Chapter 2

The kinetic theory of gases

So far, we have argued that statistical ensembles should be relevant to describe complex systems. But can we do better? Can we actually find systems that are complex enough that they are endowed with the kind of 'mixing dynamics' that we have said would guarantee the applicability of statistical mechanics and yet are simple enough that we can characterize them analytically? The answer is yes, and is largely due to the work of Boltzmann. In this chapter, we consider a dilute gas of interacting particles and construct explicitly its large-scale dynamics. We will:

- Show that it relaxes to equilibrium, in a way that we will make more precise later
- Characterize this relaxation to extract transport coefficients, such as viscosity, thermal conductivity, etc.

Explicitly, the model we consider comprises N classical particles in three space dimensions, interacting via a pair potential V and experiencing an external potential U. Its Hamiltonian is given by[1]:

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i) + \frac{1}{2}\sum_{i\neq j} V(\vec{q}_i - \vec{q}_j)\ . \tag{2.1}$$

In the Hamiltonian (2.1),

$$H_1 \equiv \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i) \tag{2.2}$$

describes the evolution of the N particles in the absence of interactions, which we will refer to as the free evolution. On the contrary, the blue term in Eq. (2.1) describes the pairwise interactions between the particles.

Our goal is to start from Eq. (2.1) and to demonstrate and characterize the relaxation to equilibrium, as illustrated in Fig. 2.1. The natural starting point to tackle this challenge is given by Hamilton's equations of motion but, clearly, the joint knowledge of the position and velocities of all particles is way too much information and we would like to construct a coarse-grained description of the system that contains only the information which is relevant at the macroscopic scale. Doing so will require identifying the right level of description, i.e. the right coarse-grained variables and to construct their dynamics.

The outline of the chapter is as follows. In Section 2.1, we will attempt to build coarse-grained variables and derive their dynamics starting from Liouville's equation. This path will fail, but it will deliver the right tools to make progress. In Section 2.2, we construct the Boltzmann equation, and in Section 2.3 we show it accounts for the evolution depicted in Fig 2.1. Finally, we characterize in Section 2.4 the relaxation to equilibrium.

[1] Note that the factor 1/2 is included to avoid double counting. Consider the dynamics of particle k, $\dot{\vec{p}}_k = -\frac{\partial U(\vec{q}_k)}{\partial \vec{q}_k} - \frac{1}{2}\sum_{i\neq j}\frac{\partial V(\vec{q}_i-\vec{q}_j)}{\partial \vec{q}_k}$. (Note that there are $N(N-1)$ terms in the last sum: i goes from 1 to N, and so does j but with $j \neq i$.) The terms in the last sum are non-vanishing whenever either i or j equals k so that $\dot{\vec{p}}_k = -\frac{\partial U(\vec{q}_k)}{\partial \vec{q}_k} - \frac{1}{2}\sum_{i\neq j}\left[\frac{\partial V(\vec{q}_k-\vec{q}_j)}{\partial \vec{q}_k}\delta_{i,k} + \frac{\partial V(\vec{q}_i-\vec{q}_k)}{\partial \vec{q}_k}\delta_{j,k}\right] = -\frac{\partial U(\vec{q}_k)}{\partial \vec{q}_k} - \sum_{j\neq k}\frac{\partial V(\vec{q}_k-\vec{q}_j)}{\partial \vec{q}_k}$, where we have relabelled the dummy variable i into j and used that V is even to obtain the last equality. Note that, this time, there are only $N-1$ terms in the last sum since k is fixed.

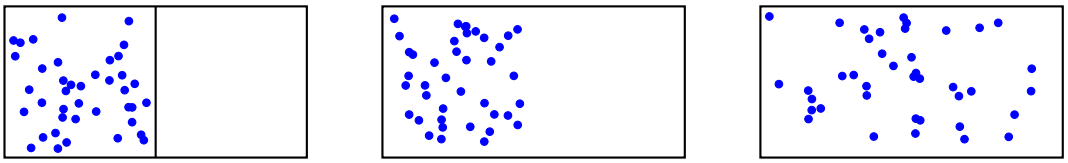

Figure 2.1: *A gas of particles is initially confined in the left half of the system. At $t = 0$, it is released and start exploring the accessible volume. At large time, it has relaxed and no macroscopic evolution can be observed.*

2.1 From Liouville's equation to the BBGKY hierarchy

2.1.1 Liouville's equation for an interacting gas

Using the Hamiltonian (2.1), Liouville's equation take the form

$$\partial_t \rho(\{\vec{q}_i, \vec{p}_i\}, t) = -\{\rho, H\} = -\sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{q}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{q}_i} \tag{2.3}$$

$$= -\sum_{i=1}^{N} \left[\frac{\partial \rho}{\partial \vec{q}_i} \cdot \frac{\partial H_1}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i} \cdot \frac{\partial H_1}{\partial \vec{q}_i} \right] - \sum_{i=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_i} \cdot \sum_{j \neq i} \frac{\partial V(\vec{q}_i - \vec{q}_j)}{\partial \vec{q}_i} \right] . \tag{2.4}$$

We can thus rewrite the evolution of the probability density ρ as

$$\partial_t \rho(\{\vec{q}_i, \vec{p}_i\}, t) + \{\rho, H_1\} = \sum_{i=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_i} \cdot \sum_{j \neq i} \frac{\partial V(\vec{q}_i - \vec{q}_j)}{\partial \vec{q}_i} \right] . \tag{2.5}$$

In this expression, the left-hand-side tells us how the particles would evolve if they were not interacting. We refer to this evolution—and thus to $\{\rho, H_1\}$—as the free evolution. On the contrary, the right-hand side gives the contribution of interactions between particles to the evolution of ρ.

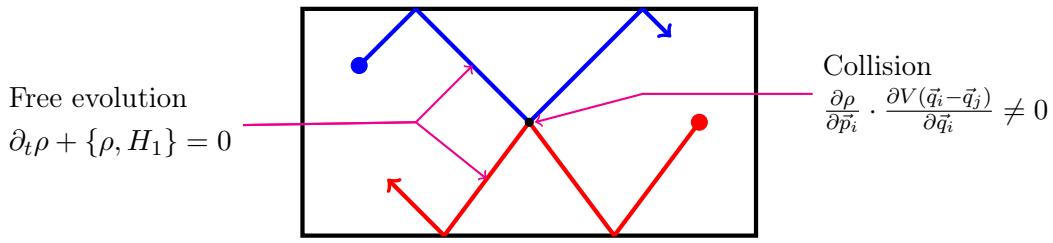

Figure 2.2: *Schematic illustration of the free evolution of two particles, interrupted by sudden collisions.*

2.1.2 Coarse-grained description

To build a coarse-grained description of the system, we need to identify a set of observables that are sufficient to describe the system at large scales and to construct a closed set of evolution equations for these observables. This is very difficult in general, but you may have already encountered examples of such descriptions, like the Navier-Stokes equations that predict the joint evolution of the density and

velocity fields of a fluid:

$$\partial_t \rho(\vec{r},t) = -\nabla\cdot[\rho(\vec{r},t)\vec{u}(\vec{r},t)], \qquad \rho(\vec{r},t)[\partial_t\vec{u}(\vec{r},t)+\vec{u}(\vec{r},t)\cdot\nabla\vec{u}(\vec{r},t)] = -\nabla p(\vec{r},t)+\mu\Delta\vec{u}(\vec{r},t)\ . \quad (2.6)$$

To use this equation, one needs to know the value of the dynamic viscosity μ and how the pressure field should be related to ρ and $\vec{u}$. For an incompressible fluid, the density field is a constant and the pressure is set by enforcing that $\nabla\cdot\vec{u}=0$, in which case Eq. (2.6) becomes a closed equation for $\vec{u}$. The viscosity can be experimentally measured and the Navier-Stokes can then be used to make predictions. However, since we have started from a macroscopic description of the fluid, it is not possible anymore to relate μ to microscopic properties of the system. We also have little control on when Eq. (2.6) is a valid description of a fluid. Statistical physics aims at fixing these problems by starting from the microscopic description of systems to build their coarse-grained description, hence yielding microscopic insight into macroscopic transport parameters.

Another example of a coarse-grained description is offered by the description of a set of particles doing a Brownian random walk in water. The random motion of the particles leads to a large-scale motion described by the diffusion equation:

$$\partial_t n(\vec{r},t) = D\Delta n(\vec{r},t)\ . \quad (2.7)$$

Here, the knowledge of D suffices to make predictions on the evolution of the number density field $n(\vec{r},t)$. Again, it can be measured experimentally but Eq. (2.7) has nothing to say on its microscopic origin.

For our interacting gas, we would like to derive an analog of Eq. (2.6) or Eq. (2.7). This means identifying what are the relevant fields that we need to characterize and to compute all relevant transport parameters. At this stage, many questions are open. How do we know if the density field will be sufficient, as in Eq. (2.7), or whether we will also need a velocity field as in Eq. (2.6)? Or some other fields? And can we even be sure that such closed, self-consistent descriptions exist?

In general, these are very difficult questions and there are many systems for which we do not know how to address them. However, there are also a number of important concepts and principles that help us construct such 'hydrodynamic' descriptions [2].

Scale separation

In principle, it is not obvious at all why the dynamics of a system at some macroscopic scale should decouple from what happens at shorter scales. The reason why we end up being able to construct such close self-contained macroscopic descriptions is that many systems have well-defined and well-separated scales that only interact with each other through the form of transport coefficients like μ and D in Eqs. (2.6) and (2.7).

Consider the case of the diffusion equation. Our small particles are moving around randomly and they travel a distance d equal to their size in a typical time τ_m, which is independent of the size of the system. Now, consider instead their density field $n(\vec{r},t)$. We can study its dynamics starting from an initial profile

[2] Because, in spirit, we are trying to achieve a description akin to what Navier and Stokes did for a fluid, we often refer to deterministic coarse-grained descriptions as 'hydrodynamic' descriptions, despite the lack of any 'water' in the system under study.

at density n_0, perturbed by a small fluctuation $\delta n(\vec{r}, t=0)$. We can then decompose the density field at all times as

$$n(\vec{r},t) = n_0 + \delta n(\vec{r},t) = n_0 + \sum_{\vec{q}} \delta n_{\vec{q}}(t) e^{-i\vec{q}\cdot\vec{r}} \,. \tag{2.8}$$

Injecting Eq. (2.8) into Eq. (2.7) shows that the Fourier modes of the perturbation relax as

$$\delta n_{\vec{q}}(t) = \delta n_{\vec{q}}(0) e^{-t/\tau_q} \quad \text{with} \quad \tau_q = \frac{1}{Dq^2} \,. \tag{2.9}$$

The relaxation time of a mode of size $\ell = \frac{2\pi}{q}$ is thus $\tau_\ell = \ell^2/(4D\pi^2)$. A perturbation of the density field at the scale of the system thus relaxes in a time $\mathcal{O}(L^2)$ that diverges with the system size. We see that the macroscopic relaxation of the density field and the microscopic motion of the particle over a distance of the order of its size take place on time scales that are well separated. We may thus hope to be able to average out what happens at the microscopic scale to create a closed description of what happens at much larger scales. This type of scale separation will be at the root of our computations for the interacting gas.

Slow fields/hydrodynamics fields

Even if we know that there is a scale separation in our system and we hope to be able to describe its macroscopic scale 'independently' of the microscopic one, how can we identify the relevant observables that one needs to characterize? Again, this is a complex question whose generic answer we do not know. But a lot of progress has been made towards identifying the guiding principles.

Conserved fields are slow. Some fields are associated with conserved quantities. Take the example above of the diffusion equation. Because particles are not created or annihilated, the dynamics of the density field has to take the form of a local conservation law, even at the microscopic scale: $\partial_t n(\vec{r},t) = -\nabla\cdot\vec{j}(\vec{r},t)$, where $\vec{j}(\vec{r},t)$ is the average particle current. At the macroscopic scale, Fick's law states that $\vec{j} = -D\nabla n$, but $\vec{j}$ can be a much more complicated quantity at the microscopic scale. Fields like $n(\vec{r},t)$, which measure the local amount of a conserved quantity, are called conserved fields. These fields are necessarily slow because relaxing a fluctuation on the scale of the system size L requires transporting the conserved observable over the same scale. If the transport is ballistic, it will take a time $\tau \sim L$. If it is diffusive, it will take a time $\tau \sim L^2$. To characterize this, one typically defines a dynamic exponent z such that

$$\tau \sim L^z \quad \text{with} \quad z > 0 \,. \tag{2.10}$$

Conserved quantities thus typically lead to hydrodynamic fields that enter the large-scale description of the system.

Spontaneous breaking of symmetry. Consider a system invariant under some symmetry group. For instance, the atomic spins $\vec{S}_i$ in a metallic alloy. At very high temperature, the interactions between the spins are irrelevant and they explore their configuration space isotropically. They thus respect the symmetry of their system and $\langle \vec{S}_i \rangle = 0$. In a ferromagnetic system, as temperature is decreased, the exchange interaction between the spins tend to align them and, at low enough temperature, they order: below a temperature T_c, called the Curie temperature, $\langle \vec{S}_i \rangle \neq 0$. The system is thus not invariant anymore

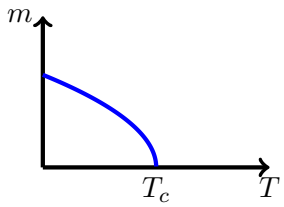

Figure 2.3: *As T is lowered below T_c, the system acquires a spontaneous magnetization. The relaxation time diverges at the transition point and a slow mode associated to the order-parameter field appears in the system.*

under the symmetry group and the symmetry is said to be 'broken'. More precisely, one can define an order parameter

$$m(T) = \left| \frac{1}{N} \sum_{i=1}^{N} \langle \vec{S}_i \rangle \right| , \tag{2.11}$$

such that, in the high temperature phase, $m = 0$, whereas m acquires a non-zero value below $T = T_c$, as shown in Fig. 2.3.

Imagine that you locally order the system in the high temperature phase by aligning all the spins in a given region of space. Each of the spins fluctuates rapidly and, in a finite time, the magnetization will vanish. One thus expects that a fluctuation $\delta m(t)$ relaxes as $\delta m(t) = \delta m(0) e^{-t/\tau}$, where τ is a finite relaxation time. As the system approaches T_c, aligned spins are less likely to fluctuate, since the interactions with their neighbors are about to make them order globally. The relaxation will thus be much slower and $\tau \to \infty$ as $T \to T_c$. At the critical point, the system relaxes infinitely slowly: it can choose any direction in space to order equivalently, due to the invariance by rotation, and this state of bewilderment prevents any form of rapid ordering or relaxation. This fate is common to all spontaneous breaking of symmetries leading to a continuous transition. In such systems, we can associate a hydrodynamic mode to the order parameter field. While we do not discuss the dynamics of phase transitions in this class, we refer the interested reader to Prof. Kardar's class 8.334, offered in the Spring term.

Let us now try to identify the fields that are relevant for our interacting gas and construct their dynamics starting from Liouville's equation.

2.1.3 One-body functions

In our interacting gas, particle number, momentum, and energy are conserved quantities and we thus expect that hydrodynamic modes should be associated with these quantities. At this stage, we know how to predict the evolution of the particle positions and momenta, $\{\vec{q}_i, \vec{p}_i\}$, using Hamilton's equations of motion, as well as the evolution of the phase-space joint probability density $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$.

Density field. Let us first try to build a density field out of these microscopic quantities. A density field $n(\vec{r}, t)$ should measure the local number of particles in any volume of space V:

$$\int_V n(\vec{r}, t) d^3\vec{r} = \text{average number of particles in V} \tag{2.12}$$

A natural object to count whether particle i is in a given volume is the Dirac distribution. Indeed, $\int_V \delta(\vec{r} - \vec{q}_i(t)) = 1$ when particle i is in V at time t, and vanishes otherwise. We can thus compute the

average number of particles in V as:

$$\int_V n(\vec{r},t)d^3\vec{r} = \Big\langle \int_V \sum_{i=1}^{N} \delta(\vec{q}_i(t)-\vec{r})d^3\vec{r} \Big\rangle \tag{2.13}$$

By definition of the probability density, the average of an observable $\langle O(\{\vec{q}_i(t),\vec{p}_i(t)\})\rangle$ is given by

$$\langle O(\{\vec{q}_i(t),\vec{p}_i(t)\})\rangle = \int \prod_k d^3\vec{q}_k d^3\vec{p}_k \, O\big(\{\vec{q}_i,\vec{p}_i\}\big)\, \rho\big(\{\vec{q}_i,\vec{p}_i\},t\big) \tag{2.14}$$

$$= \int \prod_k \mathrm{d}\Gamma_k \, O\big(\{\vec{q}_i,\vec{p}_i\}\big)\, \rho\big(\{\vec{q}_i,\vec{p}_i\},t\big)\ . \tag{2.15}$$

where $\mathrm{d}\Gamma_k \equiv \mathrm{d}^3\vec{q}_k \mathrm{d}^3\vec{p}_k$, as before. Applying the definition (2.14) to Eq. (2.13) then leads to

$$\int_V n(\vec{r},t)d^3\vec{r} = \int \prod_k \mathrm{d}\Gamma_k \Big[\int_V \sum_{i=1}^{N} \delta(\vec{q}_i-\vec{r})d^3\vec{r}\Big]\rho(\{\vec{q}_i,\vec{p}_i\},t) \tag{2.16}$$

$$= \int_V \Big[\int \prod_k \mathrm{d}\Gamma_k \sum_{i=1}^{N} \delta(\vec{q}_i-\vec{r})\rho(\{\vec{q}_i,\vec{p}_i\},t)\Big]d^3\vec{r}\,, \tag{2.17}$$

where we have commuted the order of the integrals to go from the first to the second line. Identifying the blue terms in Eq. (2.16) and (2.17) then leads to

$$n(\vec{r},t) = \int \prod_k \mathrm{d}\Gamma_k \sum_{i=1}^{N} \delta(\vec{q}_i-\vec{r})\rho(\{\vec{q}_i,\vec{p}_i\},t) = \Big\langle \sum_{i=1}^{N} \delta(\vec{q}_i(t)-\vec{r})\Big\rangle\ . \tag{2.18}$$

We note that Eq. (2.18) could have been obtained directly from Eq. (2.13) by commuting average and integrals. Whenever I will write in the following "by linearity, we can commute A and B", I will be referring to the type of computation done above, which I will thus skip from now on[3].

An appealing feature of Eq. (2.18) is that it relates directly the field $n(\vec{r},t)$ to the trajectories $\{\vec{q}_i(t),\vec{p}_i(t)\}$. Note also how, on the left-hand side of Eq. (2.14), $\{\vec{q}_i(t),\vec{p}_i(t)\}$ refer to trajectories of the system while on the right-hand side, $\{\vec{q}_i,\vec{p}_i\}$ are simply vectors that are being integrated over, with the time dependence now entering through $\rho(\{\vec{q}_i,\vec{p}_i\},t)$.

One-body functions. Let us now show how the expression (2.18) for the density field suggests a way to coarse-grain the system. Inverting the sum and integrals indeed leads to

$$n(\vec{r},t) = \sum_{i=1}^{N} \int \mathrm{d}\Gamma_i \delta(\vec{q}_i-\vec{r}) \int \prod_{k\neq i} \mathrm{d}\Gamma_k \rho(\{\vec{q}_j,\vec{p}_j\},t) \tag{2.19}$$

$$= \sum_{i=1}^{N} \int \mathrm{d}\Gamma_i \delta(\vec{q}_i-\vec{r})\rho_1^i(\vec{q}_i,\vec{p}_i,t)\ , \tag{2.20}$$

where we have introduced the one-body phase-space density

$$\rho_1^i(\vec{q}_i,\vec{p}_i,t) \equiv \int \prod_{k\neq i} \mathrm{d}\Gamma_k \rho(\{\vec{q}_j,\vec{p}_j\},t)\ . \tag{2.21}$$

[3]This will be the case for $\partial_t\langle O\rangle$ and $\langle\partial_t O\rangle$, for instance.

Since we have integrated over all the $\vec{q}_k$ and $\vec{p}_k$, $\rho_1^i(\vec{q}_i, \vec{p}_i, t)$ tells us the probability density of finding particle i at $\vec{q}_i, \vec{p}_i$ at time t, irrespective of the positions and momenta of all other particles.

At this stage, it is important to realize that, since all the gas particles are indistinguishable, their labeling is irrelevant. Relabeling all of them with different numbers should not change anything in the physics of the system. When we pick the initial condition for the probability distribution, it is thus important to choose it so that it respects the invariance by relabelling of the system. In other words, for any permutation σ, we require that $\rho(\{\vec{q}_i, \vec{p}_i\}, 0) = \rho(\{\vec{q}_{\sigma(i)}, \vec{p}_{\sigma(i)}\}, 0)$. This property is then preserved by the dynamics. As a consequence, particle i and particle $j \neq i$ have exactly the same probability to be at $\vec{q}_i, \vec{p}_i$ at time t and

$$\rho_1^i(\vec{q}_i, \vec{p}_i, t) = \rho_1^j(\vec{q}_i, \vec{p}_i, t) \equiv \rho_1(\vec{q}_i, \vec{p}_i, t) \, . \tag{2.22}$$

The function ρ_1 is called the one-body phase-space probability density function. By definition it is normalized to 1:

$$\int d^3\vec{q} d^3\vec{p} \rho_1(\vec{q}, \vec{p}) = 1 \, . \tag{2.23}$$

At this stage, we note that the variables $\vec{q}_i, \vec{p}_i$ are dummy variables in Eq. (2.20). We can relabel them $\vec{q}, \vec{p}$ and integrate over $\vec{q}$ to find:

$$n(\vec{r}, t) = \sum_{i=1}^{N} \int d^3\vec{p} \rho_1(\vec{r}, \vec{p}, t) = N \int d^3\vec{p} \rho_1(\vec{r}, \vec{p}, t) \equiv \int d^3\vec{p} f_1(\vec{r}, \vec{p}, t) \, , \tag{2.24}$$

where we have introduced the phase-space number density

$$f_1(\vec{q}, \vec{p}, t) \equiv N \rho_1(\vec{q}, \vec{p}, t) = \left\langle \sum_{i=1}^{N} \delta[\vec{q} - \vec{q}_i(t)] \delta[\vec{p} - \vec{p}_i(t)] \right\rangle \, . \tag{2.25}$$

By definition, f_1 is such that $f_1(\vec{q}, \vec{p}, t) \mathrm{d}^3\vec{q} \mathrm{d}^3\vec{p}$ represents the average number of particles with position and momenta in the (phase-space) volume element $\mathrm{d}^3\vec{q} \mathrm{d}^3\vec{p}$ near $(\vec{q}, \vec{p})$ at time t.

Starting from the joint phase-space probability density describing the N particles, $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$, we have thus introduced much lower dimensional fields, $\rho_1(\vec{q}, \vec{p}, t)$ and $f_1(\vec{q}, \vec{p}, t)$ that allow us to compute and characterize the number density $n(\vec{r}, t)$ through Eqs. (2.20) or (2.24). Thanks to Eq. (2.21), we can directly relate these objects through

$$\rho_1(\vec{q}, \vec{p}, t) = \int \prod_{k>1} \mathrm{d}\Gamma_k \rho(\vec{q}, \vec{p}, \vec{q}_2, \vec{p}_2, \ldots, \vec{q}_N, \vec{p}_N) \, . \tag{2.26}$$

Since we know how ρ evolves in time, thanks to Liouville's equation, Eq. (2.26) will allow us to construct the evolution equation of ρ_1.

Comment: Mathematically, the "dimensional" reduction of the problem can be seen by comparing the functional spaces in which ρ and ρ_1 live. ρ maps $\{\vec{p}_i, \vec{q}_i\}$ and t onto a real number, $\rho(\{\vec{p}_i, \vec{q}_i\}, t)$. Since there are N particles, ρ is a function from $\mathbb{R}^{6N} \times \mathbb{R} \to \mathbb{R}$. ρ_1 maps $\vec{p}, \vec{q}$ and t onto a real number, $\rho(\vec{p}, \vec{q}, t)$ and is thus a function from $\mathbb{R}^6 \times \mathbb{R} \to \mathbb{R}$. If you wanted to sample ρ at a given value of t for a system with $N = 10$ particles, and you wanted at least 10 values for each coordinates—which is a low-quality grid!—, you would need a grid with
$(10^6)^{10} = 10^{60} = 1\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000\,000$ points.

Using C doubles, this requires $8 \times 10^{60}/(600 \times 10^{15}) \simeq 10^{43}$ times more data than the 600 petabytes produced by LHC run 3... If you want to do the same with ρ_1, you need 1 000 000 points, which means 8Mb of storage space.

2.1.4 The BBGKY hierarchy

The dynamics of f_1.

Let us recall that the Hamiltonian describing the system is

$$H = \sum_{i=1}^{N} \Big[\frac{\vec{p}_i^{\,2}}{2m} + U(q_i) \Big] + \frac{1}{2} \sum_{i=1}^{N} \sum_{\ell \neq i} V(\vec{q}_i - \vec{q}_\ell) = H_1 + \frac{1}{2} \sum_{i=1}^{N} \sum_{\ell \neq i} V(\vec{q}_i - \vec{q}_\ell) \, , \tag{2.27}$$

where we have singled out the "free" noninteracting part H_1. The time-evolution of the probability density to find the system at a position $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$ is then given by Eq. (2.5)

$$\partial_t \rho + \{\rho, H_1\} = \sum_{i=1}^{N} \Big[\frac{\partial \rho}{\partial \vec{p}_i} \cdot \sum_{\ell \neq i} \frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i} \Big] \, . \tag{2.28}$$

In Eq. (2.28), the term in magenta tells us how the free evolution makes ρ relax while the term in blue tells us how interactions make ρ relax. We now want to integrate Eq. (2.28) over $\{\vec{q}_i, \vec{p}_i\}_{i \geq 2}$ to deduce the evolution of $\rho_1(\vec{q}_1, \vec{p}_1, t)$ from that of $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$.

Left-hand side of Eq. (2.28). Since the left hand side ignores the presence of interactions, the dynamics of particles $2, \dots, N$ cannot impact those of particle 1, and we should thus expect that

$$\int \prod_{k>1} \mathrm{d}\Gamma_k (\partial_t \rho + \{\rho, H_1\}) = \partial_t \rho_1 + \{\rho_1, H_1\} \, . \tag{2.29}$$

Let us show that this is indeed the case. By linearity, and since the domain of integration is time independent,

$$\int_{\mathbb{R}^{6N-6}} \prod_{k>1} \mathrm{d}\Gamma_k \partial_t \rho(\{\vec{q}_i, \vec{p}_i\}, t) = \partial_t \Big[\int_{\mathbb{R}^{6N-6}} \prod_{k>1} \mathrm{d}\Gamma_k \rho(\{\vec{q}_i, \vec{p}_i\}, t) \Big] = \partial_t \rho_1(\vec{q}_1, \vec{p}_1, t) \, . \tag{2.30}$$

Let us now turn to the Poisson bracket between ρ and H_1:

$$\int \prod_{k>1} \mathrm{d}\Gamma_k \{\rho, H_1\} = \int \prod_{k>1} \mathrm{d}\Gamma_k \Big[\frac{\partial \rho}{\partial \vec{q}_1} \cdot \frac{\partial H_1}{\partial \vec{p}_1} - \frac{\partial \rho}{\partial \vec{p}_1} \cdot \frac{\partial H_1}{\partial \vec{q}_1} \Big] + \sum_{i \geq 2} \int \prod_{k>1} \mathrm{d}\Gamma_k \Big[\frac{\partial \rho}{\partial \vec{q}_i} \cdot \frac{\partial H_1}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i} \cdot \frac{\partial H_1}{\partial \vec{q}_i} \Big] \, . \tag{2.31}$$

Let us first consider the term in blue. Since $\frac{\partial H_1}{\partial \vec{p}_i} = \frac{\vec{p}_i}{m}$ does not depend on $\vec{q}_i$ and $\frac{\partial H_1}{\partial \vec{q}_i} = \frac{\partial U(\vec{q}_i)}{\partial \vec{q}_i}$ does not depend on $\vec{p}_i$, it can be rewritten as:

$$\sum_{i \geq 2} \int \prod_{k>1} \mathrm{d}\Gamma_k \Big[\frac{\partial}{\partial \vec{q}_i} \cdot \Big(\rho \frac{\partial H_1}{\partial \vec{p}_i} \Big) - \frac{\partial}{\partial \vec{p}_i} \cdot \Big(\rho \frac{\partial H_1}{\partial \vec{q}_i} \Big) \Big] \, , \tag{2.32}$$

where the operators $\frac{\partial}{\partial \vec{q}_i}$ and $\frac{\partial}{\partial \vec{p}_i}$ apply to the parenthesis on their rights. We then note that $i \geq 2$ so that $\vec{q}_i$ and $\vec{p}_i$ are always integrated over. Since the integrand are total derivatives, the results of the

integrals will involve $\rho\frac{\partial H_1}{\partial \vec{q}_i}$ and $\rho\frac{\partial H_1}{\partial \vec{p}_i}$ evaluated as $|\vec{p}_i| \to \infty$ and $|\vec{q}_i| \to \infty$, respectively. Since ρ has to be normalizable, it must vanish in these limits and these boundary terms do not contribute: the overall integral vanishes[4]. This result is not surprising: The blue term tells us about how particles 2 to N make ρ evolve due to their free dynamics. While this impacts ρ, it does not impact particle 1 and should thus not impact the time evolution of ρ_1.

Consider next the term in magenta. Since $\frac{\partial H_1}{\partial \vec{p}_1} = \frac{\vec{p}_1}{m}$ and $\frac{\partial H_1}{\partial \vec{q}_1} = \frac{\partial U(\vec{q}_1)}{\partial \vec{q}_1}$ do not depend on $\{\vec{q}_k, \vec{p}_k\}$, they can be taken out of the integral. The same hold for the operators $\frac{\partial}{\partial \vec{q}_1}$ and $\frac{\partial}{\partial \vec{p}_1}$ so that one finds

$$\int \prod_{k>1} \mathrm{d}\Gamma_k \Big[\frac{\partial \rho}{\partial \vec{q}_1}\cdot\frac{\partial H_1}{\partial \vec{p}_1} - \frac{\partial \rho}{\partial \vec{p}_1}\cdot\frac{\partial H_1}{\partial \vec{q}_1}\Big] = \frac{\partial H_1}{\partial \vec{p}_1}\cdot\frac{\partial}{\partial \vec{q}_1}\int \prod_{k>1} \mathrm{d}\Gamma_k \rho - \frac{\partial H_1}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1}\int \prod_{k>1} \mathrm{d}\Gamma_k \rho \tag{2.33}$$

$$= \frac{\partial H_1}{\partial \vec{p}_1}\cdot\frac{\partial}{\partial \vec{q}_1}\rho_1(\vec{q}_1,\vec{p}_1,t) - \frac{\partial H_1}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1}\rho_1(\vec{q}_1,\vec{p}_1,t) \tag{2.34}$$

$$= \{\rho_1, H_1\} \tag{2.35}$$

All in all, we thus get Eq. (2.29) as anticipated.

Right-hand side of Eq. (2.28). We are interested in the evolution of the probability density of observing particle 1 at a given position in phase space. For the same reason as above, the interactions between particles $i \neq 1$ and $j \neq 1$ should not impact $\partial_t \rho_1(\vec{q}_1, \vec{p}_1)$. This suggests splitting the interaction term as

$$\int \prod_{k>1} \mathrm{d}\Gamma_k \sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{p}_i}\cdot\sum_{\ell\neq i}\frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i} = \int \prod_{k>1} \mathrm{d}\Gamma_k \frac{\partial \rho}{\partial \vec{p}_1}\cdot\sum_{\ell>1}\frac{\partial V(\vec{q}_1 - \vec{q}_\ell)}{\partial \vec{q}_1} + \sum_{i\geq 2}\int \prod_{k>1} \mathrm{d}\Gamma_k \frac{\partial \rho}{\partial \vec{p}_i}\cdot\sum_{\ell\neq i}\frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i}\,. \tag{2.36}$$

We first note that the term in orange always contains an integration over $\vec{p}_i$. Integrating by parts over $\vec{p}_i$ thus shows this term to vanish since $\frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i}$ does not depend on $\vec{p}_i$.The interaction term can then be rewritten as

$$\int \prod_{k>1} \mathrm{d}\Gamma_k \sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{p}_i}\cdot\sum_{\ell\neq i}\frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i} = \sum_{\ell>1}\int \mathrm{d}\Gamma_\ell \frac{\partial V(\vec{q}_1 - \vec{q}_\ell)}{\partial \vec{q}_1}\cdot\int \prod_{k\neq 1,\ell} \mathrm{d}\Gamma_k \frac{\partial \rho}{\partial \vec{p}_1}, \tag{2.37}$$

$$= (N-1)\int \mathrm{d}\Gamma_2 \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1}\int \prod_{k>2} \mathrm{d}\Gamma_k\ \rho. \tag{2.38}$$

The term in blue in Eq. (2.37) is obtained from Eq. (2.36) by noticing that $\frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i}$ does not depend on $q_{k\neq 1,\ell}$. Equation (2.38) then stems from the fact that particles $2, \ldots, N$ are indistinguishable and that the last integral does not include an integral over $\vec{p}_1$. Finally, we introduce the two-body probability density

$$\rho_2(\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2) = \int \prod_{k>2} \mathrm{d}\Gamma_k \rho(\{\vec{q}_i, \vec{p}_i\})\,, \tag{2.39}$$

which is the joint probability density that particle 1 is at $\vec{q}_1, \vec{p}_1$ and particle 2 is at $\vec{q}_2, \vec{p}_2$. This allows rewriting the interaction term in a relatively compact form:

$$\int \prod_{k>1} \mathrm{d}\Gamma_k \sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{p}_i}\cdot\sum_{\ell\neq i}\frac{\partial V(\vec{q}_i - \vec{q}_\ell)}{\partial \vec{q}_i} = (N-1)\int \mathrm{d}\Gamma_2 \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial \rho_2(\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2)}{\partial \vec{p}_1}\,. \tag{2.40}$$

[4]Note that the same result can be obtained by integrating by parts $\frac{\partial \rho}{\partial \vec{q}_i}$ and $\frac{\partial \rho}{\partial \vec{p}_i}$, using similar arguments.

All in all, the dynamics for ρ_1 read

$$\partial_t \rho_1(\vec{q}_1,\vec{p}_1) + \{\rho_1, H_1\} = (N-1)\int \mathrm{d}\Gamma_2 \frac{\partial V(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial \rho_2(\vec{q}_1,\vec{p}_1,\vec{q}_2,\vec{p}_2)}{\partial \vec{p}_1}\ . \tag{2.41}$$

Introducing $f_2 = N(N-1)\rho_2$ and multiplying Eq. (2.41) by N then gives the time evolution of the phase-space number density:

$$\partial_t f_1 + \{f_1, H_1\} = \int \mathrm{d}\Gamma_2 \frac{\partial V(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial f_2(\vec{q}_1,\vec{p}_1,\vec{q}_2,\vec{p}_2)}{\partial \vec{p}_1}\ . \tag{2.42}$$

Again, f_2 does not contain more physics than ρ_2, and it simply allows absorbing the factor $N-1$ to lighten a little bit the notations.

Comments.

At this stage, we have accomplished what we wanted: we have projected the dynamics of ρ onto that of ρ_1 and f_1, hence obtaining the time evolution of a lower dimensional object. From there, we simply have to integrate its dynamics over $\vec{p}_1$ to obtain the dynamics of the average density field. However, there are several problems with Eq. (2.42).

1. While the 'low'-dimensional nature of Eq. (2.42) almost allows us to put it in a computer to predict the evolution of f_1, we cannot do that since we do not know f_2. To solve that problem, we could derive the evolution equation for f_2: we would start from Liouville's equation and integrate it over $\{\vec{q}_k,\vec{p}_k\}_{k\geq 3}$. However, the evolution of the joint probability density of particle 1 and 2 will depend on their encounters with other particles and the interaction term will require introducing a function f_3 that couple particles 1 and 2 to particle $k\geq 3$. Proceeding further, we would build a dynamics for all f_k that involves f_{k+1} until we arrive at a closed dynamics for $f_N=\rho$, which is simply Liouville's equation. This hierarchy of equations can indeed be derived exactly, and it is called the BBGKY hierarchy. Note that it is not very surprising that we did not end up with a problem simpler than the one we started from since everything we did so far is exact: eliminating 'useless' information will require assumptions that will need to be motivated on physical grounds.

2. A second problem of the BBGKY hierarchy is that it inherits the time-reversibility of Hamilton's equations of motion. Let us review the time-reversibility of classical mechanics.

   Time-reversal symmetry of Hamilton's equations of motion. If $\{\vec{q}_i(t),\vec{p}_i(t)\}$ are solutions of Hamilton's equations of motion, then so are $\{\vec{q}_i^{\,r}(t)\equiv\vec{q}_i(t_f-t),\vec{p}_i^{\,r}(t)\equiv-\vec{p}_i(t_f-t)\}$. Indeed, if

   $$\dot{\vec{q}}_i(t) = \frac{\partial H}{\partial \vec{p}_i} \qquad \text{and} \qquad \dot{\vec{p}}_i(t) = -\frac{\partial H}{\partial \vec{q}_i}\ , \tag{2.43}$$

   then the chain rule guarantees that

   $$\dot{\vec{q}}_i^{\,R}(t) = \frac{\mathrm{d}}{\mathrm{d}t}\vec{q}_i(t_f-t) = -\dot{\vec{q}}_i|_{t_f-t} = -\left.\frac{\partial H}{\partial \vec{p}_i}\right|_{t_f-t} = \frac{\partial H}{\partial \vec{p}_i^{\,R}} \quad \text{and} \quad \frac{\mathrm{d}}{\mathrm{d}t}\vec{p}_i^{\,R}(t) = \dot{\vec{p}}_i|_{t_f-t} = -\left.\frac{\partial H}{\partial \vec{q}_i}\right|_{t_f-t} = -\frac{\partial H}{\partial \vec{q}_i^{\,R}}\ .$$

   Time-reversal symmetry of Liouville's equation. Similarly, let us show that, if $\rho(\{\vec{q}_i,\vec{p}_i\},t)$ is a solution of Liouville's equation, then so is

   $$\rho^r(\{\vec{q}_i,\vec{p}_i\},t) \equiv \rho(\{\vec{q}_i,-\vec{p}_i\},t_f-t) = \rho(\{\vec{q}_i^{\,r},\vec{p}_i^{\,r}\},t^r)\ , \tag{2.44}$$

where we have introduced $t^r(t) \equiv t_f - t$. Using the chain rule, we find that

$$\partial_t \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) = \partial_{t^r} \rho(\{\vec{q}_i{}^r, \vec{p}_i{}^r\}, t^r) \partial_t t^r \tag{2.45}$$

$$= \sum_i \frac{\partial}{\partial q_i^r} \rho(\{\vec{q}_i{}^r, \vec{p}_i{}^r\}, t^r) \cdot \frac{\partial H}{\partial p_i^r} - \frac{\partial}{\partial p_i^r} \rho(\{\vec{q}_i{}^r, \vec{p}_i{}^r\}, t^r) \cdot \frac{\partial H}{\partial q_i^r} \,, \tag{2.46}$$

where the second equality comes from applying Liouville's equation to $\rho(\{\vec{q}_i{}^r, \vec{p}_i{}^r\}, t^r)$. One then need to go back to the original variables $\vec{q}_i, \vec{p}_i, t$. To do so, we note that

$$\partial_{q_{i,\alpha}^r} \rho(\{\vec{q}_i{}^r, \vec{p}_i{}^r\}, t^r) = \partial_{q_{i,\alpha}^r} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) = \partial_{q_{i,\alpha}} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) \frac{\partial q_{i,\alpha}}{\partial q_{i,\alpha}^r} = \partial_{q_{i,\alpha}} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) \tag{2.47}$$

$$\partial_{p_{i,\alpha}^r} \rho(\{\vec{q}_i{}^r, \vec{p}_i{}^r\}, t^r) = \partial_{p_{i,\alpha}^r} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) = \partial_{p_{i,\alpha}} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) \frac{\partial p_{i,\alpha}}{\partial p_{i,\alpha}^r} = -\partial_{p_{i,\alpha}} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) \tag{2.48}$$

$$\tag{2.49}$$

Then, since $H(\{\vec{q}_i, \vec{p}_i\}) = H(\{\vec{q}_i{}^r, \vec{p}_i{}^r\})$, one finds

$$\frac{\partial H(\{\vec{q}_i{}^r, \vec{p}_i{}^r\})}{\partial_{q_{i,\alpha}^r}} = \frac{\partial H(\{\vec{q}_i, \vec{p}_i\})}{\partial_{q_{i,\alpha}^r}} = \frac{\partial H(\{\vec{q}_i, \vec{p}_i\})}{\partial_{q_{i,\alpha}}} \tag{2.50}$$

$$\frac{\partial H(\{\vec{q}_i{}^r, \vec{p}_i{}^r\})}{\partial_{p_{i,\alpha}^r}} = \frac{\partial H(\{\vec{q}_i, \vec{p}_i\})}{\partial_{p_{i,\alpha}^r}} = -\frac{\partial H(\{\vec{q}_i, \vec{p}_i\})}{\partial_{p_{i,\alpha}}} \,. \tag{2.51}$$

Together, these equations turn Eq. (2.52) into

$$\partial_t \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) = -\sum_i \frac{\partial}{\partial q_i} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) \cdot \frac{\partial H}{\partial p_i} - \frac{\partial}{\partial p_i} \rho^r(\{\vec{q}_i, \vec{p}_i\}, t) \cdot \frac{\partial H}{\partial q_i} \,, \tag{2.52}$$

which shows that $\rho^r(\{\vec{q}_i, \vec{p}_i\}, t) = \rho(\{\vec{q}_i, -\vec{p}_i\}, t_f - t)$ is also a solution of the Liouville equation. The Liouville equation can thus predict the evolution from the second panel of Fig. 2.1 to the third panel as well as the reverse dynamics.

Time-reversal symmetry of BBGKY hierarchy.

Since Liouville's equation and the BBGKY hierarchy contains the same information, the same symmetry holds and if $f_k(\{\vec{q}_i, \vec{p}_i\}_{i \le k}, t)$ is a set of solutions of the hierarchy, so is $f_k(\{\vec{q}_i, -\vec{p}_i\}_{i \le k}, t_f - t)$. Mathematically, this reversibility is due to the fact that all terms in the hierarchy include either one time derivative or one derivative with respect to a momentum variable, as can be checked in Eq. (2.42). As a result, to any solution of the BBGKY hierarchy that would describe the evolution shown in Fig. 2.1 corresponds the exact time reversed solution, and it's not clear how we can prove convergence to equilibrium—which is a time-irreversible process—in this context.

It turns out that we will solve both problems in the next section by coarse-graining our description of the system to build the Boltzmann equation. Since I will not be using higher order equation of the BBGKY hierarchy, they are not included in these notes, but an alternative route can be found in [1].