \tag{B.2}$$

B.1 Construction of the MSRJD action

The probability density P for a complete field history $(x_0, x_1, ..., x_{N+1})$ is set by the relation

$$\begin{aligned} & P(x_0, x_1, ..., x_{N+1}) dx_0 dx_1 ... dx_{N+1} \\ & \qquad = P_{\rm i}(x_{\rm i}, \dot{x}_{\rm i}) dx_{\rm i} d\dot{x}_{\rm i}\ P_{\rm n}(\xi_1, \xi_2, ..., \xi_N) d\xi_1 d\xi_2 ... d\xi_N \ . \end{aligned} \tag{B.3}$$

$P_{\rm i}$ is the initial probability distribution of the field. The probability for a given noise history to occur between times t_1 and t_N is given by

$$P_{\rm n}(\xi_1,...,\xi_N) \;=\; \mathcal{M}_N^{-1}\; e^{-\frac{1}{2}\sum_{k,l=1}^{N}\xi_k\;\beta\Gamma_{kl}^{-1}\;\xi_l} \tag{B.4}$$

with the normalization $\mathcal{M}_N \equiv \left(\frac{(2\pi)^N}{\det_{kl}\beta\Gamma_{kl}^{-1}}\right)^{1/2}$. From eq. (B.3), one gets

$$P(x_0,x_1,...,x_{N+1}) = |\mathcal{J}_N| P_{\rm i}(x_1,\frac{x_1-x_0}{\epsilon}) P_{\rm n}({\rm Eq}_0,...,{\rm Eq}_{N-1}) \;\;, \tag{B.5}$$

with the Jacobian

$$\mathcal{J}_N \equiv \det\frac{\partial(x_{\rm i},\dot{x}_{\rm i},\xi_1,\ldots,\xi_N)}{\partial(x_0,x_1,\ldots,x_{N+1})} = \det\frac{\partial(x_{\rm i},\dot{x}_{\rm i},{\rm Eq}_0,\ldots,{\rm Eq}_{N-1})}{\partial(x_0,x_1,\ldots,x_{N+1})}\;, \tag{B.6}$$

The expression (B.4) for the noise history probability reads, after a Hubbard-Stratonovitch transformation that introduces the auxiliary variables $\hat{x}_k$ ($k=1,...,N$),

$$\begin{aligned} P_{\rm n}(\xi_1,...,\xi_N) &= \mathcal{N}_N^{-1}\int d\hat{x}_1...d\hat{x}_N e^{-\sum_k i\hat{x}_k\xi_k+\frac{1}{2}\sum_{kl} i\hat{x}_k\beta^{-1}\Gamma_{kl}i\hat{x}_l} \\ &= \mathcal{N}_N^{-1}\int d\hat{x}_0...d\hat{x}_{N+1}\delta(\hat{x}_0)\delta(\hat{x}_{N+1})\; e^{-\sum_k i\hat{x}_k{\rm Eq}_{k-1}+\frac{1}{2}\sum_{kl} i\hat{x}_k\beta^{-1}\Gamma_{kl}i\hat{x}_l}\;, \end{aligned}$$

with $\mathcal{N}_N \equiv (2\pi)^N$. In the last step, we replaced ξ_k by ${\rm Eq}_{k-1}$ and we allowed integrations over $\hat{x}_0$ and $\hat{x}_{N+1}$ at the cost of introducing delta functions. Notice that the Hubbard-Stratonovitch transformation allows for some freedom in the choice of the sign in front of $i\hat{x}_k$ in the exponent. Together with eq. (B.5) this gives

$$\begin{aligned} P(x_0,x_1,...,x_{N+1}) = \mathcal{N}_N^{-1}\,|\mathcal{J}_N|\int d\hat{x}_0...d\hat{x}_{N+1} \\ \times e^{-\sum_k i\hat{x}_k{\rm Eq}_{k-1}+\frac{1}{2}\sum_{kl} i\hat{x}_k\beta^{-1}\Gamma_{kl}i\hat{x}_l+\ln P_{\rm i}\left(x_1,\frac{x_1-x_0}{\epsilon}\right)} \end{aligned} \tag{B.7}$$

that in the continuum limit becomes

$$P[x] \;=\; \mathcal{N}^{-1}e^{\ln P_{\rm i}+\ln|\mathcal{J}[x]|}\int\mathcal{D}[\hat{x}]e^{-\int du\;\; i\hat{x}(u){\rm Eq}([x],u)+\frac{1}{2}\int duv i\hat{x}(u)\beta^{-1}\Gamma(u-v)i\hat{x}(v)}\;,$$

with the boundary conditions $\hat{x}(-\mathcal{T})=\hat{x}(\mathcal{T})=0$ and where all the integrals over time run from $-\mathcal{T}$ to $\mathcal{T}$. In the following, unless otherwise stated, we will simply

denote them by $\int$. The infinite prefactor $\mathcal{N} \equiv \lim_{N\to\infty} (2\pi)^N$ can be absorbed in the definition of the measure:

$$\mathcal{D}[x,\hat{x}] = \lim_{N\to\infty} \frac{1}{(2\pi)^N} \prod_{k=0}^{N+1} dx_k d\hat{x}_k \ . \tag{B.8}$$

B.2 Evaluation of the Jacobian

In this section we take the continuum limit of the Jacobian defined in eq. (B.6). In the additive noise case, we start from

$$\begin{aligned}
\mathcal{J}_N &= \det \frac{\partial(x_{\rm i}, \dot{x}_{\rm i}, {\rm Eq}_0, \ldots, {\rm Eq}_{N-1})}{\partial(x_0, x_1, \ldots, x_{N+1})} \\
&= \det \begin{bmatrix}
0 & 1 & 0\ldots & & & \\
-1/\epsilon & 1/\epsilon & 0\ldots & & & \\
\frac{\partial {\rm Eq}_0}{\partial x_0} & \frac{\partial {\rm Eq}_0}{\partial x_1} & \frac{\partial {\rm Eq}_0}{\partial x_2} & 0\ldots & & \\
\frac{\partial {\rm Eq}_1}{\partial x_0} & \frac{\partial {\rm Eq}_1}{\partial x_1} & \frac{\partial {\rm Eq}_1}{\partial x_2} & \frac{\partial {\rm Eq}_1}{\partial x_3} & 0\ldots & \\
\ldots & & & & & 0 \\
\frac{\partial {\rm Eq}_{N-1}}{\partial x_0} & & \ldots & & & \frac{\partial {\rm Eq}_{N-1}}{\partial x_{N+1}}
\end{bmatrix} \\
&= \frac{1}{\epsilon} \det \begin{bmatrix}
\frac{\partial {\rm Eq}_0}{\partial x_2} & 0\ldots & & \\
\frac{\partial {\rm Eq}_1}{\partial x_2} & \frac{\partial {\rm Eq}_1}{\partial x_3} & 0\ldots & \\
\ldots & & & 0 \\
\frac{\partial {\rm Eq}_{N-1}}{\partial x_2} & \ldots & & \frac{\partial {\rm Eq}_{N-1}}{\partial x_{N+1}}
\end{bmatrix} = \frac{1}{\epsilon} \prod_{k=0}^{N-1} \frac{\partial {\rm Eq}_k}{\partial x_{k+2}}
\end{aligned} \tag{B.9}$$

We can safely drop the overall $1/\epsilon$ factor since it can be included in the normalization. Notice that causality manifests itself in the lower triangular structure of the last matrix involved. In the continuous notation, $\lim_{N\to\infty} \mathcal{J}_N$ reads

$$\mathcal{J}[x] = \det_{uv} \left[\frac{\delta {\rm Eq}([x],u)}{\delta x(v)} \right] \ . \tag{B.10}$$

B.2.1 Markov case

Let us first consider the Markovian case in which the friction term has no memory and the force F is a local functional of x which can carry a time-dependence. Defining F' as $\delta F_u[x_u]/\delta x_v \equiv F'_u[x_u]\delta(u-v)$, the Jacobian reads

$$\mathcal{J}[x] = \det_{uv} \left[\left(m\partial_u^2 + \gamma_0 \partial_u - F'_u[x_u] \right) \delta_{u-v} \right] \ . \tag{B.11}$$

Now let us write $\det_{uv}\left[\left(m\partial_u^2+\gamma_0\partial_u-F'_u[x_u]\right)\delta_{u-v}\right]$

$$\begin{aligned}
&= \det_{uv}\left[(m\partial_u^2+\gamma_0\partial_u)\delta_{u-v}\right]\ \det_{uv}\left[\delta_{u-v}-\int_w G_{u-w}F'_w[x_w]\delta_{w-v}\right]\\
&= \det_{uv}\left[(m\partial_u^2+\gamma_0\partial_u)\delta_{u-v}\right]\ \exp \mathrm{Tr}_{uv}\ln\left[\delta_{u-v}-G_{u-v}F'_v[x_v]\right]\\
&= \det_{uv}\left[(m\partial_u^2+\gamma_0\partial_u)\delta_{u-v}\right]\ \exp-\sum_{n=1}^{\infty}\frac{1}{n}\int_u\left(\underbrace{M\circ M\circ ...\circ M}_{n\ \text{times}}\right)_{uu}\ , \qquad \text{(B.12)}
\end{aligned}$$

where we used the matrix notation $M_{uv}\equiv G_{u-v}F'_v[x_v]$ and product $\circ$. G is the retarded Green function solution of

$$\left[m\partial_u^2+\gamma_0\partial_u\right]G(u-v)=\delta(u-v)\ , \qquad \text{(B.13)}$$

which reads

$$G(t)=\frac{1}{\gamma_0}\left[1-e^{-\gamma_0 t/m}\right]\theta(t)\ . \qquad \text{(B.14)}$$

Since $\theta(u-v)\theta(v-u)=0$, $\forall\ u\neq v$, the $n\geq 2$ terms do not contribute to the sum in eq. (B.12). Furthermore, $G(t=0)=0$ for finite values of m[24], implying that the $n=1$ term is zero as well. Therefore we established

$$\mathcal{J}[x]=\det_{uv}\left[m\partial_u^2+\gamma_0\partial_u\right]\delta(u-v)\ . \qquad \text{(B.15)}$$

This means that the functional determinant is simply a field independent constant. One can easily generalize this result for time dependent and non potential forces.

B.2.2 Non Markov case

Within the Stratonovich prescription, the determinant can be seen as the result of a Gaussian integration over Grassmannian conjugate fields c and c^*. Let us first recall the discretized expression of the Jacobian obtained in eq. (B.9):

$$\mathcal{J}_N=\frac{1}{\epsilon}\det_{kl}\left[\frac{\partial \mathrm{Eq}_k}{\partial x_{l+2}}\right]\ , \qquad \text{(B.16)}$$

[24] If we send $m\to 0$ at the end of the calculation, we still get $G(0)=0$ and a constant Jacobian. However, if m is set to 0 from the begining then $G(t)=\theta(t)/\gamma_0$ and $G(0)=1/(2\gamma_0)$ in our conventions. This leads to the so-called Jacobian extra-term in the action: $-1/(2\gamma_0)\int_u F'_u[x_u]$. It is invariant under time-reversal of the field $x_u\mapsto x_{-u}$ as long as F' is itself time-reversal invariant.

where k and l run from 0 to $N-1$. Introducing ghosts, it can be put in the form

$$\begin{aligned}\mathcal{J}_N &= \frac{1}{\epsilon}\int dc_2 dc_0^* ... dc_{N+1} dc_{N-1}^*\; e^{\sum_{k=0}^{N-1}\sum_{l=2}^{N+1} c_k^* \frac{\partial \mathrm{Eq}_k}{\partial x_l} c_l} \\ &= \frac{1}{\epsilon}\int dc_0 dc_0^* ... dc_{N+1} dc_{N+1}^*\; e^{\sum_{k=0}^{N+1}\sum_{l=0}^{N+1} c_k^* \frac{\partial \mathrm{Eq}_k}{\partial x_l} c_l}\; c_0 c_1 c_N^* c_{N+1}^* \,,\end{aligned} \tag{B.17}$$

where in the last step, we allowed integration over c_0, c_1, c_N^* and c_{N+1}^* at the cost of introducing delta functions (remember that for a Grassmann number c, the delta function is achieved by c itself). In the continuum limit, dropping the overall $1/\epsilon$ constant (and infinite) factor, this yields

$$\mathcal{J}[x] = \int \mathcal{D}[c, c^*] e^{K[c,c^*,x]} \tag{B.18}$$

with

$$K[c, c^*, x] \equiv \int_{-T}^{T} dduv c^*(u) \frac{\delta \mathrm{Eq}([x], u)}{\delta x(v)} c(v) \,, \tag{B.19}$$

and with the extra boundary conditions: $c(-T) = \dot{c}(-T) = c^*(T) = \dot{c}^*(T) = 0$. Plugging the Langevin equation (2.10), we have

$$\frac{\delta \mathrm{Eq}_u[x]}{\delta x_v} = m\partial_u^2 \delta_{u-v} - \frac{\delta F_u[x]}{\delta x_v} + \int_w \gamma_{w-v} \partial_w \delta_{w-v} \,.$$

The kinetic term in $K[c, c^*, x]$ can be re-written

$$\int_u \int_v c_u^* \, \partial_u^2 \delta_{u-v} \, c_v = \int_u c_u^* \, \partial_u^2 c_u + \frac{1}{2}\left[\dot{c}^* c - c^* \dot{c}\right]_{-T}^{T} + \frac{1}{2}\delta_0 \left[c^* c\right]_{-T}^{T} \,.$$

The last two terms in the rhs vanishes by use of the boundary conditions ($c_{-T} = \dot{c}_{-T} = c_T^* = \dot{c}_T^* = 0$). The retarded friction can be re-written

$$\int_u \int_v c_u^* \, \partial_u \gamma_{u-v} \, c_v - \frac{1}{2}\int_u c_u^* \left[\gamma_{u+T} \, c_{-T} - \gamma_{u-T} \, c_T\right] \,,$$

where the second line vanishes identically for two reasons: the boundary condition ($c_{-T} = 0$) kills the first part and the causality of the friction kernel ($\gamma_u = 0 \; \forall \, u < 0$) suppresses the second one. Notice that if there is a Dirac contribution to γ centered

at $u = 0$ like in the Markovian case, the other boundary condition ($c^*_{-T} = 0$) finishes to cancel the second part. Finally we have

$$K[c, c^* x] = \int_u c^*_u \, \partial^2_u c_u + \int_u \int_v c^*_u \left[\partial_u \gamma_{u-v} - \frac{\delta F_u[x]}{\delta x_v} \right] c_v \ . \tag{B.20}$$

B.3 Multiplicative noise

The discretized Langevin equation reads:

$$\begin{aligned} \mathrm{Eq}_k \ \equiv \ & m \frac{x_{k+2} - 2x_{k+1} + x_k}{\epsilon^2} - F_{k+2}(x_{k+2}, x_{k+1}, ...) \\ & + M'(x_k) \sum_{l=1}^{k} \gamma_{kl} M'(x_l)(x_{l+2} - x_{l+1}) = M'(\tilde{x}_k) \xi_{k+1} \ , \end{aligned} \tag{B.21}$$

with the mid-point $\tilde{x}_k \equiv (x_{k+1} + x_k)/2$. The Jacobian is:

$$\mathcal{J}_N = \frac{1}{\epsilon} \det_{kl} \left[\frac{\partial \mathrm{Eq}_k}{\partial x_{l+2}} - \frac{M''(\tilde{x}_k)}{M'(\tilde{x}_k)} \mathrm{Eq}_k \ \frac{\delta_{k+1\, l+2} + \delta_{k\, l+2}}{2} \right] \ , \tag{B.22}$$

where k and l run from 0 to $N - 1$. Introducing ghosts, it can be put in the form

$$\mathcal{J}_N \ = \ \int dc_0 dc^*_0 ... dc_{N+1} dc^*_{N+1} \, c_0 c_1 c^*_N c^*_{N+1} \, e^{K_N} \ ,$$

with

$$K_N \ \equiv \ \sum_{k=0}^{N+1} \sum_{l=0}^{N+1} c^*_k \frac{\partial \mathrm{Eq}_k}{\partial x_l} \, c_l - \sum_{k=0}^{N+1} c^*_k \frac{M''(\tilde{x}_k)}{M'(\tilde{x}_k)} \mathrm{Eq}_k \ \frac{c_{k+1} + c_k}{2} \ . \tag{B.23}$$

In the continuum limit,

$$K \ \equiv \ \lim_{N \to \infty} K_N = \int_u \int_v c^*_u \frac{\delta \mathrm{Eq}_u[x]}{\delta x_v} \, c_v - \int_u c^*_u \frac{M''(x_u)}{M'(x_u)} \mathrm{Eq}_u[x] \, c_u \ , \tag{B.24}$$

with the boundary conditions $c(-\mathcal{T}) = \dot{c}(-\mathcal{T}) = 0$ and $c^*(\mathcal{T}) = \dot{c}^*(\mathcal{T}) = 0$.

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