1.2.4) Conserved quantities and statistical independence of macroscopic volumes

See Landau & Lifschitz, Statistical Mechanics

Liouville's equation Consider a classical system comprising N particles whose position and momenta are denoted as

$$\vec{q}_i = \begin{pmatrix} q_{i,x} \\ q_{i,y} \\ q_{i,z} \end{pmatrix} \quad \& \quad \vec{p}_i = \begin{pmatrix} p_{i,x} \\ p_{i,y} \\ p_{i,z} \end{pmatrix}.$$

We write the dynamics as

$$\dot{\vec{q}}_i = \frac{\partial H}{\partial \vec{p}_i} \quad \& \quad \dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{q}_i} \quad \text{where} \quad \frac{\partial}{\partial \vec{q}_i} = \begin{pmatrix} \frac{\partial}{\partial q_{i,x}} \\ \frac{\partial}{\partial q_{i,y}} \\ \frac{\partial}{\partial q_{i,z}} \end{pmatrix} \quad \& \quad \frac{\partial}{\partial \vec{p}_i} = \begin{pmatrix} \frac{\partial}{\partial p_{i,x}} \\ \frac{\partial}{\partial p_{i,y}} \\ \frac{\partial}{\partial p_{i,z}} \end{pmatrix}$$

Imagine that you sample an initial condition with a probability density $\rho(\{\vec{q}_i, \vec{p}_i\}, t=0) \Longrightarrow \rho(\{\vec{q}_i, \vec{p}_i\}, t) = ?$

Since $\vec{q}_i(t)$ & $\vec{p}_i(t)$ are advected by the flow given by (3), one can define a probability current $\vec{J}(\{\vec{q}_i, \vec{p}_i\}, t) = \rho(\{\vec{q}_i, \vec{p}_i\}, t) \begin{pmatrix} \dot{q}_{1,x} \\ \dot{q}_{1,y} \\ \vdots \\ \dot{p}_{N,z} \end{pmatrix}$.

The conservation equation for probability then reads

$$\partial_t \varrho(\underbrace{\vec{q}_i, \vec{p}_i}_{\text{fixed values}}, t) = -\vec{\nabla}_{\{\vec{q}_i,\vec{p}_i\}} \cdot \vec{J}(\vec{q}_i, \vec{p}_i, t)$$

$$= -\sum_{i=1}^{N} \sum_{\alpha=x,y,z} \left\{ \frac{\partial}{\partial q_{i,\alpha}} \left[\dot{q}_{i\alpha}\, \varrho(\vec{q}_i, \vec{p}_i, t) \right] + \frac{\partial}{\partial p_{i\alpha}} \left[\dot{p}_{i\alpha}\, \varrho(\vec{q}_i, \vec{p}_i, t) \right] \right\}$$

$$= -\sum_{i=1}^{N} \frac{\partial}{\partial \vec{q}_i} \cdot \Big[\underbrace{\dot{\vec{q}}_i}_{\frac{\partial H}{\partial \vec{p}_i}} \varrho \Big] + \frac{\partial}{\partial \vec{p}_i} \cdot \Big[\underbrace{\dot{\vec{p}}_i}_{-\frac{\partial H}{\partial \vec{q}_i}} \varrho \Big]$$

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

where we have introduced the POISSON BRACKET

$$\{A, B\} \equiv \sum_{i=1}^{N} \sum_{\alpha=x,y,z} \frac{\partial A}{\partial q_{i,\alpha}} \frac{\partial B}{\partial p_{i,\alpha}} - \frac{\partial A}{\partial p_{i,\alpha}} \frac{\partial B}{\partial q_{i,\alpha}}$$

Liouville's theorem: $\varrho(\underbrace{\{\vec{q}_i(t), \vec{p}_i(t)\}}_{\text{trajectory}}, t)$ is a constant of motion. Using the chain rule:

$$\frac{d}{dt} \varrho(\{\vec{q}_i, \vec{p}_i\}, t) = \partial_t \varrho + \sum_i \dot{\vec{q}}_i \cdot \frac{\partial \varrho}{\partial \vec{q}_i} + \dot{\vec{p}}_i \cdot \frac{\partial \varrho}{\partial \vec{p}_i}$$

$$= -\{\varrho, H\} + \underbrace{\sum_i \frac{\partial \varrho}{\partial \vec{q}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \varrho}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{q}_i}}_{\{\varrho, H\}} = 0$$

$\ln \rho$ is "additive": Two subsystems $S_1 = \{\vec{q}_1, \vec{p}_1\}$ & $S_2 = \{\vec{q}_2, \vec{p}_2\}$ that are very large and thus assumed uncorrelated:

$$\rho_{1 \cup 2}(\{\vec{q}_1, \vec{q}_2, \vec{p}_1, \vec{p}_2\}) \simeq \rho_1(\{\vec{q}_1, \vec{p}_1\})\, \rho_2(\{\vec{q}_2, \vec{p}_2\})$$

$$\Rightarrow \ln \rho_{1 \cup 2} = \ln \rho_1 + \ln \rho_2$$

Landau's trick: . $\ln \rho$ is an additive constant of motion

. If E is the only additive constant of motion, then $\ln \rho \propto E$.

$\Rightarrow$ Boltzmann weight

This is a second appealing justification of the Boltzmann weight. Still not a derivation $\Rightarrow$ KINETIC THEORY OF GASES.

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 $\mathcal{U}$, so

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

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

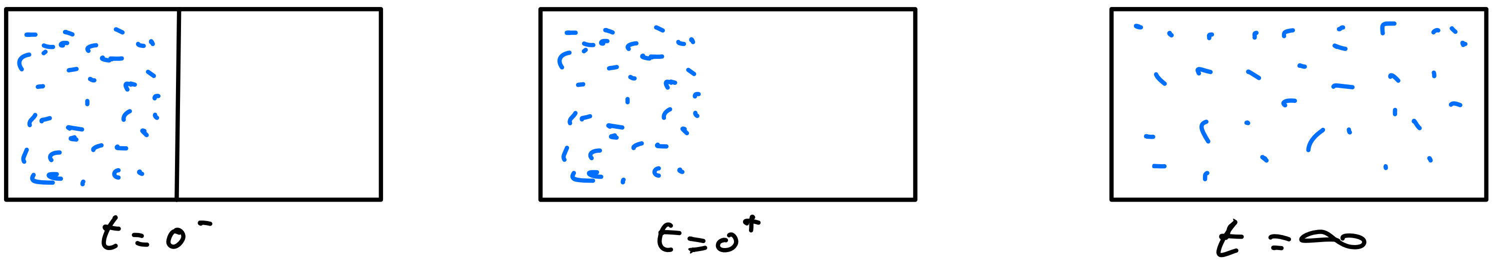
$$\dot{\vec{p}}_k = -\frac{\partial \mathcal{U}}{\partial \vec{q}_k} - \frac{\partial}{\vec{q}_k}\left[\frac{1}{2}\sum_{i\neq k} V(\vec{q}_i - \vec{q}_k) + \frac{1}{2}\sum_{j\neq k} V(\vec{q}_k - \vec{q}_j)\right]$$

dummy $j \to$ dummy i

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

$\Rightarrow$ No double counting.

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



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

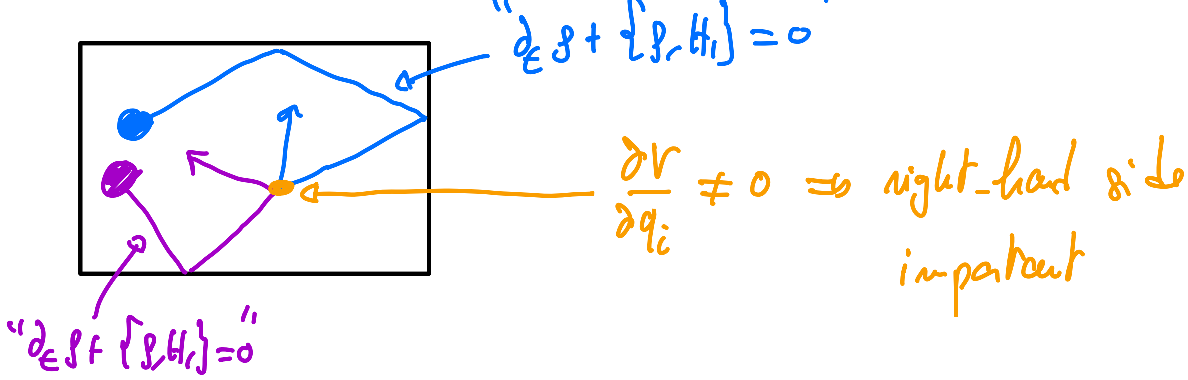
$$\partial_t \rho = -\{\rho, H\} = -\sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{q}_i} \cdot \frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i} \cdot \frac{\partial H}{\partial \vec{q}_i}$$

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

All in all

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

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

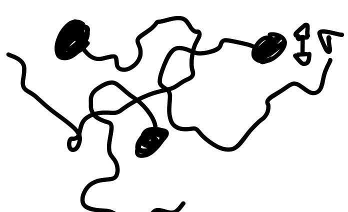
$\Rightarrow$ Q: How? Which observables should we use?

General idea:

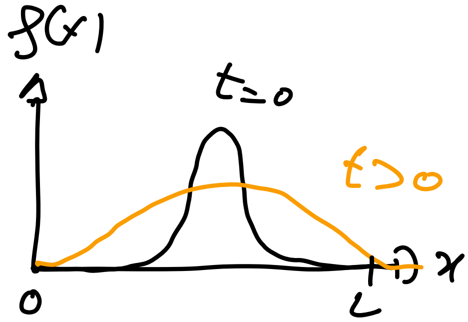
We need to identify the fields that allow us to derive a closed, self consistent description of the system at large scales

$\Rightarrow$ Very difficult task in general

Example:



$\Rightarrow$



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

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