Chapter 2: The kinetic theory of gases

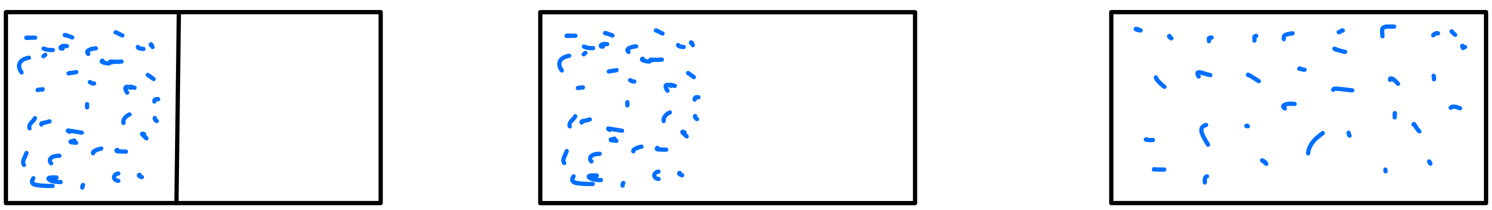
So far, we have argued that statistical ensembles should be relevant to describe complex systems $\Rightarrow$ Can we do better?

System: Dilute gas of N interacting particles & construct its dynamics explicitly to:

(i) Show that it relaxes to equilibrium

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

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



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

First challenge: what is the right level of description?

* The joint knowledge of all $\vec{q}_i$ & $\vec{p}_i$, and their probability density $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$ is way too much information, but that a simple starting point since we have Liouville's equation.

$\Rightarrow$ How can we build & characterize the relevant coarse grained variable (e.g. density field) ?

2.1) From Liouville's equation to the BBGKY hierarchy

2.1.1) Coarse-grained descriptions

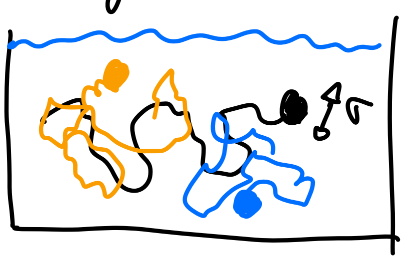
Idea:

We want to identify the fields that allows us to derive a closed, self consistent description of the system at large scale.

$\Rightarrow$ very difficult in general !

Examples:

Microscopic scale	Macroscopic description
pollen grains in water doing random walks (Brown 1827)	diffusion equation



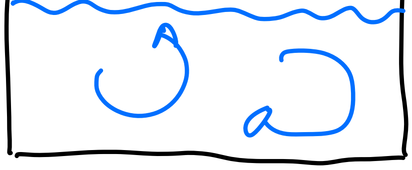
$\Rightarrow$

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

n: number density field

D: diffusivity

Microscopic scale	Macroscopic description
liquid water	Navier-Stokes equations



$\Rightarrow$

$$\begin{cases} \partial_t \rho(\vec{r},t) = -\vec{\nabla} \cdot \left[\rho(\vec{r},t)\,\vec{u}(\vec{r},t)\right] \\ \rho \partial_t \vec{u} + \rho \vec{u} \cdot \vec{\nabla} \vec{u} = -\vec{\nabla} p + \mu \Delta \vec{u} \end{cases}$$

ρ : density field ; $\vec{u}$ velocity field

μ: dynamic viscosity

Comments:

* How do we know what are the right fields? Why no $\vec{u}(\vec{r})$ for the pollen grains? Why no $T(\vec{r})$ for Navier-Stokes?

* If you know D or μ, then you have closed equations. They can be measured experimentally, but where do they come from microscopically? Can we predict their value?

* By reference to the Navier-Stokes equation, such closed, large-scale descriptions are called hydrodynamic equations & the fields they describe hydrodynamic fields (or modes), even when no water is involved.

Why does it work? Scale separation

Microscopic scale	well separated from	Macroscopic scale
particle size σ		diffusion over scale L
time to travel $\tau = \frac{\sigma}{v}$		in $T = \frac{L^2}{D} \gg \tau$
		if $L \gg \sigma$

We say that the system admits scale separation if there are time scales $\tau \ll t \ll T$ such that most observables have relaxed, since $t \gg \tau$, while a few hydrodynamic fields have not since $t \ll T$.

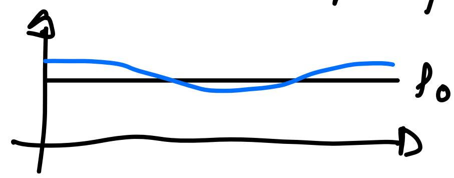
How do we identify the slow fields?

Hard in general, but there are some rules

Conserved fields are slow

It takes time to move stuff without teleportation...

ex: diffusion equation $\partial_t \rho = D \Delta \rho$ & consider a macroscopic fluctuation



$\rho(x, t=0) = \rho_0 + \delta\rho \cos\left(\frac{2\pi x}{L}\right)$

$D \Delta \rho = -D \delta\rho \cos\left(\frac{2\pi x}{L}\right) \cdot \frac{4\pi^2}{L^2}$

Solution of the dynamics $\rho(x,t) = \rho_0 + \delta\rho \cos\left(\frac{2\pi x}{L}\right) e^{-\frac{4\pi^2 D}{L^2} t}$

This relax to $\rho \simeq \rho_0$ when $t \gg T = \frac{L^2}{4\pi^2 D} \xrightarrow[L \to \infty]{} \infty$

Intuition: to relax a conserved field, you need to transport it over a distance $L \Rightarrow T \sim L^z$; z dynamic exponent.

Diffusion $z = 2$

Ballistic transport $z = 1$

Richer physics exists. Kardar–Parisi–Zhang $z = 3/2$

Spontaneous breaking of symmetry & critical slowing down

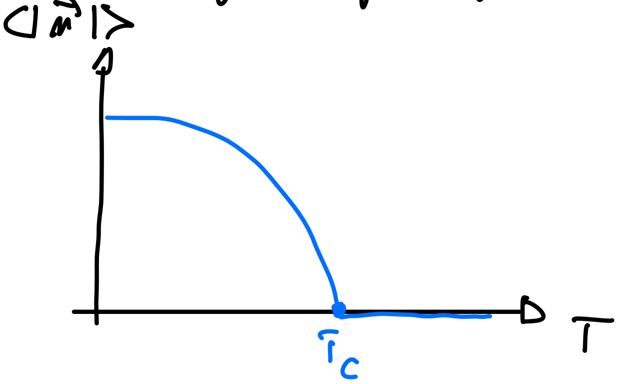
Consider a system invariant under some symmetry group that becomes ordered as the temperature is lowered.

E.g. Ferromagnets, atoms with spins $\vec{S}_i$.

Isotropy of space, all $\vec{S}_i$ are equally likely $\Rightarrow$ $O(3)$ symmetry.

At high temperature, the system is disordered and $\langle \vec{m} \rangle = \frac{1}{N} \langle \sum_{i=1}^{N} \vec{S}_i \rangle = \vec{0}$

At low temperature, exchange interactions between the spins lead to the emergence of magnetisation $\vec{m}_0$ that breaks the symmetry



At T_c, the system wants to order, but very weakly $\Rightarrow$ very large fluctuations that are very slow.

The magnetization field $\vec{m}(\vec{r})$ is then a slow mode.

$\Rightarrow$ generic for continuous transition associated with spontaneous symmetry breaking.

Let's try to build a hydrodynamic description of an dilute gas

2.1.2) Liouville's equation

N classical particles, interacting via a pair potential V and experiencing an external potential $\mathcal{U}$.

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

Comment:

$$\frac{1}{2} \sum_{i \neq j} V(\vec{q}_i - \vec{q}_j) = \sum_{i<j} V(\vec{q}_i - \vec{q}_j) \Rightarrow \text{No double counting}$$

$$\dot{\vec p}_k = -\frac{\partial U}{\partial \vec q_k} - \frac{1}{2}\frac{\partial}{\partial \vec q_k}\left[\sum_{i\neq j} V(\vec q_i - \vec q_j)\,\Big[\delta_{ik} + \underbrace{\delta_{jk}}_{V \text{ even}}\Big]\right]$$

$$= -\frac{\partial U}{\partial \vec q_k} - \frac{1}{2}\underbrace{\sum_j \frac{\partial V(\vec q_k - \vec q_j)}{\partial \vec q_k}}_{j \text{ dummy} \Rightarrow j=i} - \frac{1}{2}\sum_i \frac{\partial V(\vec q_k - \vec q_i)}{\partial \vec q_k} = -\frac{\partial U}{\partial \vec q_k} - \sum_{i=1}^{N}\frac{\partial V}{\partial \vec q_k}(\vec q_k - \vec q_i)$$

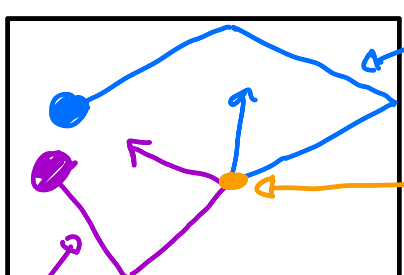
Liouville's equation

$$\partial_t \rho = -\{\rho, H\} = -\sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec q_i}\cdot\frac{\partial H}{\partial \vec p_i} - \frac{\partial \rho}{\partial \vec p_i}\cdot\frac{\partial H}{\partial \vec q_i}$$

$$= -\sum_{i=1}^{N} \underbrace{\frac{\partial \rho}{\partial \vec q_i}\cdot\frac{\vec p_i}{m} - \frac{\partial \rho}{\partial \vec p_i}\cdot\frac{\partial U}{\partial \vec q_i}}_{-\{\rho, H_1\} \text{ describes the "free" evolution of the particles, when they do not interact}} - \underbrace{\frac{\partial \rho}{\partial \vec p_i}\cdot\sum_{k\neq i}\frac{\partial V(\vec q_i - \vec q_k)}{\partial \vec q_i}}_{\text{evolution of } \rho \text{ due to interactions.}}$$

$$\boxed{\partial_t \rho + \{\rho, H_1\} = \sum_{i=1}^{N}\left[\frac{\partial \rho}{\partial \vec p_i}\cdot\sum_{k\neq i}\frac{\partial V(\vec q_i - \vec q_k)}{\partial \vec q_i}\right]} \qquad (LE)$$

Illustrate with $N=2$



"$\partial_t \rho + \{\rho, H_1\} = 0$"

$\frac{\partial V}{\partial q_i} \neq 0 \Rightarrow$ right-hand side important

"$\partial_t \rho + \{\rho, H_1\} = 0$"

Let's start from (LE) & coarse-grain things out!

2.1.3) One-body density

Conserved quantities: particle number, momentum, energy $\Rightarrow$ how do we characterize the corresponding fields starting from $\rho(\{\vec{q}_i, \vec{p}_i\}, t)$

Number density field: $n(\vec{r}, t)$ such that, for any volume V

$$\int_V d^3\vec{r}\; n(\vec{r}, t) = N_V(t)\,,$$ the average # of particles in V.

$$\int_V \delta(\vec{q}_i(t) - \vec{r})\, d^3\vec{r} = 1 \text{ if } \vec{q}_i(t) \in V \;\&\; 0 \text{ otherwise}$$

$$\Rightarrow N_V(t) = \left\langle \int_V \sum_{i=1}^{N} \delta(\vec{q}_i(t) - \vec{r})\, d^3\vec{r} \right\rangle$$

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

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

$$= \int_V d^3\vec{r}\; \left\langle \sum_{i=1}^{N} \delta(\vec{q}_i(t) - \vec{r}) \right\rangle$$

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

One-body function:

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

$$= \sum_{i=1}^{N} \int \underbrace{d^3\vec{q}_i\, d^3\vec{p}_i}_{d\Gamma_i}\; \delta(\vec{q}_i - \vec{r}) \underbrace{\int \prod_{k \neq i} d^3\vec{q}_k\, d^3\vec{p}_k\; \rho(\{\vec{q}_j, \vec{p}_j\}, t)}_{\equiv \rho_i(\vec{q}_i, \vec{p}_i, t)}$$

$\rho_i(\vec{q}_i, \vec{p}_i, t)$ is the marginal of ρ over all particles $h \neq i$. It is the one-body probability density to find the particle i at $\vec{q}_i, \vec{p}_i$ at time t.

Particle indistinguishability All particles in the gas are indistinguishable so that ρ is invariant by permutations of $\vec{q}_i, \vec{p}_i$ & $\vec{q}_j, \vec{p}_j$.

Thus $\rho_i(\vec{q}, \vec{p}, t) = \rho_j(\vec{q}, \vec{p}, t) \equiv \rho_1(\vec{q}, \vec{p}, t)$

One-body density

One thus has

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

$$\boxed{n(\vec{r}, t) = \int d^3\vec{p} \; f_1(\vec{r}, \vec{p}) \quad ; \quad f_1(\vec{r}, \vec{p}) = N \rho_1(\vec{r}, \vec{p})}$$