Two ways to Boltzmann Eq.

1 Intuitive Derivation:

a – "the Dilute billiard gas".

b – μ-space vs Γ-space.

c – Collision rates and B. Equation.

d – Reminder: Physics of Elastic collisions.

2. Formal Derivation

a – The BBGKY hierarchy (for a binary interaction potential)

b – Dilute gas approximation.

c – Chaotic Hypothesis.

d – Observations

Reference:

Physics: Huang – Statistical Mechanics, chapt.

Math: Cercignani – Theory and Application of the B. equations.

Spohn: Large-Scale Dynamics of interacting particles.

1

Ambition is to derive a coarse-grained description of a system composed of an assembles of N undistinguishable particles, say described microscopically through the Hamiltonian:

$$H_N = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + V[q_i] + \sum_{i<j} \mathcal{U}_{ij}$$

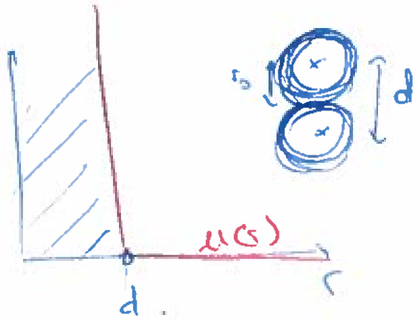
with $\mathcal{U}_{ij} = u[r_{ij}]$; $r_{ij} = q_i - q_j$

① Intuitive derivation: The Dilute gas of (spinless) billiard balls.

It corresponds to the specific choice:

$$V(\vec{q}) = \begin{cases} \infty & \vec{q} \in \partial D \\ 0 & \vec{q} \in D \end{cases}$$

$$u(r) = \begin{cases} \infty & r \leq d \\ 0 & \text{otherwise} \end{cases}$$



Together with the following modeling assumptions:

(i) • Binary collisions: dilute gas $\rho \ll 1$

(ii) • Collisions are instantaneous: $\tau_{coll} \to 0$.

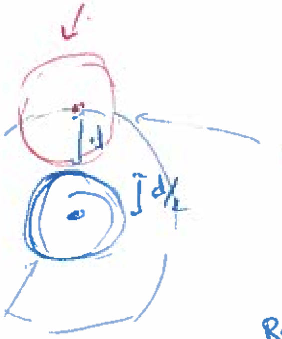
(iii) • Balls are rigid

(iv) • Any possible × between velocities prior and after collisions are neglected. [" molecular chaos"; "Stosszahl hypothesis"].

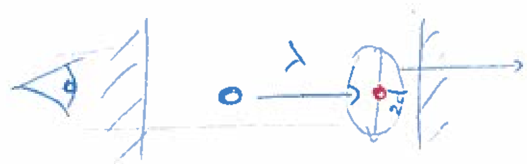
Items i) and ii) can be quantified in terms of measurable parameters:

<u>In particular</u>:

- λ : mean free path : "average distance travelled between two successive collisions".



<u>ixed target</u>



<u>Interaction sphere</u> : sphere of radius $\underset{\text{Ôm}}{\underline{d}}$ enclosing a particle with diameter d, with cross section $\sigma = \pi d^2$.

Rough estimate gives:

$$\lambda \pi d^2 N = V \implies \boxed{\lambda = \frac{1}{\pi d^2 \rho}}. \qquad \rho \ll 1 \Rightarrow \lambda \gg 1$$

- <u>Instantaneous collision</u>:

$$\tau_{coll} \ll \tau_\lambda$$

τ_λ : average time spent between two collisions,

$$\tau_\lambda = \frac{\lambda}{\langle u \rangle}.$$

<u>With numbers</u>:

<u>Air</u> (Room Temp) : $\rho \sim 10^{25}$ molecules$/m^3$.
$d \sim 10^{-10}$ m
$u \sim 10 m/s$.

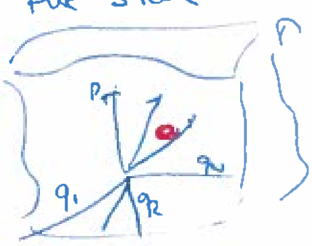
$\Rightarrow$ • $\lambda \sim 10^{20-25} \sim 10^{-5}$ m.
$\underline{\lambda \sim 10^5 d}$. i.e. $\frac{\lambda}{d} \gg 1$.
• $\tau_\lambda \sim 10^{-6}$ s.

- How to describe the gas?

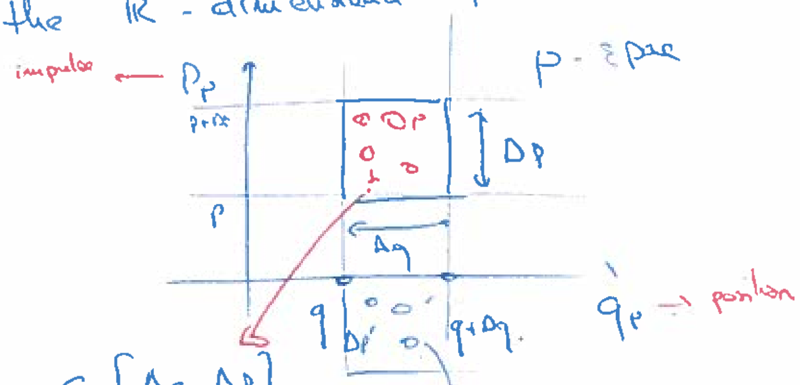
From Γ-space to μ-space description.

Γ-space : One point $(\vec{P}, \vec{Q}) \in \mathbb{R}^{2n}$ represents the state of the N molecules

$\longrightarrow$ Too precise!



μ-space : state of the gas = N points in the $\mathbb{R}^{2d}$-dimensional space.



μ-space densities:

$$f_1(\vec{p}, \vec{q}, t)\, \Delta^3 q\, \Delta^3 p$$
$= \#$ molecules $\in [\Delta q, \Delta p]$

$$f_2(q, p, p', t)\, \Delta^3 q\, \Delta^3 p\, \Delta^3 p'$$
$= \#$ pairs with impulses $\in [\Delta p\ \Delta p']$ @ q.

We will assume

$$\boxed{f_2(q, p, p', t) \simeq f_1(q, p, t)\, f_1(q, p', t)}$$

chaotic hypothesis

The quantity f_1 can be used to describe various measurable quantities, at a local level.

Density : $n_1(q, t) \doteq \frac{1}{V} \int f_1(p, q, t)\, d^3p$ $\Rightarrow \int n_1 dq = \frac{N}{V} = \rho$

Velocity : $\vec{u}(q, t) \doteq \int d^3p\, f_1(p, q, t) \frac{\vec{p}}{m}$

etc.

Obs : in terms of the full Liouville density: $f_1(p, q, t) = N \int \prod_{i=2}^{N} d\vec{q}_i\, d\vec{p}_i\, \rho(q_1 \ldots q_N, p \ldots)$

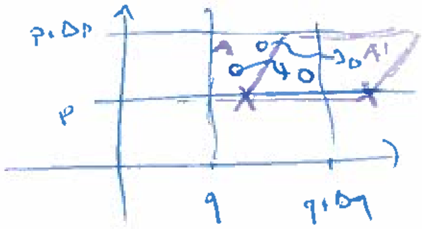
[illegible] $\int \prod d\vec{q}_i\, d\vec{p}_i\, \rho(\vec{q}, \vec{p})$

[L]

Equation for f_1

During two collisional events, the assembly of N particles evolve as a perfect gas:

$|A'| = |A|$



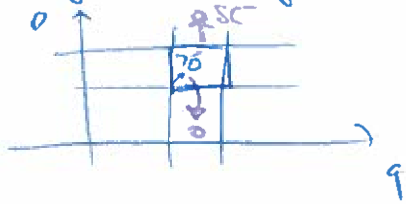
$$(*)\quad f_1[q+\dot{q}\tau,\ p+\dot{p}\tau,\ t+\tau]\ \underbrace{\Delta^3 q'\,\Delta^3 p'}_{=\Delta q\,\Delta p}$$

$$= f_1[q,p,t]\,\Delta^3 q\,\Delta^3 p$$

$$+\ \delta C^+ \quad - \ \delta C^-$$

$$+\ \delta W^+ \quad - \ \delta W^-$$

← number of binary collisions either yielding or removing p-particle at q



reflections due to collisions with wall yielding p-part

reflection removing p-particle.

Specifically:

collision rate

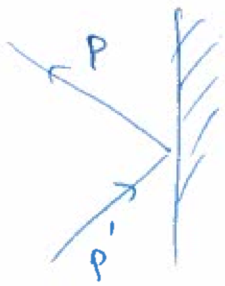
$$\delta C^+ = \tau\,\Delta^3 q\,\Delta^3 p \int dp' dp'_* dp_*\ \chi(q,\ p'p'_* \to p p_*)\ f_1[p', q, t]\, f_1[p'_*, q, t]$$

$$\delta C^- = \tau\,\Delta^3 q\,\Delta^3 p \int dp\, dp_* dp_*\ \chi(p p_* \to p' p'_*)\ f_1[p_*, q, t]\, f_1[p, q, t]$$

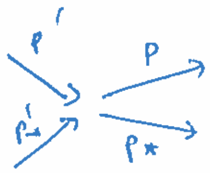
$$\delta W^+ = \tau\,\Delta^3 q\,\Delta^3 p \int dp'\ \chi^{\omega}_{p'\to p}\, f_1[p', q, t].$$

$$\delta W^- = \tau\,\Delta^3 q\,\Delta^3 p \int dp\ \chi^{\omega}_{p\to p'}\, f_1[p, q, t].$$

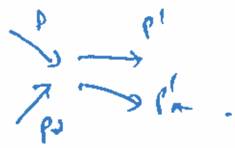
δW^+



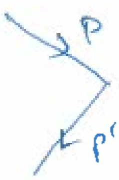
δC^+



δC^-



δW^-



Rmq: $\chi^{\omega}_{p'\to p}\,\Delta^3 p\,\tau$ = fraction of particles with p' that ~~transfer~~ reflect to p.

$\int \chi_{p'\to p}\,\Delta p = 1$

Discrete symmetries of Hamiltonian dynamics impose symmetries of the collision rates:

Time-Reversal: $\chi^{(\vec{q})}_{p_0 p_1 \to p_0' p_1'} = \chi^{(\vec{q})}_{-p_0'-p_1' \to -p_0-p_1}$

Parity Invariance: $\chi^{(+\vec{q})}_{p_0 p_1 \to p_0' p_1'} = \chi^{(-q)}_{-p_0-p_1 \to -p_0'-p_1'}$.

This implies, assuming spatial homogeneity:

$$\boxed{\chi_{p_0 p_1 \to p_0' p_1'} = \chi_{p_0' p_1' \to p_0 p_1}} \quad (S)$$

Expanding (4) and using (S) yields the

Boltzmann equation:

$$\partial_t f_1 + \frac{\vec{p}}{m}\cdot\partial_q f_1 = \phi(f_1, f_1) + L f_1$$

with

$$\phi(f_1, f_1) = \int_{p_1' p_*' p_*} \chi_{p_*' p' \to p_* p}\left(f_1' f_{1*}' - f_1 f_{1*}\right)$$

$$L f_1 = \int_{p'} \chi^{0}_{p' \to p}\left(f_1' - f_1\right) dp'.$$

and the shorthand notations:

$$f_1' \equiv f_1[\vec{q}, \vec{p}\,', t]$$

$$f_1 = f_1[q, \vec{p}, t]$$

$$f_{1*} = f_1[q, p_*, t]$$

$$f_{1*}' = f_1[q, p_*', t].$$

(Bo)

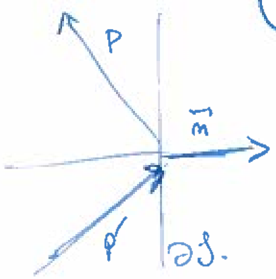
Obs: • This equation is an integro-differential equation.

• Ressembles a master equation [Chapman-K], as seen in the Ehrenfest Lottery, with the notable exception that it is quadratic in the argument.

To substantiate (Bo), we will render the collision rate explicit.

Collision rates for elastic collisions

Ⓐ Reflexion at the wall.



$$\Delta^3 p \cdot \chi^{\omega}_{p' \to p} \doteq \mathbb{1}_{\vec{q} \in \partial\mathcal{S}} \, (p' \cdot n) \, \mathbb{1}_{p' \cdot n > 0} \qquad p = p' - 2(p' \cdot n) n .$$

Ⓑ Binary collisions:

$$\Delta^3 p \, \Delta^3 p_* \, \chi_{p' p'_* \to p p_*} = \int_{\mathbb{R}^2} d\tilde{\chi}_{p' p'_* \to p p_*}(\sigma)$$

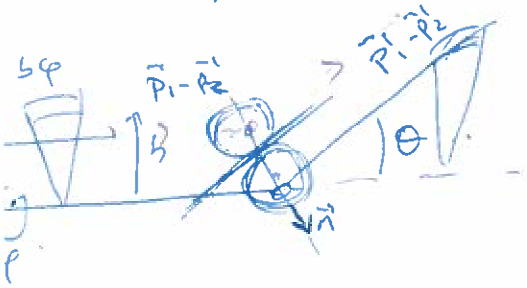
with $d\tilde{\chi}_{p' p'_* \to p p_*}(\sigma) = \mathbb{1}_{\substack{\Pi = \Pi' \\ \Delta p = \Delta p' - 2(\Delta p' \cdot n)}} |\Delta p'| \, d\sigma$.

$= |\Delta p'| \, d\sigma$

↑

Abuse

σ = impact parameter



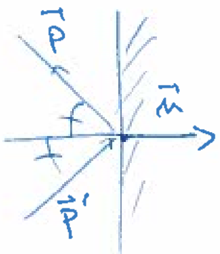
<u>Exercise</u>: • Show the formulae (A) and (B).

• Check the symmetry property (8) for these cases.

<u>Solution</u>:

• <u>Formula (A)</u> [Reflexion].

<u>Hard wall</u> = particle with impulse $\vec{p}'$ reflects with impulse $\vec{p}$:



$$\vec{p} = \vec{p}' - 2(p'.n)\,n$$

[specular reflexion]

<u>Obs</u>: Energy is conserved: $\frac{\vec{p}^{\,2}}{2m} = \frac{1}{2m}\left[\vec{p}' - 2(p'.n)n\right]^2 = \frac{\vec{p}'^{\,2}}{2m}$ (check).

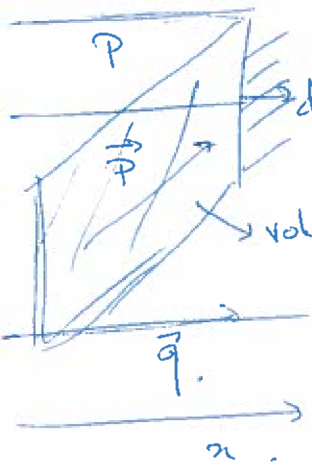
Momentum is not conserved.

Yet the |vertical / parallel| component is!

$$p'_{/\!/} = p_{/\!/} \quad \text{with} \quad p_{/\!/} = \vec{p} - (p.n)\,n .$$

$$\left(p_{/\!/} = \vec{p} - (p.n)n = \vec{p}' - 2\cancel{(p'.n)}n - (p'.n)n + 2\cancel{(p'.n)} = p'_{/\!/} \right)$$

We can now estimate:



$$\delta W^+ = \int_{\mathbb{1}_{p'.n>0}} d^3p'\ f_1(p',q,t)\ \frac{\vec{p}.n}{m}\ \tau\ dA\ \Delta x\ \mathbb{1}_{x\in\partial S}$$

dA.

volume: $\left(\frac{\vec{p}.n}{m}\tau\right) dA$

$$= \tau \int dp'\ \Delta^3 x\ \mathbb{1}_{x\in\partial S}\ \frac{|p'.n|}{m}\ f_1(p',q,t)\ \mathbb{1}_{p'.n>0}$$

$$= \tau \int dp'\, f_1(p',q,t)\ \chi^{\omega}_{p'\to p}\ \Delta^3 x\, \Delta^3 p .$$

<u>with</u>
$$\boxed{\chi^{\omega}_{p'\to p}\,\Delta^3 p = \mathbb{1}_{x\in\partial S}\ \frac{|p'.n|}{m}\ \mathbb{1}_{p'.n>0} .}$$

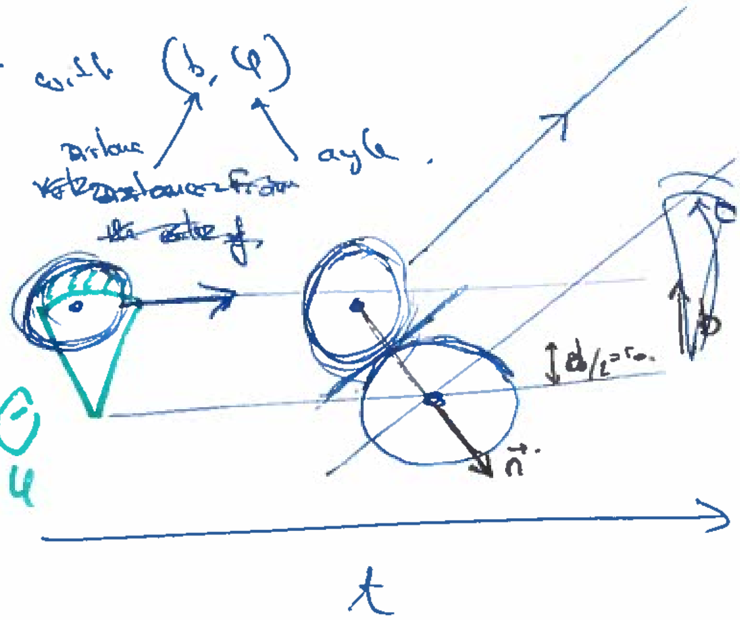
• Formula B:

Elastic collision $\stackrel{\text{def}}{=}$ A collision which preserves energy & momentum.

Binary elastic collision:
$$\left|\begin{array}{ll} \vec{p}_1 + \vec{p}_2 \to \vec{p}_1' + \vec{p}_2' & (3\text{ eq}) \\ p_1^2 + p_2^2 \Rightarrow p_1'^2 + p_2'^2 & (1\text{ eq}) \end{array}\right. \quad (E)$$

Obs: in 3d, p_1' and p_2' are not entirely prescribed by (E).
The missing parameter $\sigma \in \mathbb{R}^2$ is the impact parameter.
in our case, we identify σ with (b, φ)
distance ~~from the axis of~~ angle.

Def: Rest frame of ② [Target].



$d\sigma = b\,db\,d\varphi$.
(θ, φ) : scattering parameters.
$d\Omega$: $\sin\theta\, d\theta\, d\varphi$ (solid) scattering angle
$d\sigma = \left|\frac{d\sigma}{d\Omega}\right| d\Omega$

" Differential cross section " [Jargon].

$\sigma_T = \int \left|\frac{d\sigma}{d\Omega}\right| d\Omega$.

Hard sphere: $\sigma_T = \int_0^d b\,db\,d\varphi = 2\pi \frac{d^2}{2} = \pi d^2$.
X-section of interaction sphere

For prescribed $b \in]0; d[$, the outgoing impulses are:

$$\Delta\vec{p} = \vec{p}_1 - \vec{p}_2$$

$$p_1' = p_1 - (\Delta p)\cdot n\, \vec{n}$$

$$p_2' = p_2 + (\Delta p)\cdot n\, \vec{n}.$$

The fundamental observation is $\Delta p' = \Delta p - 2(\Delta p)\cdot n\, \vec{n}$.

In the rest frame of the target particle the incident particle undergoes " specular reflection "

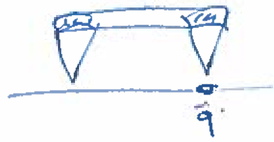
$$\alpha = \frac{(\Delta p \cdot n)\cos}{(\Delta p)}.$$

6'''

$\Rightarrow$ the angle between the relative velocities before and after collision is bisected by the line joining both centers of mass!

To determine the scattering rates, it now suffices to count the number of collisions $p_1 p_2 \to p_1' p_2'$ within τ.

$\frac{\Delta p}{m}\tau$



This number is:

$$dN^+_{p_1p_2}(\sigma) = \overbrace{b\,db\,d\varphi}^{d\sigma}\ \tau\ \frac{|\Delta p|}{m}\ \underbrace{f_1(p_1,q,t)\,f_1(p_2,q,t)}_{\text{in fact } f_2(p_1 x, q, t)}\ \Delta^3 p_1 \Delta^3 p_2 \Delta^3 q$$

$$\mathbb{1}_{\substack{\Delta p' = \Delta p - 2(\Delta p\cdot n) \\ \pi = \pi'}}.$$

$$= \tau\, d\chi_{p_1p_2\to p_1'p_2'}(\sigma)\quad f_1(p_1)\,f_1(p_2)\qquad \Delta^3 p_1\, \Delta^3 p_2\, \Delta^3 q$$

with $d\chi(\sigma)_{p_1p_2\to p_1'p_2'} = \mathbb{1}_{\substack{\Delta p' = \Delta p - 2\Delta p\cdot n \\ \pi = \pi'}}\ \frac{|\Delta p|}{m}\, d\sigma.$

Hence:

$$dN^+_{p_1p_2\to p_1'p_2'} = \int_{\mathbb{R}^2} d\chi(\sigma)\quad f_1(p_1)\,f_1(p_2)\ \Delta p_1 \Delta p_2 \Delta q.$$

$$= \cancel{\chi_{p_1p_2}}\ \chi_{p_1p_2\to p_1'p_2'}\ \Delta p_1' \Delta p_2'\quad \Delta p_1 \Delta p_2 \Delta q.$$

with

$$\boxed{\chi_{p_1p_2\to p_1'p_2'}\ \Delta p_1' \Delta p_2' = \int d\sigma\ \frac{|\Delta p|}{m}\ \mathbb{1}_{\substack{\Delta p' = \Delta p - 2(\Delta p\cdot n)n \\ \pi = \pi'}}}$$

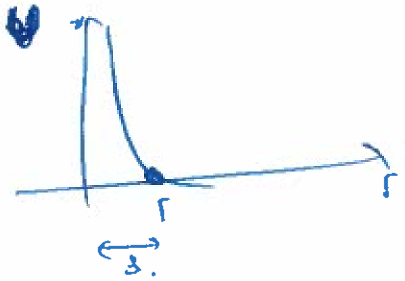
② Formal Derivation of the Boltzmann-Equation

(A) via the "BBGKY" hierarchy.

↳ Bogoliubov, born, green, Kirkwood Yvon.

- the objective of this section is to give a 2nd, but this time "generic" derivation of the (BE) : Involving explicitly the Liouville equation and smooth potentials.

- We assume again that $\mathcal{U}$ is short range: $\mathcal{U} = 0$ for $r > d$.



Def: - $H_N(\vec{q}, \vec{p}, t) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + V[q_i] + \sum_{j>i} \mathcal{U}_{ij}$, $\quad \mathcal{U}_{ij} = \mathcal{U}[r_{ij}]$, $r_{ij} = \|q_i - q_j\|$

- $\rho_N[\{\vec{q}, \vec{p}\}, t]$ = Distribution of $\{\vec{q}, \vec{p}\}$ in Γ-space at time t.

[Recall: At equilibrium, we expect $\rho_N \propto \delta[\mathcal{H}_N[\vec{q}, \vec{p}] - E]$]

- we use interchangeably $z \leftrightarrow (\vec{q}, \vec{p})$ $\quad dz = d\vec{q}\, d\vec{p}$ (shorthand).

- $Z!$ Assume ρ_N is symmetric under exchange of two particles:

i.e. $\rho_N[z_{\sigma(1)} \cdots z_{\sigma(N)}] = \rho_N[z_1 \cdots z_N]$

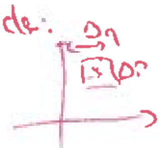
We now define: the normalized "coarse-grained densities: (in μ_k-space)

$$\rho_1 = \int \prod_{i \geq 2} \underbrace{dz_i}_{d\vec{p}_i\, d\vec{q}_i} \rho_N[\{q, p\}, t] \qquad \rho_k = \int \prod_{i \geq k+1} dz_i\, \rho_N[\{q\}, t]$$

It is more convenient to introduce the local $\overset{\text{rigorous}}{\vee}$ densities:

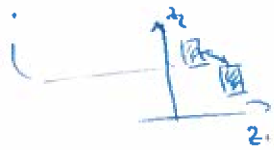
$$f_1 = N \int \prod_{i \geq 2} d\vec{p}_i \, d\vec{q}_i \; \rho_N(\{p,q\}_i^t) = N \rho_1(p,q,t).$$

[local number of particles in $f_1 \Delta p \Delta q$]



$$f_2 = N(N-1) \int \prod_{i \geq 3} d\vec{z}_i \; \rho_N(\{p,q\}^t) = N(N-1)\rho_2.$$

[# p-uples]



$\vdots$

$$f_p = N(N-1)\cdots(N-p+1) \int \prod_{i \geq p+1} d\vec{z}_i \; \rho_N = \frac{N!}{(N-p)!} \rho_p.$$

obs:
$$f_1(p,q) = N \int \Big(\prod_{i \neq k} d\vec{z}_i \Big) \rho_N(\{p,q\},t) \qquad \forall k \in [\![1;N]\!]$$

$(p_k,q_k) = (p,q)$.

$$f_2(p,q,p',q') = \int \prod_{i \neq k,k'} dz_i \; \rho_N(\{p,q\}) \, (N-1)N \qquad \forall k \neq k'$$

obs: another way of writing:

$$f_1(p,q) = N \int \Big(\prod_{i=1}^{N} dz_i\Big) \rho_N(\{p,q\},t) \, \delta(p_k - p)\delta(q_k - q)$$
$$= N \langle \delta(p_k - p)\delta(q_k - q) \rangle \qquad (\forall k \in [\![1;N]\!]).$$

$$\int f_1 \, dp\,dq = N.$$

$$\int f_2 \, dp\,dq\,dp'\,dq' = N(N-1) \langle \delta(p_k - p)\delta(q_k - q)\delta(p_{k'} - p')\delta(q_{k'} - q') \rangle$$

Our goal is to find an equation for $f_1, f_2, \dots f_N$.

The final answer turns out to be the so-called

<u>BBGKY - Hierarchy</u>:

$$\partial_t f_1 + \{f_1, H_1\} = \int dz_2 \{U_{12}, f_2\}$$

$$\partial_t f_2 + \{f_2, H_{12}\} = \int dz_3 \left[\{U_{13}, f_3\} + \{U_{23}, f_3\}\right]$$

$$\vdots$$

$$\partial_t f_p + \{f_p, H_{1\to p}\} = \sum_{i=1}^{p} \int dz_{p+1} \{U_{i\,p+1}, f_{p+1}\}$$

<u>obs</u>:

- $\partial_t f_N + \{f_N, H_N\} = 0.$
  The hierarchy is not closed due to the binary collision term
- As $N \to \infty$, the hierarchy becomes an infinite set of equations!

<u>BE</u> corresponds to a specific truncation of the hierarchy ⊕ some ad-hoc assumptions, which in general <u>are not</u> rigorously justified.

<u>Exercise:</u> Derive the BBGKY hierarchy. $\lfloor 9'$

<u>Sol</u>:

Most easily done in terms of observable.

$$G : (\vec{p},\vec{q}) = z \in \mathbb{R}^{2M} \longrightarrow G_1(p_1,q_1) \;\dots\; O_2(p_1,q_1,p_2,q_2) \text{ etc.}$$

- <u>Eq for a general observable</u>: [From Liouville].

$$\frac{d}{dt}\langle O\rangle \doteq \int dz\, O(\bar{z})\,\partial_t \rho_N(\bar{z},t) = -\int O\,\{\rho,H\}$$

$$\boxed{\frac{d}{dt}\langle G\rangle = \langle\{G,H\}\rangle}$$

- <u>Eq for an observable $G : \bar{z} \to G_1$</u>

$$\frac{d}{dt}\langle G\rangle = \int G_1(z_1)\,dz_1\,\partial_t \overbrace{\int \prod_{i>1}\rho_N(z)\,dz}^{\rho_1} = \int G_1\,\partial_t\rho_1(z_1,t)\,dz_1$$

$$\langle\{O,H\}\rangle = \int \rho_N\,dz\Big[\{O_1,H_1^{(z_1)}\} + \sum_{i>1}\{O_1(z_1),H_1(z_i)\}. + \sum_{i>1}\{O_1,U_{1i}\}. + \sum_{\substack{i>1\\ j>i}}\{O_1(z_1),U_{ij}\}.\Big].$$

0 . 0

$$= \int dz_1\,\rho_1\,\{O_1,H_1\} + \sum_{i>1}\int dz_1\,dz_i\,\{O_1,U_{1i}\}\underbrace{\prod_{\substack{k\neq i\\ k>1}} dz_k\,\rho_N(z)}_{\doteq\,\rho_2(z_1,z_i)}$$

$$= \underbrace{\int dz_1\,\rho_1\,\{O_1,H_1\}}_{=\int dz_1\,O_1\{H_1,\rho_1\}.} + (N-1)\underbrace{\int dz_1\,dz_2\,\{O_1,U_{12}\}\,\rho_2(z_1,z_2)}_{=\int dz_1\,dz_2\{U_{12},\rho_2\}\,O_1}.$$

$$\Longrightarrow \left|\,\partial_t\rho_1 + \{\rho_1,H_1\} = (N-1)\int dz_2\,\{U_{12},\rho_2\}\,\right|$$

- To obtain ρ_2, consider: $O: z \longrightarrow O_2(z_1, z_2)$

$$\frac{d}{dt}\langle O\rangle = \int O_2(z_1,z_2)\, dz_1 dz_2\, \partial_t \underbrace{\rho_2(z_1,z_2)}_{\int \prod_{i>2} \rho_N\, dz_i}$$

$$\{O, H\}\rangle = \int dz_1\, dz_2 \ldots dz_N\, \rho_N \Big[\{ O_2(z_1,z_2), H_{12}(z_1,z_2)\} + \sum_{j\geq 3} \{O_2, u_{1j}\} + \sum_{j\geq 3}\{O_2, u_{2j}\}\Big]$$

$$= \int dz_1 dz_2\, \rho_2 \{O_2, H_{12}\} + (N-2)\int \rho_3\, dz_1\, dz_2\, dz_3 \Big[\{O_2, u_{13}\} + \{O_2, u_{23}\}\Big]$$

$$\Longrightarrow \times N(N-1) \quad \boxed{\partial_t \rho_2 + \{\rho_2, H_{12}\} = (N-2)\int dz_3 \{u_{13} + u_{23}, \rho_3\}}$$

$$\partial_t f_2 + \{f_2, H_{12}\} = \int dz_3 \{u_{13} + u_{23}, f_3\}.$$

Etc:

$$\left(\frac{N!}{(N-k)!} \times\right) \partial_t \rho_k + \{\rho_k, H_{1\to k}\} = (N-k)\int dz_{k+1} \{u_{1k+1} \cdots u_{kk+1}, \rho_{k+1}\},$$

$$\partial_t f_k + \{f_k, H_{1\to k}\} = \int dz_{k+1} \Big\{\sum_{i\leq k} u_{ik+1}, f_{k+1}\Big\}.$$

L10

③ BE from BBGKY (Dilute gas approximation)

The Boltzmann equation can now be obtained by manipulating the BBGKY hierarchy. Essentially: truncating to order 2 and dropping physically subdominant terms. Let's see the general philosophy.

BBGKY: order 2:

$$
\begin{cases}
(1) \quad \partial_t f_1 + \{f_1, H_1\} = \overbrace{\int dz_2 \{U_{12}, f_2\}}^{\doteq\, \Phi_{12} \;(\doteq\, \partial_t f)_{coll}} \\
(2) \quad \partial_t f_2 + \{f_2, H_{12}\} = \int dz_3 \{U_{13}, f_3\} \\
\qquad \{f_2, H_1\} + \{f_2, H_2(z_2)\} + \{f_2, U_{12}\} \qquad \underbrace{+\{U_{23}, f_3\}}_{\tilde{Q}_{123}}
\end{cases}
$$

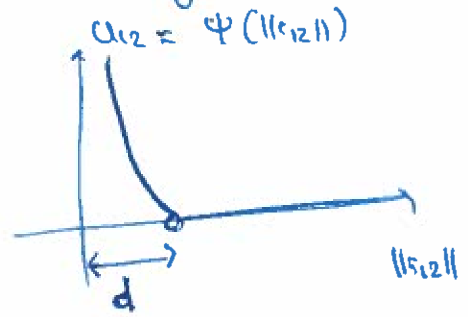
Obs: Dimensional analysis:

- Several terms appear:
  - streaming terms: $\{f_1, H_1\} \sim \dfrac{f_1}{\tau_s}$ with τ_s either streaming i.e. $\tau_s \sim \dfrac{d}{\delta u}$, or collision time with walls (τ_c)
  - collision terms: $\{f_2, U_{12}\} \sim \dfrac{f_2}{\tau_{coll}}$

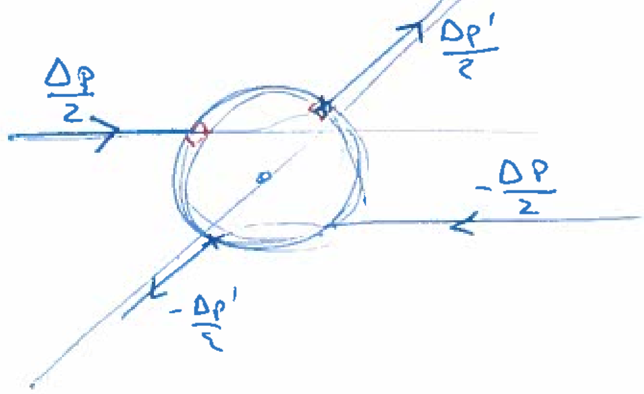
    $\{f_3, U_{13}\} \sim \dfrac{f_3}{\tau_{coll}}$.

- Recall $f_1 \simeq N \int f_2 \, dp_2 dq_2$. $f_2 = N \int f_3 \, dp_3 dq_3$

For short range potentials, as considered here, the potential is non zero only when $\|r_{12}\| < d$, in which case it varies tremendously



In the center of mass ref. frame



→ We can now provide useful dimensional estimate!

- $\mathcal{Q}_{12} \hat{=} \int dz_2 \{\mathcal{U}_{12}, f_2\} \sim \frac{1}{\tau_{coll}} \int_{|r_{12}|<d} d\vec{q}_2\, d\vec{p}_2\, f_2 \sim \frac{N f_1}{\tau_{coll}} \left(\frac{d}{L}\right)^3.$

- $\tilde{\mathcal{Q}}_{123} = \frac{N f_2}{\tau_{coll}} \left(\frac{d}{L}\right)^3.$

→ We observe that $\mathcal{Q}_{12}$ can be large, or rather that it can in general not be neglected in Eq 1 as τ_{coll} is small but so should be $N\left(\frac{d}{L}\right)^3$.

Yet, on dimensional grounds:

$$\underbrace{\{f_2, \mathcal{U}_{12}\}}_{\frac{f_2}{\tau_{coll}}} \gg \underbrace{\tilde{\mathcal{Q}}_{123}}_{\frac{N f_2}{\tau_{coll}}\left(\frac{d}{L}\right)^3} \quad \text{when} \quad N\left(\frac{d}{L}\right)^3 \ll 1.$$

Explicitly:

For a gas at room temperature:

$d \sim 10^{-10} m$, $\frac{N}{V} \sim 10^{-2} mol/L \sim 10^{25}/m^3$. $\Rightarrow N\left(\frac{d}{L}\right)^3 \sim 10^{-5}$ → small!

For H_2O: $N\left(\frac{d}{L}\right)^3 \sim 10^{-2}, 10^{-1}$ → not so small!

($\simeq \sim 55\, mol/L$)

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To describe a dilute gas such as air at room temperature, it seems physically reasonable to assume:

$$\tilde{\Phi}_{123} \ll \{ f_2, U_{12} \} .$$

Thus yielding the closed systems:

Dilute-gas BBGKY

$$\boxed{\begin{aligned} \partial_t f_1 + \{ f_1, H_1 \} &= \int dz_2 \{ U_{12}, f_2 \} . \\ \partial_t f_2 + \{ f_2, H_{12} \} &= 0 . \end{aligned}}$$

Obs. The system above is valid even in the presence of walls. (Check)

However in that case one can further decompose the streaming terms into:

$$\{ f_1, H_1 \} = \left\{ f_1, \frac{p_1^2}{2m} \right\} + \{ f_1, V(q_1) \} \sim \frac{f_1}{\tau_{wall}} .$$

$$\{ f_2, H_{12} \} \sim \left\{ f_2, \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U_{12} \right\} + \{ f_2, V_1 + V_2 \}$$

And argue $\int \{ f_2, V_1 + V_2 \} dz_2 \sim \int \frac{f_2}{\tau_c} dz_2 \sim N\left(\frac{d}{L}\right)^3 f_1/\tau_c \ll \{ f_1, V_1 \}$.

Here yielding:

$$\left[\begin{aligned} \partial_t f_1 + \left\{ f_1, \frac{p_1^2}{2m} \right\} + \{ f_1, V_1 \} &= \Phi . \\ \partial_t f_2 + \left\{ f_2, \frac{p_1^2}{2m} + \frac{p_2^2}{2m} + U_{12} \right\} &= 0 . \end{aligned} \right.$$

the contribution of the walls is linear in f_1, as previously found in the full derivation.

6- Massaging the dilute systems : (χ hypothesis)

We forget about the walls (without loss of generality)

Objective: closed equation for f_1

To achieve this, we assume that f_2 reaches equilibrium faster than f_1. [Justified provided Φ is the main mechanism to reach equilibrium and $\Phi_{23} \ll \Phi_{12}$].

$\Longrightarrow$ This implies (*)

$$\begin{cases} \{f_2, H_{12}\} = 0 . \\ \text{i.e.} \\ \{f_2, U_{12}\} + \{f_2, H_1\} + \{f_2, H_1(2')\} = 0 \end{cases}$$

- Let us now transform to the center of mass. The equilibrium conditions (*) become: (**)

$$-\underbrace{\{f_2, U_{12}\}}_{\sim f_2/\tau_c} + \underbrace{\left\{\frac{P^2}{2M}, f_2\right\}}_{\sim f_2/\tau_s} + \underbrace{\left\{\frac{\Delta p^2}{2\mu}, f_2\right\}}_{\sim f_2/\tau_c} = 0 . \quad (**)$$

$2M \to 2m$, $\quad \mu \to \frac{m}{2} = \frac{1}{\frac{1}{m}+\frac{1}{m}}$

with:
$$\Delta p = \frac{p_1 - p_2}{2} .$$
$$P = p_1 + p_2 ,$$
$$Q = \frac{q_1 + q_2}{2} .$$
$$r_{12} = q_1 - q_2 = \Delta q = r .$$

$$\boxed{\{\ ,\ \} = \partial_Q \partial_P - \partial_P \partial_Q + \partial_{\delta q}\partial_{\delta p} - \partial_{\delta p}\partial_{\delta q} .}$$

Exercise: check!. [cf Alexei's course, first week].

The assumption $\tau_c \ll \tau_s$ implies the balance:

$$\boxed{\{f_2, U_{12}\} = \left\{\frac{\Delta p^2}{2\mu}, f_2\right\} .}$$

Injecting into the collision term yields:

$$Q_{12} = \int dz_2 \{u_{12}, f_2\} = \int dz_2 \left\{ f_2, \frac{\Delta p^2}{2\mu} \right\}. \quad \mu \to m/2$$

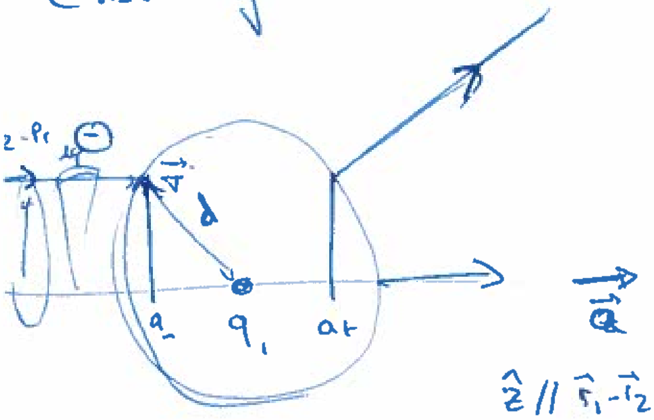
$$= \int d\vec{p}_2 \int d\vec{q}_2 \; \frac{\overset{p_1-p_2/2}{\Delta \vec{p}}}{\underset{m/2}{\mu}} \cdot \partial_{\vec{r}} f_2 .$$

$$= \frac{1}{4} \int d\vec{p}_2 \int_{|q_1-q_2|<d} d\vec{q}_2 \; (\vec{p}_1 - \vec{p}_2) \cdot \partial_r f_2 . = \frac{1}{4} \int d\vec{p}_2 \int_{|r|<d} d\vec{r} \cdot [\vec{p}_2 - \vec{p}_1] \cdot \partial_r f$$

$d\vec{q}_2 = -d\vec{r}$

Choice of a convenient coordinate system to evaluate Q.

$\vec{r} = \vec{r}_1 - \vec{r}_2$



$$\Longrightarrow Q_{12} = +\frac{1}{4} \int d\vec{p}_2 \int_{|q_1-q_2|<d} d\vec{\sigma} \; |p_2 - p_1| \int_{a_-}^{a_+} da \, \partial_a f_2$$

$\hat{z} \parallel \vec{r}_1 - \vec{r}_2$

$$(*) \quad \boxed{Q_{12} = \frac{1}{4} \int d\vec{p}_2 \int d\vec{\sigma} \, |p_2 - p_1| \left[f_2(p_1, p_2, a^+, \vec{\sigma}, t) - f_2(p_1, p_2, a^-, \vec{\sigma}, t) \right]}$$

$a \parallel \hat{z}$

obs: $d\vec{\sigma} = b\,db\,d\varphi$, $= \pi d^2 = 4\pi \left(\frac{d}{2}\right)^2$

. At this point, one invokes the time-reversibility of f_2 to write $f_2(p_1, p_2, \sigma, +) = f_2(p_1', p_2', \sigma, -)$

where p_1', p_2' are the elastic v rates satisfying
$$\begin{cases} p_1' + p_2' = p_1 + p_2 . \\ E = p_1' + p_2' . \end{cases}$$

(At a_+, a_- the interaction potential is zero)

. obs: this is necessary circumvolution as putting $f_2 = f_1 f_1$ in (*) yields.

$Q_{12} = 0$!!!

. We can now invoke the molecular chaos hypothesis,

... which states that before collisions, particles are randomized, eg:

p-chaos:

$$\boxed{f_2(p_1, p_2, \sigma, \ominus) = f_1(p_1)\, f_1(p_2)}$$

$\hat{\sigma}\cdot\sigma_1$

Obs: without the $\ominus$, if we simply invoke a mean field argument to write $f_2(p_1, p_2, \sigma, +) = f_1(p_1)\, f_1(p_2)$,

then $\Phi_{12} = 0$.

This implies that the p-chaos hypothesis relates to time-irreversibility! . .

We now obtain:

Boltzmann equation:

$$\partial_t f + \{f, H_1\} = Q(f, f).$$

with
$$Q(f, f) = \int d\vec{p}_2 \int \chi(12 \to 1'2', \vec{\sigma})\, d\vec{\sigma}\, \left[f'_{(1)} f'_{(2)} - f_{(1)} f_{(2)} \right]$$

$f = f_1(q, p, t)$

$f(1) = f_1(q, p_1, t)$ $\quad f(2) = f_1(q_2, p_2, t)$. $\quad \chi$ determined!

d: Final observations

- BBGKY path makes clear that BE relies on a series of stringent assumptions:

  → Binary collisions

  → Dilute gas approximation.

  - Short range interactions. $d \ll L$. $[\tilde{Q}_{123} \ll Q_{12}]$
  - Sharp potentials. $\tau_c \ll \tau_f$.
  - Chaotic hypothesis: Before collisions particles are randomized.

- Rigorous derivation of B.E is a tough subject! One proof by Lanford in the limit $\lambda = cte$, $N \to \infty$, $d \to 0$. (Boltzmann-Grad limit).

- For 'non-spherical particles', problem of grazing collision may shatter χ-hypothesis.

- B.E is far more complicated than the Ehrenfest Master equation!

  → Non-linear.

  → PDE.

  → Boundary conditions.

  For math. perspectives, see the references on page [?].

- From a φ perspective, our objective is to trust B.E in its potential range of applicability, the breaking of time-invariance will lead to natural apparition of temperature! [And Entropy increase?].

  → cf Next course!