Chapter 2: The kinetic theory of gases

So far, we have argued that statistical ensembles should be relevant to describe complex systems

Q: Can we do better?

Here: Consider a dilute gas of interacting particles and construct its dynamics.

(i) Show that it relaxes to equilibrium

(ii) Characterize this relaxation to extract transport coefficients such as viscosity, thermal conductivity, etc.

System: N classical particles, interacting via a pair potential V and experiencing an external potential U, so

$$H = \underbrace{\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i)}_{H_1 \to \text{ non interacting dynamics}} + \underbrace{\frac{1}{2} \sum_{i \neq j} V(\vec{q}_i - q_j)}_{\text{interactions between particles}}$$

* **Comment:** $\frac{1}{2} \sum_{i \neq j} V(\vec{q}_i - \vec{q}_j) = \sum_{i<j} V(\vec{q}_i - \vec{q}_j)$ such that

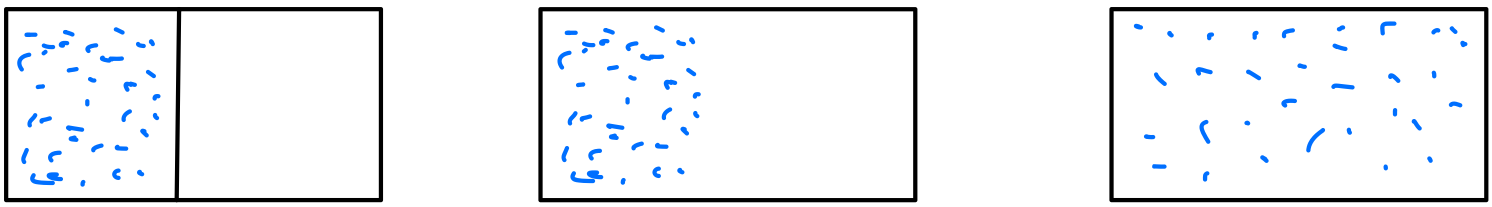
$$\dot{\vec{p}}_k = -\frac{\partial U}{\partial \vec{q}_k} - \frac{\partial}{\partial \vec{q}_k}\left[\frac{1}{2}\sum_{i \neq k} V(\vec{q}_i - \vec{q}_k) + \frac{1}{2}\sum_{j \neq k} V(\vec{q}_k - \vec{q}_j)\right]$$

dummy $j \to$ dummy i

$$= -\frac{\partial U}{\partial \vec{q}_k} - \sum_{i \neq k} \frac{\partial V(\vec{q}_k - \vec{q}_i)}{\partial \vec{q}_k}$$

$\Rightarrow$ No double counting.

Goal: Start from some initial condition & characterize the evolution of the system.



$t=0^-$ $\qquad$ $t=0^+$ $\qquad$ $t=\infty$

First challenge: The joint knowledge of all $\vec{q}_i$ & $\vec{p}_i$ is clearly too much information $\Rightarrow$ identify the right level of descriptions, i.e. the good coarse grained observables and build their dynamics (e.g. density field).

2.1) From the Liouville equation to the BBGKY hierarchy

2.1.1) The Liouville equation

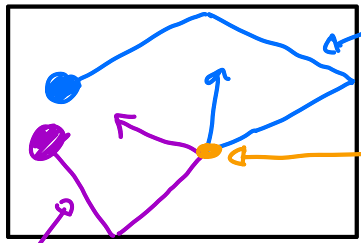
$$\partial_t \rho = -\{\rho, H\} = -\sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{q}_i}\cdot\frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i}\cdot\frac{\partial H}{\partial \vec{q}_i}$$

$$= -\sum_{i=1}^{N}\Bigg[\underbrace{\frac{\partial \rho}{\partial \vec{q}_i}\cdot\frac{\vec{p}_i}{m} - \frac{\partial \rho}{\partial \vec{p}_i}\cdot\frac{\partial U}{\partial \vec{q}_i}}_{-\{\rho, H_1\} \Rightarrow \text{ free evolution of } \rho \text{ when } V=0} \underbrace{- \frac{\partial \rho}{\partial \vec{p}_i}\cdot\sum_{\ell\neq i}\frac{\partial V(\vec{q}_i-\vec{q}_\ell)}{\partial \vec{q}_\ell}}_{\text{evolution of } \rho \text{ due to interactions}}\Bigg]$$

All in all

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

Example:



2.1.2) Coarse-grained description

The joint probability distribution $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$ contains way too much information $\Rightarrow$ introduce coarse-grained observables to describe the macroscopic evolution of the system

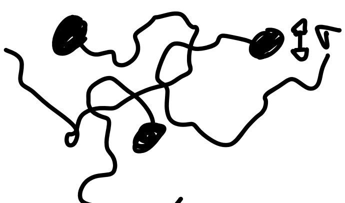
$\Rightarrow$ Q: How? Which observables should we use?

General idea:

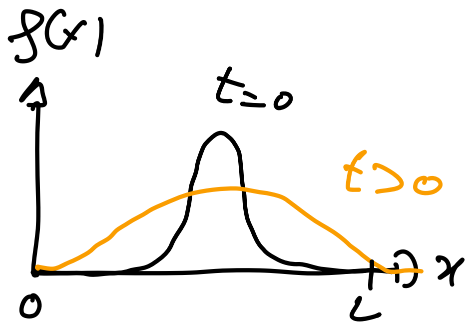
We need to identify the fields that allow us to derive a closed, self consistent description of the system at large scales

$\Rightarrow$ Very difficult task in general

Example:



$\rightarrow$



Micro: a bunch of particles doing random walks $\rightarrow$ Macro: the diffusion equation

$$\partial_t \rho(\vec{r}, t) = D \Delta \rho(\vec{r}, t)$$

If you know "D", you have a closed equation for $\rho(\vec{r},t)$ that you can solve.

Why does it work? Scale separation

Take a system described at a microscopic scale ℓ_m and that evolves on a typical time scale τ_m.

ex: $\ell_m = \sigma$ & $\tau_m =$ time it takes for a particle to move over σ.

We say that there is scale separation when we can identify some time and length scale $\tau \gg \tau_m$ & $\ell \gg \ell_m$ such that most observable relax on time scales $t \ll \tau$ while a few observables relax ———— $t \gg \tau$.

Comments:

1. Fields that relax on large time scales are called slow modes, or hydrodynamic modes. This latter denomination comes from the fact that the Navier-Stokes equations:

$$\partial_t \rho = -\vec{\nabla}\cdot[\rho\vec{u}]$$

dynamic viscosity

$$\rho\,\partial_t \vec{u} + \rho\vec{u}\cdot\vec{\nabla}\vec{u} = -\vec{\nabla}p + \mu\Delta\vec{u}$$

is one of the oldest examples of coarse grained description, that predicts the evolution of the density field, $\rho(\vec{r},t)$, and of the velocity field $\vec{v}(\vec{r},t)$, on scales much larger than the particle size.

(11) How do we identify the slow fields? Hard in general, but there are some rules.

Conserved fields are slow:

Look at the diffusion equation $\partial_t \rho = D \Delta \rho$ and consider a small perturbation $\rho(\vec{r},t) = \rho_0 + \delta\rho(\vec{r},t)$

Using Fourier decomposition in a system of size L, we find that

$$\delta\rho(\vec{r},t) = \sum_{\vec{q}} \delta\rho(\vec{q},t)\, e^{-i\vec{q}\cdot\vec{r}} \quad \text{so that}$$

$$\partial_t \delta\rho(\vec{q},t) = -|\vec{q}|^2 \delta\rho(\vec{q},t) \;\&$$

$$\delta\rho(\vec{q},t) = \delta\rho(\vec{q},0)\, e^{-q^2 t} \Rightarrow \text{relaxes in } t \sim \frac{1}{q^2}$$

Large-scale fluctuations: $|q| \sim \frac{2\pi}{L} \Rightarrow$ relaxation time $\tau \propto L^2$

$\tau \to \infty$ as $L \to \infty$ and the relaxation time is much larger than $\tau_m \approx \frac{\sigma^2}{D} \underset{L\to\infty}{\sim} O(1)$

Intuition: to relax a conserved field, you need to transport matter over a distance $\sim L \Rightarrow \tau \propto L^z$.

$z = 2$ for diffusive scaling

$z = 1$ for ballistic scaling $(\dot{x} = v)$

Richer physics exist: Kardar-Parisi-Zhang equation, which describes fluctuating interfaces, leads to $z = 3/2$. More in 8.334.

Spontaneous breaking of a symmetry.

Consider a system invariant under some symmetry group.

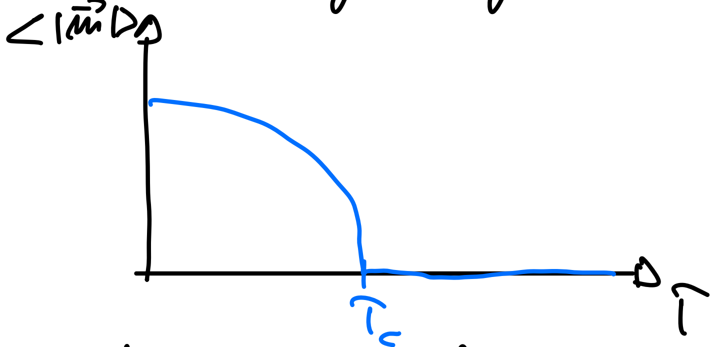
E.g. ferromagnets, atoms with spins $\vec{S}$. Isotropy of space

$\Rightarrow$ All $\vec{S}$ are equally likely $\Rightarrow$ $SO(3)$ symmetry.

As a result, at high temperatures, the system is disordered and

$$\langle \vec{m} \rangle = \langle \frac{1}{N} \sum_{i=1}^{N} \vec{S}_i \rangle = \vec{0}$$

At low temperature, because of interactions, the spins spontaneously break the symmetry and acquire a common orientation.



At T_c, the system starts to order, very weakly. Because the system does not know which direction to choose, the ordering process is very slow and take a time τ that diverges with L.

$\Rightarrow$ Spontaneous symmetry breaking is also associated with slow modes (see 8.334).

We want to start from $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$ and build the relevant coarse-grained fields associated to conserved quantities.

2.1.3) One-body density

Here: Particle number, momentum & energy are conserved quantity.

Q: How do we build a density field from $\rho(\{\vec{q}_i,\vec{p}_i\},t)$?

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

$$= \left\langle \int_V \sum_{i=1}^N \delta(\vec{q}_i-\vec{r})\,d^3\vec{r} \right\rangle \quad \text{since } \int_V \delta(\vec{q}_i-\vec{r})\,d\vec{r} = 1 \text{ if } \vec{q}_i \in V, \ 0 \text{ otherwise}$$

jump here & ask Sara to do in recitation.

$$= \int \prod_k d^3\vec{q}_k\, d^3\vec{p}_k \left[\rho(\{\vec{q}_j,\vec{p}_j\},t)\int_V d^3\vec{r}\sum_{i=1}^N \delta(\vec{q}_i-\vec{r})\right]$$

$$= \int_V \underbrace{\int \prod_k d^3\vec{q}_k\, d^3 p_k\ \rho(\{\vec{q}_j,\vec{p}_j\},t)\sum_{i=1}^N \delta(\vec{q}_i-\vec{r})}\ d^3\vec{r}$$

$$n(\vec{r},t) = \left\langle \sum_{i=1}^N \delta(\vec{q}_i-\vec{r})\right\rangle$$

$$\Rightarrow n(\vec{r},t) = \sum_{i=1}^N \int d\vec{q}_i\, d\vec{p}_i\ \delta(\vec{q}_i-\vec{r}) \underbrace{\int \prod_{k\neq i} d^3\vec{q}_k\, d^3\vec{p}_k\ \rho(\{\vec{q}_j,\vec{p}_j\},t)}_{\text{marginal over all particle } j\neq i}$$

$$\equiv \rho_i(\vec{q}_i,\vec{p}_i,t)$$

$\rho_i(\vec{q}_i,\vec{p}_i,t)$ is the "one-body" probability density of finding particle i at $\vec{q}_i,\vec{p}_i$ at time t.

Since all particles are identical $\rho_i(\vec{q}_i,\vec{p}_i,t) = \rho_k(\vec{q}_i,\vec{p}_i,t)$

$$\equiv \rho_1(\vec{q}_i,\vec{p}_i,t)$$

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