3.1 General definitions

Kinetic theory: use classical equations of motion to study the macroscopic properties of large numbers of particles.

Questions:
1. Definition of equilibrium for a system of moving particles
2. Do all systems naturally evolve towards an equilibrium state?
3. Time evolution of a system that is not quite in equilibrium.

dilute (nearly ideal) gas: The microstate corresponds to a point $\mu(t)$ in $6N$-Dim phase space $\Gamma = \prod_{i=1}^{N} \{\vec{q}_i, \vec{p}_i\}$

Canonical eqn:

$$\begin{cases} \dfrac{d\vec{q}_i}{dt} = \dfrac{\partial H}{\partial \vec{p}_i} \\ \dfrac{d\vec{p}_i}{dt} = -\dfrac{\partial H}{\partial \vec{q}_i} \end{cases}$$

$H(\bar{p}, \bar{q})$: total energy

$\bar{q} \equiv \{\vec{q}_1, \cdots, \vec{q}_N\}$

$\bar{p} \equiv \{\vec{p}_1, \cdots, \vec{p}_N\}$

$\downarrow$ property

$\boxed{\text{Time reversal symm.}}$

if all $\vec{p} \to -\vec{p}\,(t=0)$, $q(t) = q(-t)$ (retrace trajectory)

invariance of H under transformation $T(p,q) \to (-p, q)$

Space of macrostates (e.g. state funcs E, T, P and N) (M) $<$ Space of microstates (μ)

many-to-one mapping (micro $\to$ macro)

Statistical ensemble of microstates

$\mathcal{N}$ copies of a macro. described by different representative point $\mu(t)$ in the phase space Γ.

$d\mathcal{N}(\bar{p}, \bar{q}, t) \equiv$ number of $\mu(t)$s in $d\Gamma = \prod_{i=1}^{N} d^3\vec{p}_i\, d^3\vec{q}_i$ around $(\bar{p}, \bar{q})$

Density space density:

$$\boxed{\rho(\bar{p}, \bar{q}, t)}\, d\Gamma = \lim_{\mathcal{N}\to\infty} \frac{d\mathcal{N}(\bar{p}, \bar{q}, t)}{\mathcal{N}}$$

$\Rightarrow$ [objective; all microstates are equally likely]

normalized prob. density func. as $\int d\Gamma \rho = 1$

Compute macro.

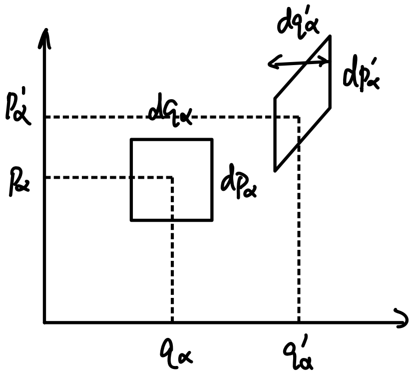
$$\mathcal{O}(\bar{p}, \bar{q}) \Rightarrow \langle \mathcal{O} \rangle = \int d\Gamma\, \rho(\bar{p}, \bar{q}, t)\, \mathcal{O}(\bar{p}, \bar{q})$$

Equilibrium:
- pure state (one $\mu(t)$): hard to distinguish as $\mu(t)$ changes constantly w.r.t. canonical eqn.
- mixed state (many $\mu(t)$s): examining the time evolution of the phase space density $\rho(t)$ (Liouville eqn.)

3.2 Liouville's theorem : (In absence of interactions with other particles)

The phase space density $\rho(\Gamma, t)$ behaves like an incompressible fluid

$$(\bar{p}, \bar{q}) \xrightarrow{\delta t} (\bar{p}', \bar{q}') \qquad q'_\alpha = q_\alpha + \dot{q}_\alpha \delta t + O(\delta t^2) \qquad p'_\alpha = p_\alpha + \dot{p}_\alpha \delta t + O(\delta t^2)$$



$d\Gamma$ get distorted, and the projected sides of the new volume element

$$dq'_\alpha = dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t + O(\delta t^2)$$

$$dp'_\alpha = dp_\alpha + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t + O(\delta t^2)$$

$$\left(d\Gamma = \prod_{i=1}^{N} d^3\vec{p}_i \, d^3\vec{q}_i \quad \Rightarrow \quad d\Gamma' = \prod_{i=1}^{N} d^3\vec{p}_i{}' \, d^3\vec{q}_i{}' \right)$$

For each conjugate coordinates: $dq'_\alpha \, dp'_\alpha = dq_\alpha dp_\alpha \left[1 + \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} \right) \delta t + O(\delta t^2) \right]$

as $\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} = \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha}$ and $\frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = \frac{\partial}{\partial p_\alpha} \left(- \frac{\partial H}{\partial q_\alpha} \right) = - \frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha}$

Therefore, $d\Gamma' = d\Gamma$

① All pures states dN are transported from $(\vec{p}, \vec{q})$ to $(\vec{p}', \vec{q}')$, but occupy the same volume

② $dN / d\Gamma$ = constant , ρ behaves like the density of an incompressible fluid.

Incompressibility condition: $\rho(\bar{p}', \bar{q}', t + \delta t) = \rho(\bar{p}, \bar{q}, t)$

$$\Rightarrow \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{dp_\alpha}{dt} + \frac{\partial \rho}{\partial q_\alpha} \frac{dq_\alpha}{dt} \right) = 0$$

↳ changes in ρ at a particular location in phase space

↳ the evolution of a volume of fluid as it moves in phase space

Therefore, $\frac{\partial \rho}{\partial t} = \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \cdot \frac{\partial H}{\partial p_\alpha} \right) = - \{\rho, H\}$

* Poisson bracket of two funcs in phase space : $\{A, B\} = \sum_{\alpha=1}^{3N} \left(\frac{\partial A}{\partial q_\alpha} \frac{\partial B}{\partial p_\alpha} - \frac{\partial A}{\partial p_\alpha} \frac{\partial B}{\partial q_\alpha} \right) = - \{B, A\}$

Consequences of Liouville's theorem :

1. Time reversal , $(\bar{p}, \bar{q}, t) \to (-\bar{p}, \bar{q}, -t)$, $\{\rho, H\}$ changes sign and the density reverses its evolution . $\rho(\bar{p}, \bar{q}, t) = \rho(-\bar{p}, \bar{q}, -t)$

2. $$\frac{d\langle \mathcal{O}\rangle}{dt} = \int d\Gamma \, \frac{\partial \rho(\bar{p}, \bar{q}, t)}{\partial t} \mathcal{O}(\bar{p}, \bar{q}) = \sum_{\alpha=1}^{3N} \int d\Gamma \, \mathcal{O}(\bar{p}, \bar{q}) \left(\frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right)$$

As ρ vanishes on the boundaries of integral $\int f \rho' = (f\rho)_{bound} - \int \rho f'$
$= -\int \rho f'$

$$\Rightarrow \frac{d\langle \mathcal{O}\rangle}{dt} = - \sum_{\alpha=1}^{3N} \int d\Gamma \, \rho \left[\frac{\partial \mathcal{O}}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} + \cancel{\mathcal{O} \frac{\partial^2 H}{\partial p_\alpha \partial q_\alpha}} - \left(\frac{\partial \mathcal{O}}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} + \cancel{\mathcal{O} \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha}} \right) \right]$$

$$= -\int d\Gamma \, \rho \{H, \mathcal{O}\} = \langle \{\mathcal{O}, H\} \rangle$$

3. At an equilibrium macroscope state, ensemble averages must be indep. of time.
(condition : $\partial \rho_{eq} / \partial t = 0$) $\Rightarrow$ $\{\rho_{eq}, H\} = 0$

A possible sol : $\rho_{eq}(\bar{p}, \bar{q}) = \rho_{eq}(H(\bar{p}, \bar{q}))$ $\leftarrow$ Similar to quantum

as $\{\rho(H), H\} = \rho'(H)\{H, H\} = 0$

basic assumption of statistical mechanics $\rightarrow$ ρ is constant on the surface of constant energy in equilibrium

E.x. microcanonical ensemble : total energy E of an isolated system is specified

All members of the ensemble must be located on the surface $H(p, q) = E$

$\frac{\partial \rho_{eq}}{\partial t} = 0 \Rightarrow$ a uniform density of points on this surface is stationary in time.

(subjective : all microstates are equally likely.)

If additional conserved quantities satisfy $\{L_n, H\} = 0$

Stationary density : $\rho_{eq}(\bar{p}, \bar{q}) = \rho(H(p,q), L_1(p,q), \cdots, L_n(p,q))$

$$\frac{dL_n(\bar{p}, \bar{q})}{dt} = \sum_{\alpha=1}^{3N} \left(\frac{\partial L_n}{\partial p_\alpha} \cdot \frac{\partial p_\alpha}{\partial t} + \frac{\partial L_n}{\partial q_\alpha} \cdot \frac{\partial q_\alpha}{\partial t} \right)$$

$$= \sum_{\alpha=1}^{3N} \left(\frac{\partial L_n}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial L_n}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right) = \{L_n, H\} = 0$$

$\hookrightarrow \frac{dL_n(\bar{p}, \bar{q})}{dt} = 0$: the value of L_n is not changed during the evolution of the system

$\Rightarrow$ the functional dependence of ρ_{eq} $\rightarrow$ accessible states are equally likely.

Above solve the definition of equilibrium

4. ~~non-stationary densities converge onto the stationary solution ρ_{eq}.~~ $\leftarrow$ contradicts time reversal symmetry: for any $\rho(t)$ converging to ρ_{eq}, there is a time-reversed solution that diverges from it.

Ergodicity $\Rightarrow$ $\rho(t)$ are in the neighbourhood of ρ_{eq} the majority of time so the time averages are dominated by the stationary solution

Ergodic theorem: the representative point comes arbitrarily close to all accessible points in phase space after a sufficient long time.

(But time intervals grow exponentially with number of particles.)

3.3 The Bogoliubov – Born – Green – Kirkwood – Yvon hierarchy

one-particle distribution refers to the expectation value of finding any of N particles at location $\vec{q}$ with mom. $\vec{p}$ at time t.

$$f_1(\vec{p},\vec{q},t) = \left\langle \sum_{i=1}^{N} \delta^3(\vec{p}-\vec{p}_i)\,\delta^3(\vec{q}-\vec{q}_i) \right\rangle$$

$$= N\int \prod_{i=2}^{N} d^3\vec{p}_i\, d^3\vec{q}_i\, \rho(\vec{p}_1=\vec{p}, \vec{q}_1=\vec{q}, \vec{p}_2, \vec{q}_2, \cdots, \vec{p}_N, \vec{q}_N, t)$$

* use first set of delta funcs to perform one set of integral. then assumed that the density is symmetric w.r.t. permuting particles

$$f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,t) = N(N-1)\int \prod_{i=3}^{N} dV_i\, \rho(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,\cdots\cdots,\vec{p}_N,\vec{q}_N,t)$$

$$f_s(\vec{p}_1,\cdots,\vec{q}_s,t) = \frac{N!}{(N-s)!}\int \prod_{i=s+1}^{N} dV_i\, \rho(\vec{p},\vec{q},t)$$

$$= \frac{N!}{(N-s)!}\boxed{\rho_s(\vec{p}_1,\vec{q}_1,\cdots,\vec{p}_s,\vec{q}_s,t)}$$

standard unconditional PDF for s particles

Evolution of few-body densities is governed by BBGKY hierarchy of equation.

$$H(\vec{p},\vec{q}) = \sum_{i=1}^{N}\left[\frac{\vec{p}_i^{\,2}}{2m} + \underbrace{U(\vec{q}_i)}_{\text{external potential}}\right] + \frac{1}{2}\sum_{(i,j)=1} \underbrace{\mathcal{V}(\vec{q}_i-\vec{q}_j)}_{\text{two-body interaction}}$$

(* higher-body interactions are ignored as dilute (ideal) gas limit.)

$$H(\vec{p},\vec{q}) = H_s + H_{N-s} + H'$$

$$H_s = \sum_{n=1}^{s}\left[\frac{\vec{p}_n^{\,2}}{2m} + U(\vec{q}_n)\right] + \frac{1}{2}\sum_{(n,m)=1}^{s}\mathcal{V}(\vec{q}_n-\vec{q}_m)$$

$$H_{N-s} = \sum_{i=s+1}^{N}\left[\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i)\right] + \frac{1}{2}\sum_{(i,j)=s+1}^{N}\mathcal{V}(\vec{q}_i-\vec{q}_j)$$

$$H' = \sum_{n=1}^{s}\sum_{i=s+1}^{N}\mathcal{V}(\vec{q}_n-\vec{q}_i)$$

$$\frac{\partial \rho_s}{\partial t} = \int \prod_{i=s+1}^{N} dV_i\,\frac{\partial \rho}{\partial t} = -\int \prod_{i=s+1}^{N} dV_i\,\{\rho, H_s + H_{N-s} + H'\}$$

First s coordinates are not integrated, the order of integrations and differentiations for Poisson bracket can be reversed

①
$$-\int \prod_{i=s+1}^{N} dV_i \{\rho, H_s\} = -\left\{\left(\int \prod_{i=s+1}^{N} dV_i\, \rho\right), H_s\right\} = -\{\rho_s, H_s\}$$

②
$$-\int \prod_{i=s+1}^{N} dV_i \{\rho, H_{N-s}\} = \int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N}\left[\frac{\partial \rho}{\partial \vec{p}_j}\cdot\frac{\partial H_{N-s}}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j}\cdot\frac{\partial H_{N-s}}{\partial \vec{p}_j}\right]$$
$$= \int \prod_{i=s+1}^{N} dV_i \sum_{j=s+1}^{N}\left[\frac{\partial \rho}{\partial \vec{p}_j}\cdot\underbrace{\left(\frac{\partial U}{\partial \vec{q}_j} + \frac{1}{2}\sum_{k=s+1}^{N}\frac{\partial \mathcal{V}(\vec{q}_j-\vec{q}_k)}{\partial \vec{q}_j}\right)}_{\text{uncorrelated to } \vec{p}_j} - \frac{\partial \rho}{\partial \vec{q}_j}\cdot\underbrace{\frac{\vec{p}_j}{m}}_{\text{uncorr. to } \vec{q}_j}\right] = 0$$

③
$$-\int \prod_{i=s+1}^{N} dV_i \{\rho, H'\} = \int \prod_{i=s+1}^{N} dV_i \sum_{j=1}^{N}\left[\frac{\partial \rho}{\partial \vec{p}_j}\cdot\frac{\partial H'}{\partial \vec{q}_j} - \cancelto{0}{\frac{\partial \rho}{\partial \vec{q}_j}\cdot\frac{\partial H'}{\partial \vec{p}_j}}\right]$$
$$= \int \prod_{i=s+1}^{N} dV_i \left[\sum_{n=1}^{s}\frac{\partial \rho}{\partial \vec{p}_n}\underbrace{\sum_{j=s+1}^{N}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_j)}{\partial \vec{q}_n}}_{\substack{\text{symmetric}\\ \text{total number } N-s}} + \underbrace{\sum_{j=s+1}^{N}\frac{\partial \rho}{\partial \vec{p}_j}\underbrace{\sum_{n=1}^{s}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_j)}{\partial \vec{q}_j}}_{\text{constant in integration}}}_{\int \cdots = 0}\right]$$
$$= (N-s)\int \prod_{i=s+1}^{N} dV_i \sum_{n=1}^{s}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\frac{\partial \rho}{\partial \vec{p}_n}$$
$$= (N-s)\sum_{n=1}^{s}\int dV_{s+1}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\cdot\frac{\partial}{\partial \vec{p}_n}\underbrace{\left[\int \prod_{i=s+2}^{N} dV_i\, \rho\right]}_{\rho_{s+1}}$$

With ①, ② & ③:
$$\frac{\partial \rho_s}{\partial t} = -\{\rho_s, H_s\} + 0 + (N-s)\sum_{n=1}^{s}\int dV_{s+1}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\frac{\partial \rho_{s+1}}{\partial \vec{p}_n}$$
$$\Rightarrow \underbrace{\frac{\partial \rho_s}{\partial t} - \{H_s, \rho_s\}}_{\text{Liouville's theorem}} = \underbrace{(N-S)\sum_{n=1}^{s}\int dV_{s+1}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\frac{\partial \rho_{s+1}}{\partial \vec{p}_n}}_{\text{collisions with } N-S \text{ particles}}$$

potential collision

probability of additional particle to collide.

or use f_s represent ρ_s (f_s : unconditional PDF for particles)

↳
$$\frac{\partial f_s}{\partial t} - \{H_s, \rho_s\} = \sum_{n=1}^{s}\int dV_{s+1}\frac{\partial \mathcal{V}(\vec{q}_n-\vec{q}_{s+1})}{\partial \vec{q}_n}\frac{\partial f_{s+1}}{\partial \vec{p}_n}$$

$\boxed{\text{Hierarchy : } \frac{\partial \rho_s}{\partial t} \text{ depends on joint PDF of } \rho_{s+1} \text{ (s+1 particles)}}$

3.4 The Boltzmann eqn.

Approximation to $\frac{\partial f_s}{\partial t} - \{H_s, f_s\} = \sum_{n=1}^{s} \int dV_{s+1} \frac{\partial \mathcal{V}(\vec{q}_n - \vec{q}_{s+1})}{\partial \vec{q}_n} \frac{\partial f_{s+1}}{\partial \vec{p}_n}$

① $$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1}\right] f_1 = \int dV_2 \frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \frac{\partial f_2}{\partial \vec{p}_1}$$

② $$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} - \frac{\partial U}{\partial \vec{q}_2} \cdot \frac{\partial}{\partial \vec{p}_2} + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m} \frac{\partial}{\partial \vec{q}_2} - \boxed{\frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right)}\right] f_2$$

$$= \int dV_3 \left[\frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_3)}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\partial \mathcal{V}(\vec{q}_2 - \vec{q}_3)}{\partial \vec{q}_2} \cdot \frac{\partial}{\partial \vec{p}_2}\right] f_3$$

* $\frac{\partial \mathcal{V}(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} = -\frac{\partial \mathcal{V}(\vec{q}_2 - \vec{q}_1)}{\partial \vec{q}_2}$ as symmetric pot. $\partial \mathcal{V}(|\vec{q}_1 - \vec{q}_2|)$

Time scales: All terms in square bracket have dimensions of inverse time. $(1/t)$

Estimate the relative magnitudes by dimension analysis.

typical speed of a gas at ambient temp.: $v_{amb} = 100 m/s$

length scales depends on the variations of the potential.

extrinsic time scale (a) [arbitrarily long by increasing system size]

$\frac{1}{\tau_U} \sim \frac{\partial U}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}}$ involves spatial variations of the external pot. $U(\vec{q})$, which take place over macroscopic distance $L \approx 10^{-3} m$. $\tau_U = L/v \approx 10^{-5} s$

intrinsic time scale (b)

$\frac{1}{\tau_c} \sim \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}}$ (collision during: 2 particles are within effective range d)

For short-range interactions (including VDW and LJ despite their power law decaying tails), $d \simeq 10^{-10} m$ (order of a typical atomic size), so $\tau_c \approx 10^{-12} s$

For long-range interactions (Coulomb gas in a plasma). For a neural plasma, the Debye screening length λ replaces d

(c) $\frac{1}{\tau_x} \sim \int dV \frac{\partial \mathcal{V}}{\partial \vec{q}} \frac{\partial}{\partial \vec{p}} \frac{f_{s+1}}{f_s} \sim \int dV \frac{\partial \mathcal{V}}{\partial \vec{q}} \cdot \frac{\partial}{\partial \vec{p}} N \frac{\rho_{s+1}}{\rho_s}$ (another collision term)

* Integrals are non-zero within the volume of the interparticle potential d^3

* $f_{s+1}/f_s \sim$ probability of finding another particle per unit time

roughly particle density $n = N/V \approx 10^{26} m^{-3}$

Mean free time: $\tau_x = \frac{\tau_c}{nd^3} = \frac{1}{nvd^2}$ (for short-range interaction: $\tau_x \gg \tau_c$)

$\longleftarrow v\tau_x \longrightarrow$

d

Only one other particle in the vol.

$d^2 v \tau_x n \sim \mathcal{O}(1)$

Boltzmann eqn is obtained for short-range interactions in the dilute regime ($\tau_c/\tau_x \simeq nd^3 \ll 1$)

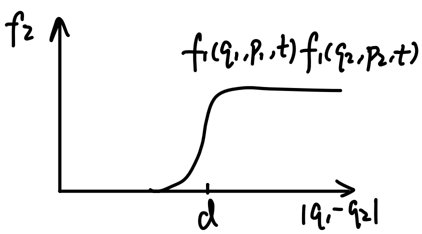
Vlasov eqn is obtained for long-range interactions ($nd^3 \gg 1$) by dropping collision terms on the left-hand side. (In problem set).

① $$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m}\frac{\partial}{\partial \vec{q}_1}\right] f_1 = \int dV_2 \, \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\,\frac{\partial f_2}{\partial \vec{p}_1}$$

lack collision term on lefthand side. Right hand side may dominate.

② $$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} - \frac{\partial U}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2} + \frac{\vec{p}_1}{m}\frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m}\frac{\partial}{\partial \vec{q}_2} - \boxed{\frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right)}\right] f_2$$
$$= \int dV_3 \left[\frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_3)}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\partial \mathcal{V}(\vec{q}_2-\vec{q}_3)}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2}\right] f_3 \to 0$$

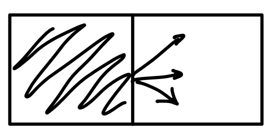
* As collision term on left hand side is larger than right hand side, let the right hand side be zero.
* The two-body density evolves as in isolated two-particle system.
* The streaming terms (red block) are proportional to both τ_U^{-1} and τ_c^{-1}
  τ_U : evolution of center of mass of two particles
  τ_c : dependence on relative coordinates.
* $f_2 \propto$ joint PDF ρ_2 for find one particle at $(\vec{p}_1,\vec{q}_1)$, and another at $(\vec{p}_2,\vec{q}_2)$ at the same time t.



True for both equilibrium and out-of-equilibrium

At distance $\gg$ the range of $\mathcal{V}$, the particles are independent.

$$\begin{cases} \rho_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,t) \to \rho_1(\vec{p}_1,\vec{q}_1,t)\,\rho_1(\vec{p}_2,\vec{q}_2,t) \\ f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{q}_2,t) \to f_1(\vec{p}_1,\vec{q}_1,t)\,f_1(\vec{p}_2,\vec{q}_2,t) \end{cases} \quad \text{for } |\vec{q}_2-\vec{q}_1| \gg d.$$



f_1 relaxation time is comparable to τ_U

f_2 is to relax to the independent func over a shorter time of the order of τ_c

Condition.

① At time intervals longer than τ_c (but shorter than τ_U)
$\frac{\partial U}{\partial \vec{q}} \to$ ignore

② "steady state":
$\frac{\partial}{\partial t} \to$ ignore

$$\left[\frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m}\cdot\frac{\partial}{\partial \vec{q}_2} - \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right)\right] f_2 = 0$$

$f_2(\vec{q}_1,\vec{q}_2)$ has low variations over center of mass coordinate $\vec{Q} = \frac{1}{2}(\vec{q}_1+\vec{q}_2)$
large variations over the relative coordinates $\vec{q} = \vec{q}_2 - \vec{q}_1$

$$\frac{\partial f_2}{\partial \vec{Q}} \ll \frac{\partial f_2}{\partial \vec{q}} \quad \text{and} \quad \underline{\frac{\partial f_2}{\partial \vec{q}_2} \simeq -\frac{\partial f_2}{\partial \vec{q}_1} \simeq \frac{\partial f_2}{\partial \vec{q}}} \quad \left(\frac{1}{m_1}\nabla_1^2 + \frac{1}{m_2}\nabla_2^2 = \frac{1}{M}\nabla_R^2 + \frac{1}{\mu}\nabla_r^2\right)$$

Atkin's mole. QM Chp3. Appendix

$$\Rightarrow \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right) f_2 = -\left(\frac{\vec{p}_2-\vec{p}_1}{m}\right)\frac{\partial f_2}{\partial \vec{q}}$$

w.r.t. f_1 & f_2 eqn.

$$\left.\frac{df_1}{dt}\right|_{coll} = \int d^3\vec{p}_2 d^3\vec{q}_2 \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\frac{\partial f_2}{\partial \vec{p}_1} = \int d^3\vec{p}_2 d^3\vec{q}_2 \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\left(\frac{\partial}{\partial \vec{p}_1}-\frac{\partial}{\partial \vec{p}_2}\right) f_2$$

$\downarrow$

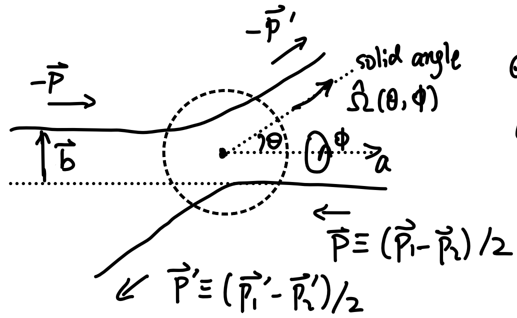
$[\cdots]$ unit is $\frac{1}{t}$

$$\backsimeq \int d^3\vec{p}_2 d^3\vec{q}\left(\frac{\vec{p}_2-\vec{p}_1}{m}\right)\frac{\partial}{\partial \vec{q}} f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,q;t)$$

$$\left(* \int \boxed{d^3\vec{p}_2} d^3\vec{q}_2 \frac{\partial \mathcal{V}(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\boxed{\frac{\partial f_2}{\partial \vec{p}_2}} \rightarrow f_2(p_2\to+\infty) - f_2(p_2\to-\infty) = 0\right)$$

Kinematics of collision and scattering

from $\left[d^3\vec{p}_2 d^3\vec{q}\left(\frac{\vec{p}_2-\vec{p}_1}{m}\right)\frac{\partial}{\partial\vec{q}}\right]$ $f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,q;t)$



elastic collision at $(\vec{a}=\vec{0})$ center of mass

conservation of momentum $\vec{P}=\vec{p}_1+\vec{p}_2=\vec{p}_1\,'+\vec{p}_2\,'$

rotate by a solid angle $\hat{\Omega}(\theta,\phi)$

($\vec{b}$ impact factor)

Hence: $$\left.\frac{df_1}{dt}\right|_{coll} = \int_{\text{over } a} d^3\vec{p}_2\, \underset{\uparrow\ \frac{d^3\vec{q}}{\partial\vec{q}}}{\underline{d^2\vec{b}}}\, \underset{\uparrow\ \left|\frac{\vec{p}_2-\vec{p}_1}{m}\right|\ \text{relative speed}}{\underline{|\vec{v}_2-\vec{v}_1|}}\left[f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,b,\underset{\uparrow}{\underline{+}};t) - f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},\underset{\uparrow}{\underline{-}};t)\right]$$

relative coordinates after collision; relative coordinates before collision

$*$ $d^2\vec{b}\,|\vec{v}_2-\vec{v}_1| \equiv$ flux of particles impinging on the element of area $d^2\vec{b}$

$f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},+;t) = f_2(\vec{p}_1\,',\vec{q}_1,\vec{p}_2\,',\vec{b},-;t)$

Through reversal time symmetry, integrating eqn of motion for particles of $-\vec{p}_1$ and $-\vec{p}_2$

☆ $$\boxed{\left.\frac{df_1}{dt}\right|_{coll} = \int d^3\vec{p}_2\, d^2\vec{b}\, |\vec{v}_2-\vec{v}_1|\left[f_2(\vec{p}_1\,',\vec{q}_1,\vec{p}_2\,',b,-;t) - f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},-;t)\right]}$$

and describe with relative momenta $\vec{p}=\vec{p}_1-\vec{p}_2$; $\vec{p}\,'=\vec{p}_1\,'-\vec{p}_2\,'$

find $\vec{p}\,'(|\vec{p}|,\vec{b})$ ☆ integrate whole equation of motion

or make statements with conservation laws :

In elastic collisions $|\vec{p}|$ is preserved,

☆ solid angle $(\theta,\phi)\equiv\hat{\Omega}(\vec{b})$ (one unit vector) $\leftrightarrow$ impact factor $\vec{b}$ (one-to-one)

$$\boxed{\left.\frac{df_1}{dt}\right|_{coll} = \int d^3\vec{p}_2\, d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_2-\vec{v}_1|\left[f_2(\vec{p}_1\,',\vec{q}_1,\vec{p}_2\,',b,-;t) - f_2(\vec{p}_1,\vec{q}_1,\vec{p}_2,\vec{b},-;t)\right]}$$

Differential cross-section $\left|\frac{d\sigma}{d\Omega}\right|$

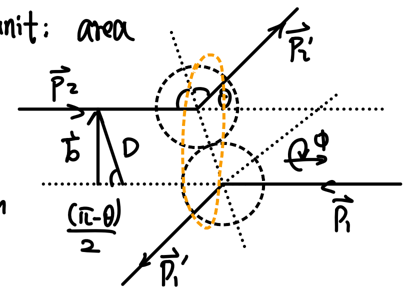
Jacobian of transformation

unit: area

conservation of momentum : $\vec{p}_1\,'+\vec{p}_2\,'=\vec{p}_1+\vec{p}_2$

conservation of energy : $\vec{p}_1\,'-\vec{p}_2\,'=|\vec{p}_1-\vec{p}_2|\,\hat{\Omega}(\vec{b})$

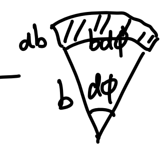
$$\Rightarrow \begin{cases}\vec{p}_1\,'=(\vec{p}_1+\vec{p}_2+|\vec{p}_1-\vec{p}_2|\,\hat{\Omega}(\vec{b}))/2\\ \vec{p}_2\,'=(\vec{p}_1+\vec{p}_2-|\vec{p}_1-\vec{p}_2|\,\hat{\Omega}(\vec{b}))/2\end{cases}$$



$\triangleleft\equiv$ see from side

diameter D of hard-sphere particle

$\cos\left(\frac{\theta}{2}\right)=\frac{b}{D}$ for all ϕ

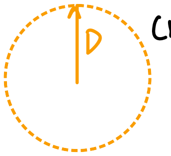


$d\Omega=\sin\theta\, d\theta\, d\phi$ (3d-Calculus)

$\downarrow$

$$|d^2\sigma| = |b\,db\,d\phi| = \left|D\cos\left(\tfrac{\theta}{2}\right) D\sin\left(\tfrac{\theta}{2}\right)\tfrac{1}{2}\,d\theta\, d\phi\right| = \frac{D^2}{4}|\sin\theta\, d\theta\, d\phi| = \frac{D^2}{4}|d^2\Omega|$$

$\equiv$ see from side



Cross-section $\sigma = \pi D^2$

$$\sigma = \iint_{-\infty}^{+\infty} \frac{D^2}{4} |d\Omega| = \frac{D^2}{4} \left| \iint_{-\infty}^{+\infty} \sin\theta \, d\theta \, d\phi \right| = \frac{D^2}{4} \left| \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\phi \right| = \left| \frac{D^2}{4} \cos\theta \Big|_0^{\pi} \cdot 2\pi \right| = \pi D^2$$

Differential cross-section:

For hard spheres, $\left|\frac{d\sigma}{d\Omega}\right|$ is independent of both θ and $|\vec{p}|$

For soft potential Ex. Coulomb potential $\mathcal{V} = \frac{e^2}{|\vec{Q}|}$ leads to

$$\left|\frac{d\sigma}{d\Omega}\right| = \left(\frac{me^2}{2|\vec{p}|^2 \sin^2(\theta/2)} \right)^2$$

* dependence on $|\vec{p}|$: the closest approach $|\vec{p}|^2/m + e^2/b \simeq 0$

Assumption of molecular chaos: $f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, b, -; t) = f_1(\vec{p}_1, \vec{q}_1, t) \, f_1(\vec{p}_2, \vec{q}_1, t)$

uncorrelated initial prob. distri. for particles → important for irreversibility.

Boltzmann eqn:

$$\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m} \frac{\partial}{\partial \vec{q}_1} \right] f_1$$

$$= -\int d^3\vec{p}_2 \, d^2\Omega \left| \frac{d\sigma}{d\Omega} \right| |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1, \vec{q}_1, t) f_1(\vec{p}_2, \vec{q}_1, t) - f_1(\vec{p}_1{}', \vec{q}_1, t) f_1(\vec{p}_2{}', \vec{q}_1, t) \right]$$

1. The prob. of finding a particle of momentum $\vec{p}_1$ at $\vec{q}_1$ is suddenly altered if it undergoes a collision with another particle of momentum $\vec{p}_2$
2. The prob. of collision is the product of kinematic
   (1) differential cross-section : $|d\sigma / d\Omega|$
   (2) the "flux" of incident particles $\propto |\vec{v}_2 - \vec{v}_1|$
   (3) joint prob. of finding two particles : $f_1(\vec{p}_1) f_1(\vec{p}_2)$
   The first-term is subtract of this prob.
3. The second-term : an addition to the prob. resulting from the inverse process two particles initially with $\vec{p}_1{}'$ and $\vec{p}_2{}'$ $\xrightarrow{\text{collide}}$ a particle suddenly with $(\vec{p}_1, \vec{q}_1)$
4. The differential cross-section and the momenta $(\vec{p}_1{}', \vec{p}_2{}')$ may have complicated dependence on $(\vec{p}_1, \vec{p}_2)$ and Ω, determined by form of interactive potential $\mathcal{V}$.

* 5. Various equilibrium properties of the gas are quite independent of the interactive potential.

3.5 The H-theorem and irreversibility

?: A collection of particles naturally evolves toward an equilibrium state

Sol: solve all steady state in phase space, but not attractors of generic non-equilibrium density.

?: unconditioned one-particle PDF suffers the same problem ; ρ_1 reflects ρ_N in some properties

H-theorem : ρ_1, governed by Boltzmann eqn. does non-reversible approach an equilibrium form.

$$\boxed{\begin{aligned}&\text{If } f_1(\vec{p},\vec{q},t) \text{ satisfies the Boltzmann eqn, then } dH/dt \le 0 \text{, where}\\ &H(t) = \int d^3\vec{p}\, d^3\vec{q}\, f_1(\vec{p},\vec{q},t) \ln f_1(\vec{p},\vec{q},t)\end{aligned}}$$

* $H(t)$ is the info. content of the one-particle PDF
* If overall constant, $\rho_1 = f_1/N$, $I(\rho_1) = \langle \ln \rho_1 \rangle$

Proof:
$$\frac{dH}{dt} = \int d^3\vec{p}_1 d^3\vec{q}_1 \frac{\partial f_1}{\partial t}(\ln f_1 + 1) = \int d^3\vec{p}_1 d^3\vec{q}_1 \ln f_1 \frac{\partial f_1}{\partial t}$$

since $\int dV_1 f_1 = N \int d\Gamma \rho = N$ is time-independent

$$\frac{dH}{dt} = \int d^3\vec{p}_1 d^3\vec{q}_1 \ln f_1 \left(\frac{\partial U_1}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\vec{p}_1}{m}\frac{\partial f_1}{\partial \vec{q}_1} \right)$$

$$- \int d^3\vec{p}_1\, d^3\vec{q}_1\, d^3\vec{p}_2\, d^2\sigma\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1,\vec{q}_1) f_1(\vec{p}_2,\vec{q}_1) - f_1(\vec{p}_1{}',\vec{q}_1) f_1(\vec{p}_2{}',\vec{q}_1) \right] \ln f_1(\vec{p}_1,\vec{q}_1)$$

* differential cross-section: $d^2\sigma$, $d^2\vec{b}$ or $d^2\Omega \left|\frac{d\sigma}{d\Omega}\right|$
* streaming parts $= 0$

$$\int d^3\vec{p}_1 d^3\vec{q}_1 \ln f_1 \frac{\partial U_1}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1} = \int d^3\vec{p}_1 d^3\vec{q}_1 \frac{\partial U_1}{\partial \vec{q}_1} \frac{\partial (f_1 \ln f_1 - f_1)}{\partial \vec{p}_1}$$

$$= \cancelto{0}{\int d^3\vec{p}_1 d^3\vec{q}_1 \frac{\partial U_1}{\partial \vec{q}_1} \frac{\partial (f_1 \ln f_1)}{\partial \vec{p}_1}} - \cancelto{0}{\int d^3\vec{p}_1\, d^3\vec{q}_1 \frac{\partial U_1}{\partial \vec{q}_1} \frac{\partial f_1}{\partial \vec{p}_1}} = 0$$

$$\int d^3\vec{p}_1 d^3\vec{q}_1 \ln f_1 \frac{\vec{p}_1}{m} \frac{\partial f_1}{\partial \vec{q}_1} = \cancelto{0}{\int d^3\vec{p}_1 d^3\vec{q}_1 \frac{\vec{p}_1}{m} \frac{\partial (f_1 \ln f_1)}{\partial \vec{p}_1}} - \cancelto{0}{\int d^3\vec{p}_1\, d^3\vec{q}_1 \frac{\vec{p}_1}{m} \frac{\partial f_1}{\partial \vec{p}_1}} = 0$$

* collision terms: $\vec{p}_1$, $\vec{p}_2$ are symmetric in integration

$$☆1 \leftarrow \frac{dH}{dt} = -\frac{1}{2}\int d^3\vec{q}\, d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1) f_1(\vec{p}_2) - f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right] \ln\left(f_1(\vec{p}_1) f_1(\vec{p}_2) \right)$$

initiators of the collision $(\vec{p}_1, \vec{p}_2, \vec{b}) \longrightarrow$ products $(\vec{p}_1{}', \vec{p}_2{}', \vec{b}')$

* Jacobian is unity due to time reversal symmetry;
* every collision has an inverse one obtained by reversing the momenta of products

$$\frac{dH}{dt} = -\frac{1}{2}\int d^3\vec{q}\, d^3\vec{p}_1{}'\, d^3\vec{p}_2{}'\, d^2\vec{b}'\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1) f_1(\vec{p}_2) - f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right] \ln\left(f_1(\vec{p}_1) f_1(\vec{p}_2) \right)$$

As $|\vec{v}_1 - \vec{v}_2| = |\vec{v}_1{}' - \vec{v}_2{}'|$, let's relabel the prime $(\vec{p}_1{}', \vec{p}_2{}', \vec{b}') \to (\vec{p}_1, \vec{p}_2, \vec{b})$

$$☆2 \leftarrow \frac{dH}{dt} = -\frac{1}{2}\int d^3\vec{q}\, d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') - f_1(\vec{p}_1) f_1(\vec{p}_2) \right] \ln\left(f_1(\vec{p}_1{}') f_1(\vec{p}_2{}') \right)$$

$(\star 1+\star 2)/2 \Rightarrow \frac{dH}{dt} = -\frac{1}{4}\int d^3\vec{q}\, d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\, |\vec{v}_1-\vec{v}_2| \left[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1{}')f_1(\vec{p}_2{}')\right]\left[\ln f_1(\vec{p}_1)f_1(\vec{p}_2) - \ln f_1(\vec{p}_1{}')f_1(\vec{p}_2{}')\right]$

If $f_1(\vec{p}_1)f_1(\vec{p}_2) > f_1(\vec{p}_1{}')f_1(\vec{p}_2{}')$: $\frac{dH}{dt} \le 0$; else $\frac{dH}{dt} \le 0$

#

Irreversibility : 2^{nd} law is an empirical formation of vast number of observations that supports the existence of an arrow of time.

Reversibility of laws (micro) $\not\longleftrightarrow$ Irreversibility of macro phonomena.
↳ exception: weak nuclear interactions & collapse of quantum wave funcs in the act of observation.

> Proponents: Reversibility of currently accepted microscopic eqn of motion (CM or QM) is indicative of their inadequacy.

> Super PC: The origin of the observed irreversibilities should be sought in the classical evolution of large collections of particles.

Boltzman eqn → not time reversible as $\frac{\partial H}{\partial t} \le 0$

How? by approx. Step 1: drop three-body collision term & the implicit coarse graining of the resolution in the spatial (T_U) and temporal ($\frac{\partial}{\partial t}$) scales

(* keep time reversal)

Step 2: Replace two-body density $f_2(-)$, evaluated before collision, with the product of two one-body densities

* If we alternatively expressed in terms of $f_2(+)$, evaluated after collision, with the product of two one-body densities, $dH/dt \ge 0$

Why using $f_1(-)$? Once the system is out of equilibrium, the coordinates after collisions are more likely to be correlated. Substitution of Eqn. for $f(+)$ doesn't make sense.

Assumption of molecular chaos: Time reversal symmetry implies that there should be subtle correlations in $f_2(+)$ that are ignored.

*
The coarse graining of space and time ⇒ The result loss of info
The info of pure state from Liouville eqn. is transported to shorter scales.
Ex. mixing two immiscible fluids
In the Boltzmann eqn., the precise info. of pure state is lost at scale of collisions
The resulting one-body density only describes space and time resolutions longer than those of a two-body collision, becoming more probabilistic.

3.6 Equilibrium properties

What is the nature of the equilibrium state described by f_1, for a homogeneous gas?

(1) Equilibrium distribution:

After the gas has reached equilibrium, the func (info) H should be zero.

$$\forall \vec{q}, \quad f_1(\vec{p}_1, \vec{q}) f_1(\vec{p}_2, \vec{q}) = f_1(\vec{p}_1{}', \vec{q}) f_1(\vec{p}_2{}', \vec{q})$$

$$\big(\underbrace{\ln f_1(\vec{p}_1, \vec{q}) + \ln f_1(\vec{p}_2, \vec{q})}_{\text{momenta before collision}} = \underbrace{\ln f_1(\vec{p}_1{}', \vec{q}) + \ln f_1(\vec{p}_2{}', \vec{q})}_{\text{momenta after collision}} \big)$$

* The equality is satisfied by any additive quantity that is conserved during elastic collision: particle number, three components of net momentum; kinetic energy

General sol. for f:

$$\ln f_1 = a(\vec{q}) - \vec{\alpha}(\vec{q}) \cdot \vec{p} - \beta(\vec{q}) (\vec{p}^2/2m)$$

$$\xrightarrow{\text{Accommodating } U(\vec{q})} \quad f_1(\vec{p}, \vec{q}) = \mathcal{N}(\vec{q}) \exp\left[-\vec{\alpha}(\vec{q}) \cdot \vec{p} - \beta(\vec{q}) \left(\frac{\vec{p}^2}{2m} + U(\vec{q}) \right) \right]$$

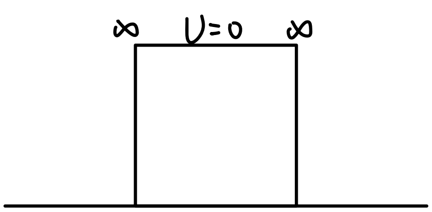
local equilibrium

* preserve during collision; evolve with time away from collisions (streaming terms)

* If $\{\mathcal{H}_1, f_1\} = 0$ $\big(f_1(\underset{\text{energy}}{\mathcal{H}_1}, \underbrace{L_1, L_2, \cdots, L_n}_{\text{conserved quantity}}) \big)$ (see 3.2 Liouville eqn)

(equivalent $\equiv$) $\mathcal{N}$ and β are independent of $\vec{q}$, and $\vec{\alpha} = 0$

Particle-in-a-box with volume V



By the definition of f_1, $\int d^3\vec{p}\, d^3\vec{q}\, f_1(\vec{p}, \vec{q}) = N$

$$N = \mathcal{N} V \left[\int_{-\infty}^{\infty} dp_i \exp\left(-\alpha p_i - \frac{\beta p_i^2}{2m}\right) \right]^3 = \mathcal{N} V \left(\frac{2\pi m}{\beta} \right)^{3/2} \exp\left(\frac{m\alpha^2}{2\beta} \right)$$

$\Rightarrow$ properly normalized Gaussian distribution for momenta

$$f_1(\vec{p}, \vec{q}) = n \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp\left[-\frac{\beta (\vec{p} - \vec{p}_0)^2}{2m} \right]$$

where $\vec{p}_0 = \langle p \rangle = m\vec{\alpha}/\beta$ mean value for mom. of gas. (0 for p-i-b)

$n = N/V$ particle density

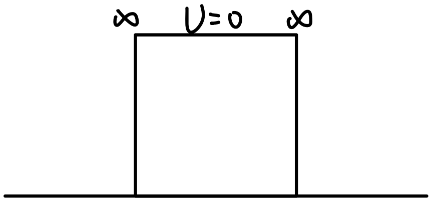
$\langle p_i^2 \rangle_c$ variance: m/β; $\langle p^2 \rangle_c = \langle p_x^2 + p_y^2 + p_z^2 \rangle_c = 3m/\beta$

(x, y, z no correlation)

(2) Equilibrium between two gases s.t. two-body interaction $\mathcal{V}_{ab}(\vec{q}^{(a)} - \vec{q}^{(b)})$

A generalized collision Integral:

$$C_{\alpha,\beta} = -\int d^3\vec{p}_2\, d^2\Omega \left|\frac{d\sigma_{\alpha,\beta}}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \left[f_1^{(\alpha)}(\vec{p}_1, \vec{q}_1)\, f_1^{(\beta)}(\vec{p}_2, \vec{q}_1) - f_1^{(\alpha)}(\vec{p}_1\,', \vec{q}_1)\, f_1^{(\beta)}(\vec{p}_2\,', \vec{q}_1) \right]$$



A simple generalized of Boltzmann eqn.

$$\begin{cases} \dfrac{\partial f_1^{(a)}}{\partial t} = \{\mathcal{H}_1^{(a)}, f_1^{(a)}\} + C_{a,a} + C_{a,b} \\[2ex] \dfrac{\partial f_1^{(b)}}{\partial t} = \{\mathcal{H}_1^{(b)}, f_1^{(b)}\} + C_{b,b} + C_{b,a} \end{cases}$$

interspecies collisions $C_{a,b} = C_{b,a} = 0$

(1) Independent stationary distributions at equilibrium ($C_{a,a} = C_{b,b} = 0$)

$$f_1^{(a)} \propto \exp(-\beta_a \mathcal{H}_1^{(a)}) \quad \& \quad f_1^{(b)} \propto \exp(-\beta_b \mathcal{H}_1^{(b)})$$

(2) $f_1^{(a)}(\vec{p}_1)\, f_1^{(b)}(\vec{p}_2) - f_1^{(a)}(\vec{p}_1\,')\, f_1^{(b)}(\vec{p}_2\,') = 0$

$\Rightarrow \beta_\alpha \mathcal{H}_1^{(a)}(\vec{p}_1) + \beta_b \mathcal{H}_1^{(b)}(\vec{p}_2) = \beta_\alpha \mathcal{H}_1^{(a)}(\vec{p}_1\,') + \beta_b \mathcal{H}_1^{(b)}(\vec{p}_2\,')$

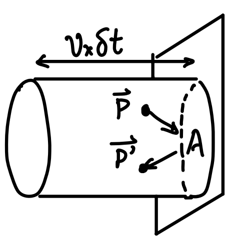
since $\mathcal{H}_1^{(a)} + \mathcal{H}_1^{(b)}$ (total energy) is conserved in a collision.

$\Rightarrow \beta_\alpha = \beta_b = \beta$

$$\left\langle \frac{p_a^2}{2m_a} \right\rangle_c = \left\langle \frac{p_b^2}{2m_b} \right\rangle_c = \frac{3}{2\beta} \qquad \text{from } \langle p^2 \rangle_c = \frac{3m}{\beta}$$

* β plays the role of an empirical temperature describing equilibrium of gas.

(3) The equation of state:



find $\beta(T)$:

Number of particles impacting the area, with momenta in the interval $[\vec{p}, \vec{p} + d\vec{p}]$ over a time period δt

$$d\mathcal{N}(\vec{p}) = (f_1(\vec{p})\, d^3\vec{p})(A v_x \delta t)$$

Each collision impacts a momentum $2p_x$ ($p_x \to -p_x$: $p_x - (-p_x) = 2p_x$) to wall

Net force exerted: ($F = \frac{dp}{dt}$)

$$F = \frac{1}{\delta t} \int_{-\infty}^{0} dp_x \int_{-\infty}^{+\infty} dp_y \int_{-\infty}^{+\infty} dp_z\, f_1(\vec{p}) \left(A \frac{p_x}{m} \delta t\right)(2p_x)$$

(only particles with velocities directly towards the wall will hit it, resulting in half of range of p_x in integral.)

* integrand is even in p_x, it equals full integral divided by 2

Pressure: $p = \frac{F}{A} = \int d^3\vec{p}\, f_1(\vec{p}) \frac{\vec{p}_x^{\,2}}{m} = \frac{1}{m}\int d^3\vec{p}\, p_x^2 \boxed{n\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left(-\frac{\beta\vec{p}^{\,2}}{2m}\right)}$ f_1 at equilibrium state.

$$= \frac{1}{m}\cdot n\left(\frac{\beta}{2\pi m}\right)^{3/2}\int_{-\infty}^{+\infty} dp_y \exp\left(-\frac{\beta p_y^2}{2m}\right)\int_{-\infty}^{+\infty} dp_z \exp\left(-\frac{\beta p_z^2}{2m}\right)\int_{-\infty}^{+\infty} dp_x\, p_x^2 \exp\left(-\frac{\beta p_x^2}{2m}\right)$$

* $x^2\exp(-ax^2) = -\frac{\partial}{\partial a}\exp(-ax^2)$ & change the sequence of derivative and integral.

$$= \frac{1}{m}\cdot n\left(\frac{\beta}{2\pi m}\right)^{3/2}\left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}}\left(\frac{2\pi m}{\beta}\right)^{\frac{1}{2}}\frac{\sqrt{\pi}}{2}\left(\frac{\beta}{2m}\right)^{-3/2} = \frac{n}{\beta}$$

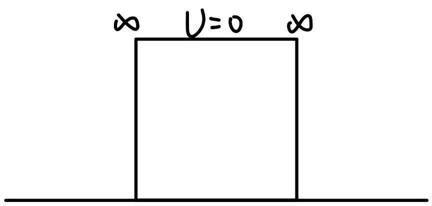
Compare $p = n/\beta$ with ideal gas law $pV = Nk_BT$, we can get * $\boxed{\beta = 1/k_BT}$

(4) Entropy:

Boltzmann H-func is related to the Info content of one-particle PDF f_1.
Define Boltzmann entropy: $S_B(t) = -k_B H(t)$

- k_B reflects historical origins of entropy.
- H-theroem implies S_B can only increase with time in approaching equili.
- works for either equilibrium or non-equilibrium

E.X.



As $f_1(\vec{p},\vec{q}) = n\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left[-\frac{\beta(\vec{p}-\vec{p}_0)^2}{2m}\right]$. (gas in equilibrium)

$$H = V\int d^3\vec{p}\, f_1(\vec{p})\ln f_1(\vec{p})$$

$(\vec{p}^{\,2} = p_x^2 + p_y^2 + p_z^2)$

$$= V\int d^3\vec{p}\,\frac{N}{V}(2\pi m k_BT)^{-3/2}\exp\left(-\frac{\vec{p}^{\,2}}{2mk_BT}\right)\left[\ln\frac{n}{(2\pi m k_BT)^{3/2}} - \frac{\vec{p}^{\,2}}{2mk_BT}\right]$$

$$= N\left[\ln\frac{n}{(2\pi m k_BT)^{3/2}} - (2\pi m k_BT)^{-3/2}\underbrace{\frac{\sqrt{\pi}}{2}\left(\frac{1}{2mk_BT}\right)^{-\frac{1}{2}}}_{\text{i.e. } \exp(x)\cdot x}\cdot\underbrace{(2\pi m k_BT)^{\frac{1}{2}\cdot 2}}_{\exp(y)\exp(z)}\cdot 3\right]$$

$$= N\left[\ln\frac{n}{(2\pi m k_BT)^{3/2}} - \frac{3}{2}\right]$$

$$\Rightarrow S_B = -k_BH = Nk_B\left[\frac{3}{2} + \frac{3}{2}\ln(2\pi m k_BT) - \ln\frac{N}{V}\right]$$

Based on thermodynamic relation: $TdS_B = dE + pdV$

$$\left.\frac{\partial E}{\partial T}\right|_V = T\left.\frac{\partial S_B}{\partial T}\right|_V = \frac{3}{2}Nk_B$$

$$p + \left.\frac{\partial E}{\partial V}\right|_T = T\left.\frac{\partial S_B}{\partial V}\right|_T = \frac{Nk_BT}{V}$$

→ monatomic ideal gas: $PV = Nk_BT$ and $E = \frac{3}{2}Nk_BT$

→ in classical gas, $S_B \to$ constant $(T\to 0)$, in violation of the third law of thermodynamics.
(depends on the density n)

3.7 Conservation laws

Third question: how the gas reaches its final equilibrium?

perturbed gas from it equilibrium: $f_1(\vec{p},\vec{q}) = n\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left[-\frac{\beta(\vec{p}-\vec{p}_0)^2}{2m}\right]$ and follows a relaxation to equili.

Approach to equilibrium: a hierarchy of mechanisms that operates at different time scales.

(i) fastest process: two-body collisions of particles over time scale τ_c
$f_2(\vec{q}_1,\vec{q}_2,t)$ relaxes to $f_1(\vec{q}_1,t)f_1(\vec{q}_2,t)$ for $|\vec{q}_1-\vec{q}_2| \gg d$
(Similar to f_s)

(ii) Next, f_1 relaxes to a **local equilibrium** form. over the time scale of the mean free time τ_X. (on the right hand side of Boltzmann eqn.)

Time-dependent local density $\quad n(\vec{q},t) = \int d^3\vec{p}\, f_1(\vec{p},\vec{q},t)$

local expectation value $\quad \langle O(\vec{q},t)\rangle = \frac{1}{n(\vec{q},t)}\int d^3\vec{p}\, f_1(\vec{p},\vec{q},t)\, O(\vec{p},\vec{q},t)$

(iii) A subsequent slower relaxation to global equilibrium over extrinsic time and length scales. (smaller streaming term on left hand side of Boltzmann eqn)

Conserved quantities: unchanged by the two-body collisions,

$$\chi(\vec{p}_1,\vec{q}_1,t) + \chi(\vec{p}_2,\vec{q}_1,t) = \chi(\vec{p}_1{}',\vec{q}_1,t) + \chi(\vec{p}_2{}',\vec{q}_1,t)$$

obeys $J_\chi(\vec{q},t) = \int d^3\vec{p}\,\chi(\vec{p},\vec{q},t)\left.\frac{df_1}{dt}\right|_{coll}(\vec{p},\vec{q},t) = 0$

Proof: Collision integral,

$$J_\chi = -\int d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\,|\vec{v}_1-\vec{v}_2|\left[f_1(\vec{p}_1)f_1(\vec{p}_2) - f(\vec{p}_1{}')f(\vec{p}_2{}')\right]\chi(\vec{p}_1)$$

similar to the changes performed in proof of H-theorem

① — $J_\chi = -\frac{1}{2}\int d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\,|\vec{v}_1-\vec{v}_2|\left[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1{}')f_1(\vec{p}_2{}')\right]\left[\chi(\vec{p}_1)+\chi(\vec{p}_2)\right]$

$(\vec{p}_1,\vec{p}_2,\vec{b}) \to (\vec{p}_1{}',\vec{p}_2{}',\vec{b}')$ and relabel the integration.

② — $J_\chi = -\frac{1}{2}\int d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\,|\vec{v}_1-\vec{v}_2|\left[f_1(\vec{p}_1{}')f_1(\vec{p}_2{}') - f_1(\vec{p}_1)f_1(\vec{p}_2)\right]\left[\chi(\vec{p}_1{}')+\chi(\vec{p}_2{}')\right]$

(①+②)/2 $\Rightarrow$ $J_\chi = -\frac{1}{4}\int d^3\vec{p}_1\, d^3\vec{p}_2\, d^2\vec{b}\,|\vec{v}_1-\vec{v}_2|\left[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1{}')f_1(\vec{p}_2{}')\right]\underbrace{\left[\chi(\vec{p}_1)+\chi(\vec{p}_2)-\chi(\vec{p}_1{}')-\chi(\vec{p}_2{}')\right]}_{0}$

$= 0$ #

Evolution of expectation values involving χ:

$$J_\chi(\vec{q},t) = \int d^3\vec{p}\,\chi(\vec{p},\vec{q},t)\left[\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}\right]f_1(\vec{p},\vec{q},t) = 0$$

$\partial_t \equiv \frac{\partial}{\partial t}$, $\partial_\alpha \equiv \frac{\partial}{\partial q_\alpha}$

$F_\alpha = -\frac{\partial U}{\partial q_\alpha}$

$$\int d^3\vec{p}\ \{ [\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha \frac{\partial}{\partial p_\alpha}](\chi f_1) - f_1 [\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}]\chi \} = 0 \qquad \left(* \int d^3\vec{p}\ F_\alpha \frac{\partial}{\partial p_\alpha}(\chi f_1) = \xrightarrow{0} \text{~~complete~~ derivative} \right)$$

$$\xrightarrow[\text{on } \vec{p}]{\text{expectation value}} \partial_t(n\langle\chi\rangle) + \partial_\alpha\left(n\langle \frac{p_\alpha}{m}\chi\rangle\right) - n\langle\partial_t\chi\rangle - n\langle\frac{p_\alpha}{m}\partial_\alpha\chi\rangle - nF_\alpha\langle\frac{\partial\chi}{\partial p_\alpha}\rangle = 0$$

5 conserved quantities → 5 corresponding hydrodynamic eqn.
- particle number, 3 components of momentum & kinetic energy

(a) Particle number. let $\chi = 1$ leads to $\partial_t n + \partial_\alpha(n u_\alpha) = 0$

$$\boxed{\text{local velocity}: \ \vec{u} \equiv \langle\frac{\vec{p}}{m}\rangle(\vec{q},t)} \quad (\text{average on } \vec{p})$$

* Time variation of the local particle density is due to particle current $\vec{J}_n = n\vec{u}$

(b) Momentum: let $\boxed{\vec{c} \equiv \frac{\vec{p}}{m} - \vec{u}}$ and substitute C_α for χ into Eqn. $(\langle C_\alpha\rangle = 0)$

any linear func of $\vec{p}$ is conserved in the collision

$$\partial_\beta(n\langle(u_\beta + C_\beta)C_\alpha\rangle) - n\langle\partial_t C_\alpha\rangle - n\langle(C_\beta+u_\beta)\partial_\beta C_\alpha\rangle - nF_\beta\langle\frac{\partial C_\alpha}{\partial p_\beta}\rangle = 0$$

$$\cancel{\partial_\beta[n u_\beta\langle C_\alpha\rangle]}^{0} + \partial_\beta[n\langle C_\alpha C_\beta\rangle] - \cancel{\frac{n}{m}\langle\partial_t p_\alpha\rangle}^{0} + \underbrace{n\langle\partial_t u_\alpha\rangle}_{①} - \cancel{n\langle(C_\beta+u_\beta)\partial_\beta\frac{p_\alpha}{m}\rangle}^{0}$$

$$\underbrace{+ n\langle u_\beta + C_\beta\rangle\partial_\beta u_\alpha}_{②} - nF_\beta\frac{\delta_{\alpha\beta}}{m} = 0$$

$$\Rightarrow \partial_t u_\alpha + u_\beta\partial_\beta u_\alpha = \frac{F_\alpha}{m} - \frac{1}{mn}\partial_\beta P_{\alpha\beta}$$

acceleration of an element of the fluid $d\vec{u}/dt$ = $\frac{\vec{F}_{net}}{m}$ (includes variations in the pressure tensor across the fluid.)

$$\boxed{\text{Pressure tensor}: \quad P_{\alpha\beta} \equiv mn\langle C_\alpha C_\beta\rangle}$$

(c) Kinetic energy:

$$\boxed{\text{average local kinetic energy}: \ \varepsilon \equiv \langle\frac{m\vec{c}^2}{2}\rangle = \langle\frac{\vec{p}^2}{2m} - \vec{p}\cdot\vec{u} + \frac{m\vec{u}^2}{2}\rangle}$$

set $\chi = mc^2/2$. For space and time derivative, $\underline{\partial\varepsilon = mC_\beta\partial C_\beta = -mC_\beta\partial u_\beta}$

$$\partial_t(n\varepsilon) + \partial_\alpha\left(n\langle(u_\alpha+C_\alpha)\frac{m\vec{c}^2}{2}\rangle\right) + \cancel{nm\langle C_\beta\rangle\partial_t u_\beta}^{0} + nm\langle(u_\alpha+C_\alpha)C_\beta\rangle\partial_\alpha u_\beta$$

$$\cancel{-nF_\alpha\langle C_\alpha\rangle}^{0} = 0 \qquad \text{and} \quad \langle C_\alpha\rangle = 0$$

$$\Rightarrow \partial_t(n\varepsilon) + \partial_\alpha(nu_\alpha\varepsilon) + \partial_\alpha\left(n\langle C_\alpha\frac{m\vec{c}^2}{2}\rangle\right) + P_{\alpha\beta}\partial_\alpha u_\beta = 0$$

Take out dependence on n: $\quad \varepsilon\partial_t n + n\partial_t\varepsilon + \varepsilon\partial_\alpha(nu_\alpha) + nu_\alpha\partial_\alpha\varepsilon + \partial_\alpha h_\alpha + P_{\alpha\beta}u_{\alpha\beta} = 0$

$$\boxed{\text{local heat flux}: \ \vec{h} \equiv \frac{mn}{2}\langle C_\alpha\vec{c}^2\rangle} \ \&\& \ \boxed{\text{rate of strain tensor}: \ u_{\alpha\beta} = \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha)}$$

As number of particle: $\partial_t n + \partial_\alpha(nu_\alpha) = 0$: $\quad \partial_t\varepsilon + u_\alpha\partial_\alpha\varepsilon = -\frac{1}{n}\partial_\alpha h_\alpha - \frac{1}{n}P_{\alpha\beta}u_{\alpha\beta}$

For solving n, $\vec{u}$ and ε, the expression for $P_{\alpha\beta}$ and $\vec{h}$ is necessary and solved from density f_1.

3.8 Zeroth-order hydrodynamics

local equilibrium approxi: $f_1^0(\vec{p},\vec{q},t) = \frac{n(\vec{q},t)}{[2\pi m k_B T(\vec{q},t)]^{3/2}} \exp\left[-\frac{\overbrace{[\vec{p}-m\vec{u}(\vec{q},t)]^2}^{m^2\vec{c}^2}}{2mk_BT(\vec{q},t)}\right]$

* $\int d^3\vec{p}\, f_1^0 = n$ and $\langle \frac{\vec{p}}{m}\rangle^0 = \vec{u}$

$$\boxed{\langle C_\alpha C_\beta\rangle} = \left\langle\left(\frac{p_\alpha}{m}-u_\alpha\right)\left(\frac{p_\beta}{m}-u_\beta\right)\right\rangle = \left\langle\frac{p_\alpha p_\beta}{m^2}\right\rangle - \left\langle\frac{p_\beta}{m}\right\rangle\left\langle\frac{p_\alpha}{m}\right\rangle - \left\langle\frac{p_\alpha}{m}\right\rangle\left\langle\frac{p_\beta}{m}\right\rangle + \left\langle\frac{p_\alpha}{m}\right\rangle\left\langle\frac{p_\beta}{m}\right\rangle$$

$$= \left\langle\frac{p_\alpha p_\beta}{m^2}\right\rangle - \left\langle\frac{p_\alpha}{m}\right\rangle\left\langle\frac{p_\beta}{m}\right\rangle = \frac{1}{m^2}\left[\langle p_\alpha p_\beta\rangle - \langle p_\alpha\rangle\langle p_\beta\rangle\right] = \frac{1}{m^2}\sigma_\alpha^2\delta_{\alpha\beta} = \boxed{\frac{k_BT}{m}\delta_{\alpha\beta}}$$

leads to

$\boxed{P_{\alpha\beta} = nk_BT\delta_{\alpha\beta}}$ and

$$\boxed{\begin{aligned}\varepsilon &= \frac{1}{2m}\langle\vec{p}^2\rangle - 3u_\alpha\langle p_\alpha\rangle + \frac{3}{2m}\langle p_\alpha\rangle^2\\ &= \frac{3}{2}k_BT - \cancel{3u_\alpha\langle p_\alpha\rangle} + \cancel{3u_\alpha\langle p_\alpha\rangle}\\ &= \frac{3}{2}k_BT\end{aligned}}$$

Density f_1^0 is even in $\vec{C}$, all odd expectation values vanish

$$\vec{h}^0 = \frac{mn}{2}\langle C_\alpha\vec{C}^2\rangle = 0$$

conservative law:

$$\begin{array}{l} n \\ \vec{u} \\ \varepsilon \end{array}\begin{cases} D_t n = -n\partial_\alpha u_\alpha & ① \\ mD_t u_\alpha = F_\alpha - \frac{1}{n}\partial_\alpha(nk_BT) & ② \\ D_t T = -\frac{2}{3}T\partial_\alpha u_\alpha & ③ \end{cases}$$

w.r.t. $\underline{D_t \equiv [\partial_t + u_\beta\partial_\beta]}$ measures the time variations of any quantities as moving along stream-lines set by $\vec{u}$

① & ③: $D_t \ln(nT^{-3/2}) = 0$

* Quantity $\ln(nT^{-3/2})$ is like a local entropy for gas
* It predicts that the gas flow is adiabatic.
* prevents the local equilibrium solution from reaching a true global equilibrium form which necessitates an increase in entropy.

Proof: A small deformation about a stationary ($\vec{u}_0=0$) state, in a uniform box ($\vec{F}=0$)

$$\begin{cases} n(\vec{q},t) = \bar{n} + \nu(\vec{q},t) \\ T(\vec{q},t) = \bar{T} + \theta(\vec{q},t)\end{cases}$$

Expand ①,②,③ to first order in the deviations (ν,θ,u) and $D_t = \partial_t + \mathcal{O}(u) \Rightarrow$ linearized 0th hydrodynamic eqn.

$$\begin{cases} \partial_t\nu = -\bar{n}\partial_\alpha u_\alpha \\ m\partial_t u_\alpha = -\frac{k_B\bar{T}}{\bar{n}}\partial_\alpha\nu - k_B\partial_\alpha\theta \\ \partial_t\theta = -\frac{2}{3}\bar{T}\partial_\alpha u_\alpha \end{cases} \xrightarrow[\text{By FT}]{\text{Normal modes}} \tilde{A}(\vec{k},\omega) = \int d^3\vec{p}\,dt\,\exp[i(\vec{k}\cdot\vec{q}-\omega t)]A(\vec{q},t)$$

A stands for any of the three fields $(\nu,\theta,\vec{u})$

$$\omega\begin{pmatrix}\tilde{\nu}\\ \tilde{u}_\alpha \\ \tilde{\theta}\end{pmatrix} = \begin{pmatrix} 0 & \bar{n}k_\beta & 0 \\ \frac{k_B\bar{T}}{m\bar{n}}\delta_{\alpha\beta}k_\beta & 0 & \frac{k_B}{m}\delta_{\alpha\beta}k_\beta \\ 0 & \frac{2}{3}\bar{T}k_\beta & 0\end{pmatrix}\begin{pmatrix}\tilde{\nu}\\ \tilde{u}_\beta \\ \tilde{\theta}\end{pmatrix}$$

$\Rightarrow$ actually that is 5×5 matrix $\tilde{u}_\alpha$ $(\alpha = x,y,z)$

$$\sim \begin{bmatrix} 0 & a & a & a & 0 \\ b & 0 & 0 & 0 & c \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & d & d & d & 0 \end{bmatrix}$$ (Calculated by mathematica)

First three with zero frequency (eigenvalues)

3 zero frequency

(a) * Two modes describe shear flows in a uniform ($n=\bar{n}$) and isothermal ($T=\bar{T}$)

* Velocity varies along a direction normal to its orientation (e.g. $\vec{u}=f(x,t)\hat{y}$)

(eigenvector $\vec{v}_S=[0,-1,0,1,0] \leftarrow \vec{u}_y$ && $[0,-1,1,0,0] \leftarrow \vec{u}_z$

* $\vec{k}\cdot\hat{\vec{u}}_T(\vec{k})=0$ indicates transverse flows are not relaxed in 0th-order approx.

(b) * The third zero frequency mode describes a stationary fluid with uniform pressure $P=nk_BT$. n and T vary across space, but product of n and T (P/k_B) is constant.

(eigenvector: $\vec{v}_E=[\bar{n},0,0,0,\bar{T}] \xleftarrow[\text{from}]{\text{comes}} \left[\frac{k_B\bar{T}}{m\bar{n}}\delta_{\alpha\beta}k_\beta,\ 0,\ \frac{k_B}{m}\delta_{\alpha\beta}k_\beta\right]$)

entropy mode

($\alpha=\beta$)

* Fluid will not move due to pressure constant.

2 non-zero frequency

(c) * The longitudinal velocity ($\vec{u}_L \parallel \vec{k}$) combines with density and temperature.

(eigenvector: $\vec{v}_L=\begin{bmatrix}\bar{n}|\vec{k}| \\ \omega(\vec{k}) \\ \frac{2}{3}\bar{T}|\vec{k}|\end{bmatrix}$ with $\omega(\vec{k})=\pm v_L|\vec{k}|$; $\boxed{v_L=\sqrt{\frac{5}{3}\frac{k_B\bar{T}}{m}}}$)

* v_L is the longitudinal sound velocity

* density and temperature variations in this mode are adiabatic so the local entropy (proportional to $\ln(nT^{-3/2})$) is unchanged.

Summary: None of the conserved quantities relaxes to equilibrium in 0th-order approx.

- Shear flow and entropy modes persist forever
- Two sound modes have undamped oscillations

3.9 First-order hydrodynamics

$f_1^0(\vec{p},\vec{q},t)$ sets the right-hand side of the Boltzmann eqn to zero. → not a full sol'n (left side causes its form to vary

Left-hand side is a linear differential operator

$$\mathcal{L}[f] \equiv \left[\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha \frac{\partial}{\partial p_\alpha}\right] f = \left[D_t + c_\alpha \partial_\alpha + \frac{F_\alpha}{m}\frac{\partial}{\partial c_\alpha}\right] f \qquad ①$$

$$\ln f_1^0 = \ln\left(nT^{-3/2}\right) - \frac{m\vec{c}^{\,2}}{2k_BT} - \frac{3}{2}\ln(2\pi m k_B) \qquad ②$$

As $\partial(\vec{c}^{\,2}/2) = c_\beta \partial c_\beta = -c_\beta \partial u_\beta$

① & ②

$$\mathcal{L}[\ln f_1^0] = D_t \ln\left(nT^{-3/2}\right) + \frac{m\vec{c}^{\,2}}{2k_BT^2} D_t T + \frac{m}{k_BT} c_\alpha D_t u_\alpha + c_\alpha\left(\frac{\partial_\alpha n}{n} - \frac{3}{2}\frac{\partial_\alpha T}{T}\right) + \frac{m\vec{c}^{\,2}}{2k_BT^2} c_\alpha \partial_\alpha T + \frac{m}{k_BT} c_\alpha c_\beta \partial_\alpha u_\beta - \frac{F_\alpha}{m}\frac{mc_\alpha}{k_BT}$$

let n, T, and u_α satisfy the 0th order hydrodynamics

$$\mathcal{L}[\ln f_1^0] = 0 - \frac{m\vec{c}^{\,2}}{3k_BT}\partial_\alpha u_\alpha + c_\alpha\left[\left(\frac{F_\alpha}{k_BT} - \frac{\partial_\alpha n}{n} - \frac{\partial_\alpha T}{T}\right) + \left(\frac{\partial_\alpha n}{n} - \frac{3}{2}\frac{\partial_\alpha T}{T}\right) - \frac{F_\alpha}{k_BT}\right] + \frac{m\vec{c}^{\,2}}{2k_BT^2} c_\alpha \partial_\alpha T + \frac{m}{k_BT} c_\alpha c_\beta u_{\alpha\beta}$$

$$= \frac{m}{k_BT}\left(c_\alpha c_\beta - \frac{\delta_{\alpha\beta}}{3}\vec{c}^{\,2}\right) u_{\alpha\beta} + \left(\frac{m\vec{c}^{\,2}}{2k_BT} - \frac{5}{2}\right)\frac{c_\alpha}{T}\partial_\alpha T$$

In 0th-order approx. with $\tau_\times/\tau_U \to 0$ (intrinsic/extrinsic characteristic time → 0)

⇒ in a perturbation series in $\tau_\times/\tau_U$

set $\boxed{f_1 = f_1^0(1+g)}$ and linearize the collision operator

$$C[f_1,f_1] = -\int d^3\vec{p}_2\, d^3\vec{q}\, d^2\vec{b}\, |\vec{v}_1 - \vec{v}_2|\, f_1^0(\vec{p}_1) f_1^0(\vec{p}_2)\left[g(\vec{p}_1) + g(\vec{p}_2) - g(\vec{p}_1{}') - g(\vec{p}_2{}')\right]$$

$$\equiv -f_1^0(\vec{p}_1)\, C_L[g]$$

1st: single collision time approx. $\quad C_L[g] \approx \dfrac{g}{\tau_\times}$ (characteristic magnitude)

2nd: keep only leading term $\quad$ As $\mathcal{L}[f_1] = -f_1^0 C_L[g]$, $\quad g = -\tau_\times \dfrac{1}{f_1^0}\mathcal{L}[f_1] \approx -\tau_\times \mathcal{L}[\ln f_1^0]$

$$f_1^1(\vec{p},\vec{q},t) = f_1^0(\vec{p},\vec{q},t)\left[1 - \frac{\tau_\mu m}{k_BT}\left(c_\alpha c_\beta - \frac{\delta_{\alpha\beta}}{3}\vec{c}^{\,2}\right) u_{\alpha\beta} - \tau_K\left(\frac{m\vec{c}^{\,2}}{2k_BT} - \frac{5}{2}\right)\frac{c_\alpha}{T}\partial_\alpha T\right]$$

In single collision time approx., $\tau_\mu = \tau_K = \tau_\times$; however, $\tau_\mu \neq \tau_K$ in sophisticated treatment (but both times are still of order of $\tau_\times$)

Easy to check that $\int d^3\vec{p}\, f_1^1 = \int d^3\vec{p}\, f_1^0 = n$

proof: $C_\alpha C_\beta - \frac{\delta_{\alpha\beta}}{3}\vec{C}^2$ $\nearrow$ $C_\alpha C_\beta$ (odd) : $C_x C_y$

$\searrow$ $C_\alpha^2 - \frac{C^2}{3}$: $C_x^2 - \frac{C^2}{3} + C_y^2 - \frac{C^2}{3} + C_z^2 - \frac{C^2}{3} = 0$

&& $\left(\frac{m\vec{c}^2}{2k_BT} - \frac{5}{2}\right)\frac{C_\alpha}{T}$ (odd) $\Rightarrow \int d^3\vec{p}\, g f_1^0 = 0$

local expectation values w.r.t. first order

$$\boxed{\langle O\rangle^1 = \frac{1}{n}\int d^3\vec{p}\, O f_1^0 (1+g) = \langle O\rangle^0 + \langle gO\rangle^0}$$

Wick's theorem

Expectation value of the product is the sum over all possible products of paired expectation values.

Use Wick's theorem to calculate averages of products of C_α according to Gaussian weight of f_1^0.

E.x. $\langle C_\alpha C_\beta C_\gamma C_\delta\rangle_0 = \left(\frac{k_BT}{m}\right)^2(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma})$ $\quad \# = \binom{4}{2}/2!$

* Expectation values involving a product of an odd number of C_α's are zero by symmetry.

local velocity:

$$\left\langle \frac{\overset{\text{odd}}{p_\alpha}}{m}\right\rangle^1(\alpha) = u_\alpha - \tau_K \frac{\partial T}{T}\left\langle\left(\frac{m\vec{c}^2}{2k_BT} - \frac{5}{2}\right)C_\alpha C_\beta\right\rangle^0 = u_\alpha \quad (\alpha \text{ has been decided})$$

* $\vec{C}^2 = C_x^2 + C_y^2 + C_z^2 \Rightarrow \langle C_x^2 C_\alpha C_\beta\rangle + \langle C_y^2 C_\alpha C_\beta\rangle + \langle C_z^2 C_\alpha C_\beta\rangle = 5(k_BT/m)^2$

If $\alpha=\beta=x$, $\langle C_x^4\rangle = 3(k_BT/m)^2$, $\langle C_y^2 C_x^2\rangle = (k_BT/m)^2$, $\langle C_z^2 C_x^2\rangle = (k_BT/m)^2$

* has proved $\langle C_\alpha C_\beta\rangle^0 = (k_BT/m)\delta_{\alpha\beta}$

Pressure tensor:

$$P_{\alpha\beta}^1 = nm\langle \overset{\text{even}}{C_\alpha} C_\beta\rangle^1 = nm\left[\langle C_\alpha C_\beta\rangle^0 - \frac{\tau_\mu m}{k_BT}\left\langle C_\alpha C_\beta\left(C_\mu C_\nu - \frac{\delta_{\mu\nu}}{3}\vec{C}^2\right)\right\rangle^0 u_{\mu\nu}\right]$$

$$= nk_BT\delta_{\alpha\beta} - 2nk_BT\tau_\mu\left(u_{\alpha\beta} - \frac{\delta_{\alpha\beta}}{3}u_{\gamma\gamma}\right)$$

* $\langle C_\alpha C_\beta C_\mu C_\nu\rangle(\alpha,\beta)$ (α, β are decided at the begining in the definition of $P_{\alpha\beta}$)

if $\mu=\alpha$, $\nu=\beta$ or $\mu=\beta$, $\nu=\alpha$; $\langle C_\alpha^2 C_\beta^2\rangle = \langle C_\beta^2 C_\alpha^2\rangle = (k_BT/m)^2$

$\Rightarrow \langle C_\alpha C_\beta C_\mu C_\nu\rangle u_{\mu\nu} = 2(k_BT/m)^2 u_{\alpha\beta}$

from local velocity and the proof of pressure tensor before

* $\langle C_\alpha C_\beta(\delta_{\mu\nu}/3)\vec{C}^2\rangle(\alpha,\beta)$

As $\mu=\alpha$, $\nu=\beta$ or $\mu=\beta$, $\nu=\alpha$ and $\langle C_\alpha C_\beta \vec{C}^2\rangle = \langle C_\alpha^2 C_\beta^2\rangle + \langle C_\beta^2 C_\alpha^2\rangle = 2(k_BT/m)^2$

But it only exist when $\alpha=\beta$, so here there are 3 cases,

$\alpha=\beta=x$, $\alpha=\beta=y$, $\alpha=\beta=z$ $\Rightarrow$ substitute $\alpha=\beta=\gamma$ into $u_{\mu\nu}$

$\Rightarrow \left\langle C_\alpha C_\beta \frac{\delta_{\mu\nu}}{3}\vec{C}^2\right\rangle = 2\left(\frac{k_BT}{m}\right)^2 \frac{\delta_{\alpha\beta}}{3}u_{\gamma\gamma}$

$\boxed{\text{average local kinetic energy}}$ $\varepsilon' = \langle \frac{m\vec{c}^2}{2} \rangle' = \frac{3}{2} k_B T$

$$* \ \langle \vec{c}^2 \rangle = 3\langle c_i^2 \rangle = 3\langle c_\alpha c_\beta \rangle \delta_{\alpha\beta} = 3\frac{k_B T}{m} - 2n k_B T \tau_\mu \big(u_{xx} - \tfrac{1}{3}u_{xx} - \tfrac{1}{3}u_{yy} - \tfrac{1}{3}u_{zz} + u_{yy} - \tfrac{1}{3}u_{xx} - \tfrac{1}{3}u_{yy} - \tfrac{1}{3}u_{zz} + u_{zz} - \tfrac{1}{3}u_{xx} - \tfrac{1}{3}u_{yy} - \tfrac{1}{3}u_{zz} \big) = 3 k_B T/m$$

$\boxed{\text{local heat flux:}}$

$$h'_\alpha = n\left\langle c_\alpha \frac{m\vec{c}^2}{2} \right\rangle' = 0 - \frac{nm\tau_k}{2}\frac{\partial_\beta T}{T}\left\langle \left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right) c_\alpha c_\beta \vec{c}^2 \right\rangle^0$$

$$= -\frac{5}{2}\frac{nk_B^2 T\tau_k}{m}\partial_\alpha T$$

from local velocity: $* \ \langle c_\alpha c_\beta \vec{c}^2 \rangle = 5 (k_BT/m)^2$

$* \ \langle c_\alpha c_\beta \vec{c}^4 \rangle = 35 (k_BT/m)^3$

$\sim \langle x^6 \rangle$ reduced to 3 sets of pairs

If we let $\alpha = x$, $\beta = \alpha = x$ or $\beta \neq \alpha$ (all 0)

Configuration:

$\underline{xx}\,\underline{xx}\,\underline{xx}$: $\frac{1}{3!}\cdot\frac{6!}{2!2!2!} = 15$ | $\underline{xx}\,\underline{xx}\,\underline{yy}$: $\frac{1}{2!}\frac{4!}{2!2!} = 3$ | $\underline{xx}\,\underline{xx}\,\underline{zz}$: 3

$\underline{xx}\,\underline{yy}\,\underline{xx}$: 3 | $\underline{xx}\,\underline{yy}\,\underline{yy}$: 3 | $\underline{xx}\,\underline{yy}\,\underline{zz}$: 1

$\underline{xx}\,\underline{zz}\,\underline{xx}$: 3 | $\underline{xx}\,\underline{zz}\,\underline{yy}$: 1 | $\underline{xx}\,\underline{zz}\,\underline{zz}$: 3

$= 35$

Spatial variations in temperature generates heat flow that tends to smooth it out, while shear flows are opposed by the off-diagonal terms in the pressure tensor. $\Longrightarrow$ relaxation to equilibrium

(a) Pressure tensor has an off-diagonal term

$$P'_{\alpha\neq\beta} = -2nk_BT\tau_\mu u_{\alpha\beta} \equiv -\mu(\partial_\alpha u_\beta + \partial_\beta u_\alpha)$$

$\boxed{\text{viscosity coefficient: } \mu \equiv n k_B T \tau_\mu}$

A shearing of the fluid (e.g., described by a velocity $\vec{u}_y(x,t)$)

$\longrightarrow$ a viscous force that opposes it ($\propto \mu\partial_x^2 u_y$)

$\longrightarrow$ diffusive relaxation.

(b) A temperature gradient → a heat flux

$\vec{h} = -K\nabla T$

$\boxed{\text{coefficient of Thermal conductivity of gas: } K = (5nk_B^2 T\tau_K)/(2m)}$

The gas is at rest ($\vec{u}=0$, and uniform $P = nk_BT$)

$$n\partial_t\varepsilon = \frac{3}{2}nk_B\partial_t T = -\partial_\alpha h_\alpha = -\partial_\alpha(-K\partial_\alpha T)$$

$$\Rightarrow \partial_t T = \frac{2K}{3nk_B}\nabla^2 T$$

$\boxed{\text{Fourier eqn. temperature variations relax by diffusion}}$

linearizing the eqn. of motion

Momentum: $\partial_t u_\alpha + u_\beta\partial_\beta u_\alpha = D_t u_\alpha = \frac{F_\alpha}{m} - \frac{1}{mn}\partial_\beta P_{\alpha\beta}$ (conservation law)

has been derived

1st order contribution $D_t u_\alpha \simeq \partial_t u_\alpha$ (δ^1: only calcu. the perturbation 1)

$$\delta^1(\partial_t u_\alpha) \equiv \frac{1}{mn}\partial_\beta\delta^1 P_{\alpha\beta} = -\frac{\mu}{m\bar{n}}\partial_\beta\delta^1\left(\partial_\alpha u_\beta + \partial_\beta u_\alpha - \frac{2}{3}\delta_{\alpha\beta}\partial_\gamma u_\gamma\right)$$

$$\simeq \boxed{-\frac{\mu}{m\bar{n}}\left(\frac{1}{3}\partial_\alpha\partial_\beta + \delta_{\alpha\beta}\partial_\gamma\partial_\gamma\right)u_\beta} \leftarrow ???$$

with $\mu \equiv \bar{n}k_B\bar{T}\tau_\mu$

Energy: $\partial_t\varepsilon + u_\alpha\partial_\alpha\varepsilon = -\frac{1}{n}\partial_\alpha h_\alpha - \frac{1}{n}P_{\alpha\beta}u_{\alpha\beta}$ $\boxed{\text{ignore change of } P_{\alpha\beta}} \leftarrow ???$

$$D_t T = -\frac{2}{3}T\partial_\alpha u_\alpha - \frac{2}{3k_Bn}\partial_\alpha h_\alpha$$

1st order contribution $D_t T \simeq \partial_t\theta$

$$\delta^1(\partial_t\theta) \equiv -\frac{2}{3k_Bn}\partial_\alpha h_\alpha \simeq -\frac{2K}{3k_B\bar{n}}\partial_\alpha\partial_\alpha\theta$$

with $K = (5\bar{n}k_B^2\bar{T}\tau_K)/(2m)$

Fourier transform ↓ Modified Matrix from 0th order approx.

$$\omega\begin{pmatrix}\tilde{\nu}\\ \tilde{u}_\alpha\\ \tilde{\theta}\end{pmatrix} = \begin{pmatrix} 0 & \bar{n}\delta_{\alpha\beta}k_\beta & 0\\ \frac{k_B\bar{T}}{mn}\delta_{\alpha\beta}k_\beta & -i\underline{\frac{\mu}{m\bar{n}}}\left(\vec{k}^2\delta_{\alpha\beta} + \frac{1}{3}k_\alpha k_\beta\right) & \frac{k_B}{m}\delta_{\alpha\beta}k_\beta\\ 0 & \frac{2}{3}\bar{T}\delta_{\alpha\beta}k_\beta & -i\frac{2K\vec{k}^2}{3k_B\bar{n}}\end{pmatrix}\begin{pmatrix}\tilde{\nu}\\ \tilde{u}_\beta\\ \tilde{\theta}\end{pmatrix}$$

Transverse (shear) normal modes ($\vec{k}\cdot\tilde{\vec{u}}_T = 0$) have frequency $\omega_T = -i\frac{\mu}{m\bar{n}}k^2$

imaginary frequency implies modes are damped over a
$\Rightarrow$ characteristic time $\tau_T(k) \sim 1/|\omega_T| \sim \frac{\lambda^2}{\tau_\mu \bar{v}^2}$

$\lambda \sim$ corresponding wavelength ; $\bar{v} \sim \sqrt{\frac{k_BT}{m}}$ typical gas velocity

* time scales grow as the square of wavelength $\Rightarrow$ diffusive processes

the velocity is parallel to $\vec{k}$ $\Rightarrow$ $\omega\begin{pmatrix}\tilde{\nu}\\ \tilde{u}_\beta\\ \tilde{\theta}\end{pmatrix} = \begin{pmatrix} 0 & \bar{n}k & 0 \\ \frac{k_B\bar{T}}{m\bar{n}}k & -i\frac{4\mu k^2}{3m\bar{n}} & \frac{k_B}{m}k \\ 0 & \frac{2}{3}\bar{T}k & -i\frac{2Kk^2}{3k_B\bar{n}}\end{pmatrix}\begin{pmatrix}\tilde{\nu}\\ \tilde{u}_\beta\\ \tilde{\theta}\end{pmatrix}$

$\det(M) = i\frac{2Kk^2}{3k_B\bar{n}}\cdot\bar{n}k\cdot\frac{k_B\bar{T}}{m\bar{n}}k + O(\tau_x^2)$ = product of all eigenvalues

Two sound modes: $\omega_\pm^0(k) = \pm v_l k$ at zeroth order approx. ; $v_L = \sqrt{\frac{5}{3}\frac{k_B\bar{T}}{m}}$

frequency of isobaric mode : $\omega_e^1(k) \simeq \frac{\det(M)}{-v_l^2k^2} = -i\frac{2Kk^4\bar{T}}{3m\bar{n}}\cdot\frac{3m}{5k_B\bar{T}}\cdot\frac{1}{k^2} = -i\frac{2Kk^2}{5k_B\bar{n}} + O(\tau_x^2)$

longitudinal sound modes : turn into damped oscillations with frequency $\omega_\pm^1(k) = \pm v_l k - i\gamma$
with the help of trace (the sum of diagonal = the sum of eigenvalue)

$$\omega_\pm^1(k) = \pm v_l k - i\frac{1}{2}\frac{4\mu k^2}{3m\bar{n}} - i\frac{1}{2}\left(\frac{2Kk^2}{3k_B\bar{n}} - \frac{2}{5}\frac{Kk^2}{k_B\bar{n}}\right)$$

$$= \pm v_l k - ik^2\left(\frac{2\mu}{3m\bar{n}} + \frac{2K}{15k_B\bar{n}}\right) + O(\tau_x^2)$$

* The slow damping of all normal modes
$\Rightarrow$ approach of the gas to its final uniform and stationary equilibrium state