One-particle Distribution

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

Assume the density is symmetric upon exchanging particles.

$$\to \quad f_1(\vec{p},\vec{q},t) = N \int \prod_{i=2}^{N} d^3p_i\, d^3q_i \;\; \rho(\vec{p}_1=\vec{p}, \vec{q}_1=\vec{q}; \{\vec{p}_{i\neq 1}, \vec{q}_{i\neq 1}\}, t)$$

$$= N \rho_1(\vec{p},\vec{q},t),$$

where $\rho_1(\vec{p},\vec{q},t)$ = unconditional PDF for one of the particles.

Suppose the Hamiltonian is of the form,

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

external potential 2-body interactions

(assume $V(\vec{q}_i-\vec{q}_j) = V(\vec{q}_j-\vec{q}_i)$)

Write $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_{N-1} + \mathcal{H}'$, where

$$\mathcal{H}_1 = \frac{\vec{p}_1^{\,2}}{2m} + U(\vec{q}_1)$$

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

$$\mathcal{H}' = \sum_{i=2}^{N} V(\vec{q}_n - \vec{q}_1)$$

$$\frac{\partial \rho_1}{\partial t} = \int \prod_{i=2}^{N} d^3p_i \, d^3q_i \, \frac{\partial \rho}{\partial t}$$

$$= -\int \prod_{i=2}^{N} d^3p_i \, d^3q_i \, \{\rho, H_1 + H_{N-1} + H'\}$$

First term:

$$-\int \prod_{i=2}^{N} d^3p_i \, d^3q_i \, \{\rho, H_1\} = -\{\rho_1, H_1\}$$

$$= \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial \rho_1}{\partial \vec{p}_1} - \frac{\vec{p}_1}{m} \cdot \frac{\partial \rho_1}{\partial \vec{q}_1}$$

Second term:

$$-\int \prod_{i=2}^{N} d^3p_i \, d^3q_i \, \{\rho, H_{N-1}\}$$

$$= \int \prod_{i=2}^{N} d^3p_i \, d^3q_i \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \frac{\partial H_{N-1}}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \frac{\partial H_{N-1}}{\partial \vec{p}_j} \right]$$

$$= \int \prod_{i=2}^{N} d^3p_i \, d^3q_i \sum_{j=2}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \underbrace{\left(\frac{\partial U}{\partial \vec{q}_j} + \frac{1}{2} \sum_{k=2}^{N} \frac{\partial V(\vec{q}_j - \vec{q}_k)}{\partial \vec{q}_j} \right)}_{\text{indep of } \vec{p}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \cdot \underbrace{\frac{\vec{p}_j}{m}}_{\text{indep. of } \vec{q}_j} \right]$$

$$\overset{\text{by parts}}{=} 0$$

Final term:

$$+ \int \prod_{i=2}^{N} d^3p_i \, d^3q_i \sum_{j=1}^{N} \left[\frac{\partial \rho}{\partial \vec{p}_j} \cdot \frac{\partial H'}{\partial \vec{q}_j} - \frac{\partial \rho}{\partial \vec{q}_j} \cdot \frac{\partial H'}{\partial \vec{p}_j} \right]$$

$$= \int \prod_{i=2}^{N} d^3p_i \, d^3q_i \left[\frac{\partial \rho}{\partial \vec{p}_1} \cdot \sum_{j=2}^{N} \frac{\partial V(\vec{q}_j - \vec{q}_1)}{\partial \vec{q}_1} \right]$$

$$\prod_{i=2}^{N} d^3p_i\, d^3q_i \left[\frac{\partial \rho}{\partial \vec{p}_1} \cdot \sum_{j=2}^{N} \frac{\partial V(\vec{q}_j - \vec{q}_1)}{\partial \vec{q}_1}\right]$$

$$= (N-1) \int \prod_{i=2}^{N} d^3p_i\, d^3q_i\, \frac{\partial V(\vec{q}_2 - \vec{q}_1)}{\partial \vec{q}_1} \cdot \frac{\partial \rho}{\partial \vec{p}_1}$$

$$= (N-1) \int d^3p_2\, d^3q_2\, \frac{\partial V(\vec{q}_2 - \vec{q}_1)}{\partial \vec{q}_1} \cdot \frac{\partial}{\partial \vec{p}_1}\left(\int \prod_{i=3}^{N} d^3p_i\, d^3q_i\, \rho\right)$$

Define $\int \prod_{i=3}^{N} d^3p_i\, d^3q_i\, \rho \equiv \rho_2(\vec{p}_1, \vec{p}_2; \vec{q}_1, \vec{q}_2, t)$

= unconditional PDF for 2 particles.

Putting all of the terms together

$$\Rightarrow \boxed{\frac{\partial \rho_1}{\partial t} - \{H_1, \rho_1\} = (N-1) \int d^3p_2\, d^3q_2\, \frac{\partial V(\vec{q}_2 - \vec{q}_1)}{\partial \vec{q}_1} \cdot \frac{\partial \rho_2}{\partial \vec{p}_1}}$$

To determine ρ_1, we need ρ_2.
Similarly, to determine ρ_2, we need ρ_3, etc.

— This is the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy

n-particle density

Defining $f_n(\vec{p}_1, \ldots, \vec{q}_n, t) \equiv \frac{N!}{(N-n)!} \rho_n(\vec{p}_1, \ldots, \vec{q}_n, t)$

$$\frac{\partial f_1}{\partial t} - \{H_1, f_1\} = \int d^3p_2\, d^3q_2\, \frac{\partial V(\vec{q}_2 - \vec{q}_1)}{\partial \vec{q}_1} \cdot \frac{\partial f_2}{\partial \vec{p}_1}$$

For the 1-particle density f_1, we have

$$\underbrace{\frac{\partial f_1}{\partial t} - \{H_1, f_1\}}_{\substack{\text{streaming terms -} \\ \text{depend on } \vec{p}_1, \vec{q}_1 \\ \text{only}}} = \underbrace{\int d^3p_2\, d^3q_2\, \frac{\partial V(\vec{q}_2 - \vec{q}_1)}{\partial \vec{q}_1} \cdot \frac{\partial f_2}{\partial \vec{p}_1}}_{\substack{\text{Collision term - describes} \\ \text{effect of collisions due to} \\ V(\vec{q}_i - \vec{q}_1).}}$$

We can repeat this analysis for the time evolution of the 2-particle density $f_2(\vec{q}_1, \vec{q}_1; \vec{p}_2, \vec{q}_2; t) \equiv N(N-1)\rho_2$.

Again, consider $H = H_2 + H_{N-2} + H'$, where now

$$H_2 = \frac{\vec{p}_1^{\,2}}{2m} + U(\vec{q}_1) + \frac{\vec{p}_2^{\,2}}{2m} + U(\vec{q}_2) + V(\vec{q}_2 - \vec{q}_1)$$

$$H_{N-2} = \sum_{i=3}^{N} \left(\frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_i) \right) + \frac{1}{2} \sum_{i \neq j = 3}^{N} V(\vec{q}_i - \vec{q}_j)$$

$$H' = \sum_{i=3}^{N} V(\vec{q}_1 - \vec{q}_i) + \sum_{i=3}^{N} V(\vec{q}_2 - \vec{q}_i)$$

Following the discussion of $\frac{\partial f_1}{\partial t}$ based on application of Liouville's Equation, we now find,

$$\frac{\partial f_2}{\partial t} - \{H_2, f_2\} = \int d^3p_3\, d^3q_3 \left[\frac{\partial V(\vec{q}_1 - \vec{q}_3)}{\partial \vec{q}_1} \cdot \frac{\partial f_3}{\partial \vec{p}_1} + \frac{\partial V(\vec{q}_2 - \vec{q}_3)}{\partial \vec{q}_2} \cdot \frac{\partial f_3}{\partial \vec{p}_2} \right]$$

The Boltzmann Equation

With $\mathcal{H}_s = \sum_{n=1}^{s} \frac{\vec{p}_n^{\,2}}{2m} + U(\vec{q}_n)$, we have

$$\boxed{\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1}\right] f_1 = \int d^3\vec{p}_2\, d^3\vec{q}_2\, \frac{\partial V(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\frac{\partial f_2}{\partial \vec{p}_1}}$$

and

$$\boxed{\begin{aligned}&\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} - \frac{\partial U}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2} + \frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1} + \frac{\vec{p}_2}{m}\frac{\partial}{\partial \vec{q}_2}\right.\\ &\qquad\left. - \frac{\partial V(\vec{q}_1-\vec{q}_2)}{\partial \vec{q}_1}\cdot\left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right)\right] f_2 \\ &= \int d^3\vec{p}_3\, d^3\vec{q}_3 \left[\frac{\partial V(\vec{q}_1-\vec{q}_3)}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\partial V(\vec{q}_2-\vec{q}_3)}{\partial \vec{q}_2}\cdot\frac{\partial}{\partial \vec{p}_2}\right] f_3\end{aligned}}$$

Consider the relative magnitudes of the various terms.
Suppose gas particles move at speed $v \approx 10^2\ \mathrm{m/s}$ at room temp.

The external potential $U(\vec{q})$ varies over macroscopic distances, say $L \approx 10^{-3}$ m.

$$\boxed{\frac{1}{\tau_U} \sim \frac{\partial U}{\partial \vec{q}}\cdot\frac{\partial}{\partial \vec{p}} \sim \frac{v}{L}} \sim \frac{1}{10^{-5}\,\mathrm{s}} \quad \leftarrow \text{Extrinsic time scale.}$$

The interatomic potential V is often short-ranged, over a distance $d \approx 10^{-10}\,m$ (interatomic spacing)

$$\boxed{\frac{1}{\tau_c} \sim \frac{\partial V}{\partial \underline{q}} \cdot \frac{\partial}{\partial \underline{p}} \sim \frac{v}{d} \sim \frac{1}{10^{-12}\,s}}$$

– Only relevant for eqs. for $\frac{\partial f_s}{\partial t}$, $s > 1$.

$\rightarrow \tau_c \ll \tau_U$ in this case.

Exceptions! The Coulomb gas in a plasma can be long range, with characteristic Debye screening length λ

The collision terms lead to an inverse time scale

$$\frac{1}{\tau_\times} \sim \left(\int d^3p\, d^3q\, \frac{\partial V}{\partial \underline{q}} \cdot \frac{\partial}{\partial \underline{p}} f_{s+1}\right) \cdot \frac{1}{f_s}$$

by comparing w/ other terms in the eqn for $\frac{\partial f_s}{\partial t}$.

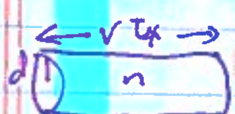
Integrals over range of V give a factor of d^3,

$\frac{f_{s+1}}{f_s} \sim$ prob of finding another particle per unit volume $\sim n = \frac{N}{Vd} \sim 10^{26}\,m^{-3}$

All together, we estimate $\frac{1}{\tau_\times} \sim n d^3 \frac{v}{d}$

$$\rightarrow \boxed{\tau_\times \approx \frac{\tau_c}{n d^3} \approx \frac{1}{n v d^2}} \sim 10^4\, \tau_c \gg \tau_c$$

(for short-ranged interactions)



$d^2 \cdot v \tau_\times \cdot n \sim O(1)$

If $\frac{\tau_c}{\tau_\times} \ll 1$, we obtain the Boltzmann Equation

by dropping the right hand side of the equation for $\frac{\partial f_1}{\partial t}$, truncating the BBGKY hierarchy.

(Can't drop collision term yet in eqn for $\frac{\partial f_2}{\partial t}$ because $\exists$ interatomic potential

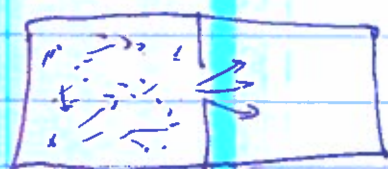
At distances $\gg$ range of potential V, we can treat the particles as independent:

$$\rho_2(\vec{p}_1, \vec{q}_1; \vec{p}_2, \vec{q}_2; t) \to \rho_1(\vec{p}_1, \vec{q}_1, t)\, \rho_1(\vec{p}_2, \vec{q}_2, t)$$

and

$$f_2(\vec{p}_1, \vec{q}_1; \vec{p}_2, \vec{q}_2; t) \to f_1(\vec{p}_1, \vec{q}_1, t)\, f_1(\vec{p}_2, \vec{q}_2, t) \quad \text{for } |\vec{q}_2 - \vec{q}_1| \gg d$$

This is valid even out of equilibrium



Open a barrier between two regions in a box, one of which has a gas originally.

Evolution of f_1 is initially complicated, relaxes in time $\gtrsim \tau_U$.

2-particle density f_2 also relaxes to final value in time $\gtrsim \tau_U$, but reaches factorized independent-particle form in shorter time $\sim \tau_c$.

Dropping the collision term depending on f_3, we have

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

In steady state, $\frac{\partial f_2}{\partial t} = 0$. (Examine state w/ resolution $\gg \tau_c$)

with $\frac{1}{\tau_c} \gg \frac{1}{\tau_U}$, we approximately have

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

If variations over center-of-mass $\vec{Q} = \frac{\vec{q}_1 + \vec{q}_2}{2}$ are slow

compared to variations of relative coordinate $\vec{q} = \vec{q}_2 - \vec{q}_1$, then

$$\frac{\partial f_2}{\partial \vec{q}_2} \approx -\frac{\partial f_2}{\partial \vec{q}_1} \approx \frac{\partial f_2}{\partial \vec{q}}.$$

$$\rightarrow \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right) f_2 \approx -\left(\frac{\vec{p}_1 - \vec{p}_2}{m}\right) \cdot \frac{\partial f_2}{\partial \vec{q}}$$

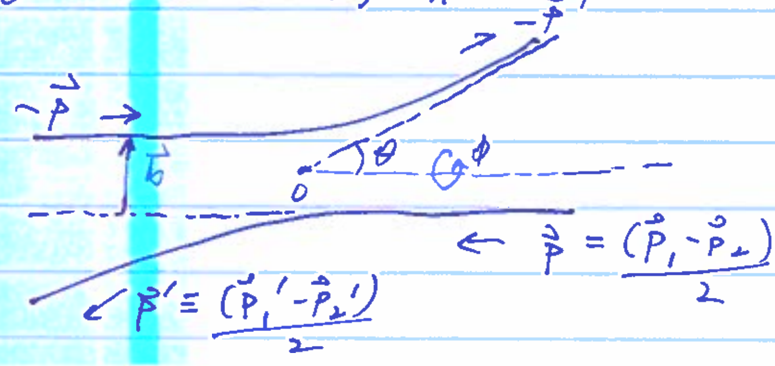
The collision term in the equation for $\frac{\partial f_1}{\partial t}$ is now

$$\left.\frac{df_1}{dt}\right|_{coll} \approx \int d^3p_2\, d^3q\, \frac{\partial V(\vec{q}_1 - \vec{q}_2)}{\partial \vec{q}_1} \cdot \left(\frac{\partial}{\partial \vec{p}_1} - \frac{\partial}{\partial \vec{p}_2}\right) f_2$$

Added a total derivative that integrates to zero.

$$\approx \int d^3p_2\, d^3q \left(\frac{\vec{p}_2 - \vec{p}_1}{m}\right) \cdot \frac{\partial}{\partial \vec{q}} f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}; t)$$

To perform this integral, choose coordinates w/ one axis along $\vec{p}_2 - \vec{p}_1$, with coordinate $a < 0$ before collision, $a > 0$ after collision.



Center-of-mass frame.

Impact vector $\vec{b}$, $\vec{b}=0$ for head-on collision
$(\vec{p}_1-\vec{p}_2 \parallel \vec{q}_1-\vec{q}_2)$

Integrate over q:

$$\left.\frac{df_1}{dt}\right|_{coll} = \int d^3p_2\, d^2b\, |\vec{v}_1-\vec{v}_2| \Big[f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, +; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \Big]$$

$|\vec{v}_1-\vec{v}_2| = \dfrac{|\vec{p}_1-\vec{p}_2|}{m}$ relative speed of the 2 particles

$(\vec{b}, -)$ before collision
$(\vec{b}, +)$ after collision.

Densities f_2 before and after collision are related by streaming

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

where $(\vec{p}_1{}', \vec{p}_2{}', \vec{b}) \longrightarrow (\vec{p}_1, \vec{p}_2, \vec{b})$ due to collision

Time-reversal symmetry: can determine $\vec{p}_1{}', \vec{p}_2{}'$ by integrating eqs. of motion backwards w/ initial momenta $-\vec{p}_1, -\vec{p}_2$.

$$\left.\frac{df_1}{dt}\right|_{coll} = \int d^3p_2\, d^2b\, |\vec{v}_2-\vec{v}_1| \Big[f_2(\vec{p}_1{}', \vec{q}_1, \vec{p}_2{}', \vec{b}; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \Big]$$

Elastic collisions: $|\vec{p}|$ preserved, $\vec{p}$ rotates to direction indicated by $(\theta,\phi) = \hat{\Omega}(\vec{b})$

$\vec{b} \to$ solid ∢ Ω $\Rightarrow$ Change variables from $\vec{b}$ to $\Omega(\vec{b})$

$$\left.\frac{df_1}{dt}\right|_{coll} = \int d^3p_2\, d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \Big[f_2(\vec{p}_1', \vec{q}_1, \vec{p}_2', \vec{b}, -; t) - f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) \Big]$$

Jacobian of transformation $\vec{b} \to \Omega(\vec{b})$

$\frac{d\sigma}{d\Omega}$ = differential cross section.
~ area presented to an incoming beam that scatters into solid ∢ Ω.

If we assume that before the collision the colliding particles are independent, then

$$f_2(\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{b}, -; t) = f_1(\vec{p}_1, \vec{q}_1, t)\, f_1(\vec{p}_2, \vec{q}_1, t)$$

– "Assumption of molecular Chaos" – Refers to past of collision.
= "Stosszahlansatz"

The equation for $\frac{\partial f_1}{\partial t}$ now becomes:

$$\boxed{\left[\frac{\partial}{\partial t} - \frac{\partial U}{\partial \vec{q}_1}\cdot\frac{\partial}{\partial \vec{p}_1} + \frac{\vec{p}_1}{m}\cdot\frac{\partial}{\partial \vec{q}_1}\right] f_1 = -\int d^3p_2\, d^2\Omega \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_1 - \vec{v}_2| \Big\{ f_1(\vec{p}_1, \vec{q}_1, t)\, f_1(\vec{p}_2, \vec{q}_1, t) - f_1(\vec{p}_1', \vec{q}_1, t)\, f_1(\vec{p}_2', \vec{q}_1, t) \Big\}}$$

– The Boltzmann Equation.

Interpretation of the Boltzmann Eq.

Streaming terms on left-hand side — motion of a single particle in the external potential U.

Collisions change the distribution of momenta of particles.

$(\vec{p}_1, \vec{p}_2) \to (\vec{p}_1', \vec{p}_2')$ Decreases density of particles w/ momentum $\vec{p}_1$.

But the inverse process does the reverse:

$\exists (\vec{p}_1', \vec{p}_2')$ s.t. $(\vec{p}_1', \vec{p}_2') \to (\vec{p}_1, \vec{p}_2)$

— Increases density of particles w/ momentum $\vec{p}_1$.

These processes correspond to the two terms on the right-hand side of the Boltzmann Equation.

Prob(collision) ~ (differential cross section) × (flux of incident particles) × (joint prob of 2 particles meeting)

$$\sim \left|\frac{d\sigma}{d\Omega}\right| |\vec{v}_2 - \vec{v}_1| \, f_1(\vec{p}_1) \, f_1(\vec{p}_2)$$

Note:

$\vec{p}_1'$ and $\vec{p}_2'$ depend on $V(\vec{q}_1 - \vec{q}_2)$.

Conservation of momentum $\vec{p}_1 + \vec{p}_2 = \vec{p}_1' + \vec{p}_2'$

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

unit vector in final direction of $\vec{p}_1' - \vec{p}_2'$