$$\boxed{\partial_t f_1(\vec{q}_1,\vec{p}_1,t) + \{f_1, H_1\} = \int d\vec{q}_1 d\vec{p}_2 \, \frac{\partial V(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1} \cdot \frac{\partial f_2(\vec{q}_1,\vec{p}_1,\vec{q}_2,\vec{p}_2)}{\partial \vec{p}_1}} \qquad \text{(F1)}$$

free evolution — interaction term

## (IV) Time reversibility

Liouville's equation is also time-reversible

If $\rho(\vec{q},\vec{p},t)$ is solution of $\partial_t \rho = -\sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{q}_i}\cdot\frac{\partial H}{\partial \vec{p}_i} - \frac{\partial \rho}{\partial \vec{p}_i}\cdot\frac{\partial H}{\partial \vec{q}_i}$, then

so is $\rho^R(\vec{q},\vec{p},t) = \rho(\vec{q},-\vec{p},t_f-t) \equiv \rho(\vec{Q},\vec{\pi},T)$ with

$\vec{Q}(\vec{q},\vec{p},t) = \vec{q}$ ; $\vec{\pi}(\vec{q},\vec{p},t) = -\vec{p}$ & $T(\vec{q},\vec{p},t) = t_f - t$

Using the chain rule, we find

$$\partial_t \rho^R = \partial_T \rho \cdot \frac{\partial T}{\partial t} = -\partial_T \rho = \sum_{i=1}^{N} \frac{\partial \rho}{\partial \vec{Q}_i}\cdot\frac{\partial H}{\partial \vec{\pi}_i} - \frac{\partial \rho}{\partial \vec{\pi}_i}\cdot\frac{\partial H}{\partial \vec{Q}_i}$$

Then, 
$$\partial_{Q_\alpha}\rho(\vec{Q},\vec{\pi},T) = \partial_{Q_\alpha}\rho^R(\vec{q}(\vec{Q},\cancel{\vec{\pi}},\cancel{T}),\vec{p}(\cancel{\vec{Q}},\vec{\pi},\cancel{T}),t(\cancel{\vec{Q}},\cancel{\vec{\pi}},T))$$
$$= \partial_{q_\alpha}\rho^R\cdot\frac{\partial q_\alpha}{\partial Q_\alpha} = \partial_{q_\alpha}\rho^R(\vec{q},\vec{p},t)$$

Similarly $\partial_{\pi_\alpha}\rho(\vec{Q},\vec{\pi},T) = \partial_{p_\alpha}\rho^R(\vec{q},\vec{p},t)\cdot\frac{\partial p_\alpha}{\partial \pi_\alpha} = -\partial_{p_\alpha}\rho^R(\vec{q},\vec{p},t)$

Last, since $H(\vec{Q},\vec{\pi}) = H(\vec{q},\vec{p})$ : $\partial_{\pi_\alpha}H = \partial_{p_\alpha}H\cdot\frac{\partial p_\alpha}{\partial \pi_\alpha} = -\partial_{p_\alpha}H$ & $\partial_{Q_\alpha}H = \partial_{q_\alpha}H$

All in all, $\partial_t \rho^R = \sum_{i=1}^{N} \frac{\partial \rho^R}{\partial \vec{q}}\cdot\left(-\frac{\partial H}{\partial \vec{p}}\right) + \frac{\partial \rho^R}{\partial \vec{p}}\cdot\frac{\partial H}{\partial \vec{q}} = -\{\rho^R, H\}$

## BBGKY is also reversible!

$$f_1^R(\vec q_1,\vec p_1,t) = f_1(\vec Q_1,\vec \pi_1,T) \qquad \vec Q_1 = \vec q_1\,;\ \vec\pi_1 = -\vec p_1\,;\ T = t_f - t$$

$$\partial_t f_1^R + \{f_1^R, H\}_{\vec q_1,\vec p_1} = \underbrace{-\partial_T f_1 - \{f_1, H\}_{\vec Q_1,\vec \pi_1}}_{\text{as for Liouville's eq}^\circ} = -\int d\vec q_2\, d\vec p_2\, \frac{\partial V(\vec Q_1 - \vec q_2)}{\partial \vec Q_1}\cdot \frac{\partial f_2(\vec Q_1,\vec \pi_1,\vec q_2,\vec p_2)}{\partial \vec \pi_1}$$

$$= \int d\vec q_2\, d\vec p_2\, \frac{\partial V(\vec q_1 - \vec q_2)}{\partial \vec q_1}\cdot \frac{\partial}{\partial \vec p_1} \underbrace{f_2(\vec q_1, -\vec p_1, \vec q_2, \vec p_2, t_f - t)}_{f_2^R}$$

the BBGKY is also reversible, so it's not going to explain why the gas relaxes to equilibrium!

**Good news:** We will solve both problems at the same time by deriving the Boltzmann equation.

## 2.2) The Boltzmann equation

### 2.2.1) the relevant time scales

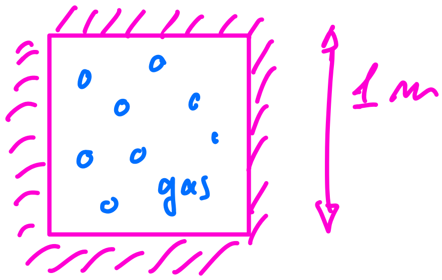
$$\boxed{\underbrace{\partial_t f_1(\vec q_1,\vec p_1,t) + \{f_1, H_1\}}_{\text{free evolution}} = \underbrace{\int d\vec q_1\, d\vec p_2\, \frac{\partial V(\vec q_1 - \vec q_2)}{\partial \vec q_1}\cdot \frac{\partial f_2(\vec q_1,\vec p_1,\vec q_2,\vec p_2)}{\partial \vec p_1}}_{\text{interaction term}}} \tag{F1}$$

**Comment:** for $V=0$, $\partial_t f_1 + \{f_1, H_1\} = 0$ is a closed equation; this is the "collision-free Boltzmann equation" studied in Part 2.
The difficulty is to deal with the right-hand side.

## Relevant time scales:

**The free evolution.** The macroscopic length & time scales are set by $\mathcal{U}(\vec{q})$ & boundary conditions.

E.g.




The time scale $\tau_F$ of the free evolution $\partial_t f_1 + \{f_1, H_1\} = 0$ corresponds to crossing the box.

$\tau_F = \frac{L}{v} \Rightarrow v = ?$ $\quad \frac{1}{2} m_{N_2} \langle \vec{v}^2 \rangle = \frac{3}{2} k_B T$ & $m_{N_2} = \frac{2 \times 14 \times 10^{-3}}{\mathcal{N}_A}$

$$\Rightarrow v \simeq \sqrt{\langle \vec{v}^2 \rangle} = \sqrt{\frac{3 k_B T}{m_{N_2}}} = 500 \ m/s \Rightarrow \tau_F \simeq 2.10^{-3} s$$

More generally $[\{f_1, H_1\}] = \frac{[f_1]}{\tau_F}$ ; $\partial_t f_1 + \frac{f_1}{\tau_F} = 0 \Rightarrow f_1 \propto e^{-t/\tau_F}$

$\tau_F$ is the time scale over which $\{f_1, H_1\}$ makes $f_1$ relax.

**Interaction term** Similarly $\left[ \int d\vec{q}_2 \, d\vec{p}_2 \, \frac{\partial f_2}{\partial \vec{p}_1} \cdot \frac{\partial V}{\partial \vec{q}_1} \right] = \frac{[f_1]}{\tau}$

$\Rightarrow$ what are the relevant time scales?

In a dilute gas, collisions are rare and sudden $\Rightarrow$ two time scales.

① duration of a collision $\tau_{col} \simeq \frac{d}{v}$, with d the particle size.

$$d \sim 3 \, \text{Å} \Rightarrow \tau_{col} \simeq 6.10^{-13} s = 0{,}6 \ ps$$

But most of the time, there are no collisions!

## ① time between collisions $\tau_{MFP}$

In a time $t$, a particle explores a volume $V(t) = \pi d^2 \bar{v} t$, and it thus encounters $n V(t) = \pi d^2 \bar{v} t n$ particles, where $n$ is the gas density. By definition $n V(\tau_{MFP}) = 1 \Rightarrow \tau_{MFP} = \dfrac{1}{\pi d^2 \bar{v} n}$

For the air in the classroom, $n = P/(k_B T)$, with

$P = 10^5 \, N.m^{-2}$, $T = 300K \Rightarrow n \simeq 2.10^{25} m^{-3}$, leading to

$$\tau_{MFP} \simeq 3 \; 10^{-10} s$$

## Three well separated time scales

$$\tau_{col} \simeq 6.10^{-13} \ll \tau_{MFP} \simeq 3.10^{-10} s \ll \tau_F \simeq 2.10^{-3} s$$

## Boltzmann equation

Describe the evolution over a time $\tau$ such that $\tau_{col} \ll \tau \ll \tau_{MFP}$

$\rightarrow$ collisions look instantaneous

$\rightarrow$ ——— are rare & random events, leading to small variations to $f_1$