Kinetic Theory – Boltzmann Equation and H-Theorem

Goal: Statistical theory of many body system.

Example: Dilute, Monatomic Gas! – Simplest!

Approach:

- basic assumptions
- BBGKY hierarchy ⇒ Boltzmann Eqn.
- H-Theorem
- Applications

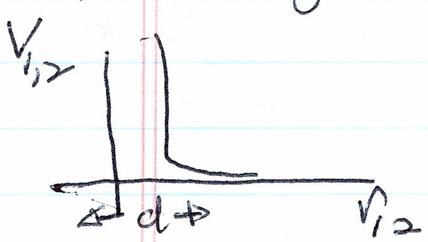
1.) Basics

Ideal, monatomic gas:

- molecules move freely
- interact only during brief encounter
- translational dof, only

Scales:

a) d → range of inter-molecular interaction



i.e. hard sphere, range d.

i.e. $\rightarrow d < \bar{r} \Rightarrow nd^3 \sim \frac{d^3}{\bar{r}^3} < 1$

diluteness

volume interaction << mean spacing volume.

$\rightarrow \ell_{mfp} \sim 1/n\sigma$

$\sim \bar{r}\,(\bar{r}/d)^2$

$\ell_{mfp} > \bar{r} > d \Rightarrow$ ideal gas, infrequent collisions.

$\rightarrow \ell_{mfp} < L \Rightarrow$ collisional system $\rightarrow$ many collisions in 1 macro-relaxation

$\Rightarrow$ approach is:
- Chapman-Enskog theory
- local transport
- hydro description.

if $L < \ell_{mfp} \Rightarrow$ collisionless system

transport non-local

kinetic / Vlasov description required

Describe dilute gas in:

→ phase space: dof's, translational only

i.e. $\underline{p}, \underline{x}$

→ phase space distribution:

$f(\Gamma)\, d\Gamma \Rightarrow$ # particles in $d\Gamma$ neighborhood of pt Γ in phase space.

$d\Gamma = d^3x\, d^3p$

→ neglect rotation, internal.

so point molecules → translation dof, only.

i.e.

$$\boxed{\begin{aligned} f &= f(\underline{x}, \underline{p}, t) \\ d\Gamma &= d^3x\, d^3p \end{aligned}}$$

Seek eqn. for $f(\underline{x}, \underline{p}, t)$

⇒ <u>Boltzmann equation</u>.

B.E. ⇒

- dynamical equation for phase space distribution – $f(\underline{x}, \underline{p}, t)$, not Liouvillean

- rests on two ideas

  → detailed balance (time reversibility of basic interaction)

  → molecular chaos

allow:
- H-Thm.
- moment / fluid eqns.
- transport eqns. and coeffs.

Two ideas:

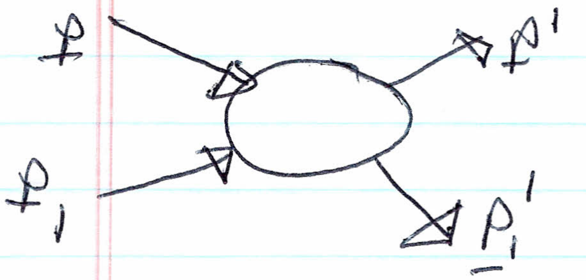
a.) Detailed Balance

Detailed Balance ⇒

in statistical equilibrium, # collisions
$\underline{p}, \underline{p}_1 \rightarrow \underline{p}', \underline{p}_1'$

$=$ # collisions $\underline{p}_1', \underline{p}' \rightarrow \underline{p}, \underline{p}_1$

i.e. $\quad w(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1') \equiv$ transition probability



then equality of # collisions:

$$w(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1')\, f_{1,2}(\underline{p}, \underline{p}_1)\, d^3\underline{p}_1\, d^3\underline{p}\, d^3\underline{p}_1'\, d^3\underline{p}'$$

$$= w(\underline{p}', \underline{p}_1'; \underline{p}, \underline{p}_1)\, f_{1,2}(\underline{p}', \underline{p}_1')\, d^3\underline{p}'\, d^3\underline{p}_1'\, d^3\underline{p}_1\, d^3\underline{p}$$

$f_{1,2}(\underline{p}, \underline{p}_1) \equiv$ two particle distribution
i.e. prob. particle (1) at $\underline{p}$,
particle (2) at $\underline{p}_1$

i.e.

particles at $\underline{p}$ which interact with others at $\underline{p}_1$ is:

$$f_{1,2}(\underline{p}, \underline{p}_1)\, d^3\underline{p}\, d^3\underline{p}_1 .$$

Now, in statistical equilibrium and, anticipating molecular chaos

$$f(\underline{p}, \underline{p}_1) = f(\underline{p})\, f(\underline{p}_1)$$

and $f = f_0$ (to be shown)

$$f(\underline{p}) = c \exp\left[- \frac{\epsilon + \underline{p} \cdot \overset{\text{macro-flow}}{\underline{V}}}{T} \right]$$

and

$$f(\underline{p})\, f(\underline{p}_1) \stackrel{?}{=} f(\underline{p}')\, f(\underline{p}_1')$$

$$\exp\left[- \frac{(\epsilon_1 + \epsilon)}{T} + \frac{(\underline{p}_1 + \underline{p}) \cdot \underline{V}}{T} \right] =$$

$$\exp\left[- \frac{(\epsilon' + \epsilon_1')}{T} + \frac{(\underline{p}_1' + \underline{p}') \cdot \underline{V}}{T} \right]$$

but energy/momentum conservation in collision $\Rightarrow$

$$\epsilon + \epsilon_1 = \epsilon' + \epsilon_1'$$

$$\underline{p} + \underline{p}_1 = \underline{p}' + \underline{p}_1'$$

so $\quad f(\mathbf{p}, \mathbf{p}_1) = f(\mathbf{p}', \mathbf{p}_1')$ in stat. eqlbrm.

as $\quad f_0(\mathbf{p})\, f_0(\mathbf{p}_1) = f_0(\mathbf{p}')\, f_0(\mathbf{p}_1')$ ✓

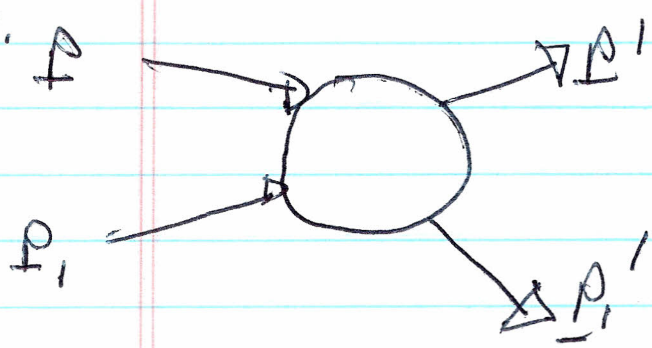
thus $\quad \# \; \mathbf{p}, \mathbf{p}_1 \rightarrow \mathbf{p}', \mathbf{p}_1'$

$\quad = \# \; \mathbf{p}', \mathbf{p}_1' \rightarrow \mathbf{p}, \mathbf{p}_1$

<u>if</u>

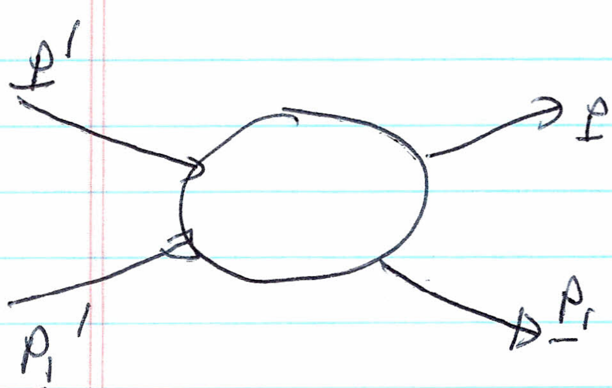
$$\boxed{W(\mathbf{p}, \mathbf{p}_1 ; \mathbf{p}', \mathbf{p}_1') = W(\mathbf{p}', \mathbf{p}_1' ; \mathbf{p}, \mathbf{p}_1)}$$

<u>i.e.</u>



probability

=



probability

$\Rightarrow$ detailed balance is a consequence of time-reversal invariance of basic interaction dynamics!

parity inv.

i.e.

$$\boxed{W(\underline{p}, \underline{p}_1 ; \underline{p}_1', \underline{p}') = W(\underline{p}', \underline{p}_1' ; \underline{p}, \underline{p}_1)}\ \overline{T}$$

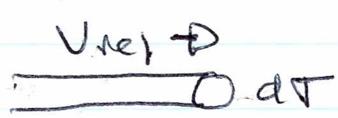
n.b.:

- σ, $\underline{p} \cdot \underline{v}$ invariant under T!
- requires no stereoisomerism.

  (i.e. gives a new substance upon parity inversion of molecular structure).
- can relate w to cross-section by:

$$d\sigma(v_{rel}) = w(\underline{p}, \underline{p}_1 ; \underline{p}', \underline{p}_1')\, d\underline{p}'\, d\underline{p}_1'$$

$\frac{d}{dt}$ (Volume Interaction) $\Leftrightarrow$ trans prob.



(b) Molecular Chaos – part of Sto

i.e $f(1,2) = f(1)\, f(2)$

valid if: ~ chaos

$\sim \tfrac{1}{2} m v_{th}^2 \gg \overline{V(1,2)}$

n.b: see discussion of Stosszahlansatz, next lecture.

i.e works for gas, not crystal.

(2.) How Construct B.E. ⇒ BBGKY Hierarchy.

– consider N particle Hamiltonian system, with $N \gg 1$.

then system completely described by:

$f(t, \underline{x}_1, \underline{p}_1, \underline{x}_2, \underline{p}_2, \ldots \underline{x}_N, \underline{p}_N) \rightarrow$ N particle distribution

This satisfies full Liouville Eqn, i.e.

$$\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \left\{ \frac{\partial}{\partial \underline{x}_i}\left(\dot{\underline{x}}_i f^N\right) + \frac{\partial}{\partial \underline{p}_i}\left(\dot{\underline{p}}_i f^N\right) \right\} = 0$$

and as $\underline{\nabla} \cdot \underline{V}_{1,N} = 0$

$$\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N}\left(\dot{\underline{x}}_i \cdot \frac{\partial}{\partial \underline{x}_i} f^N + \dot{\underline{p}}_i \cdot \frac{\partial f^N}{\partial \underline{p}_i} \right) = 0$$

from familiar Liouville Thm $\Rightarrow$ phase space flow of Hamiltonian system is incompressible.

Now, $f^N \rightarrow$ exact, but useless

seek: $f^{(1)}, f^{(2)} \rightarrow$ pdf for a particle
$\downarrow$
optimal

approach: integrate out additional particles

catch: basic interaction is 2 body!

i.e. $\quad \dot{\underline{x}}_i = \underline{v}_i$

$$\dot{\underline{p}}_i = -\partial \sum_{j<i} V_{ij} / \partial x_i$$

So

$$\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \underline{v}_i \cdot \frac{\partial f^N}{\partial \underline{x}_i} - \frac{\partial f^N}{\partial \underline{p}_i} \cdot \sum_{j<i} \frac{\partial V_{ij}}{\partial x_i} = 0.$$

Now:

$$f(t, \underline{x}_1, \underline{p}_1) = \int d\Gamma_2 \, d\Gamma_3 \ldots d\Gamma_N \, f^N$$

$\underline{x}$ and $\underline{p}$

$\rightarrow$ 1 particle distribution

$$f(t, \underline{x}_1, \underline{p}_1, \underline{x}_2, \underline{p}_2) = \int d\Gamma_3 \ldots d\Gamma_N \, f^N$$

$\rightarrow$ 2 particle distribution

So for $N = 1$

kills $N \neq$ by S.T.

$$\int d\Gamma_2 \, d\Gamma_3 \ldots d\Gamma_N \left(\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \frac{\partial}{\partial x_i} (\underline{v}_i f^N) + \sum_{i=1}^{N} \frac{\partial}{\partial p_i} \left(\left(\sum_{j<i} \frac{\partial V_{ij}}{\partial x_i} \right) f^N \right) \right) = 0$$

depends on particle 2.

$\Rightarrow$

$$\frac{\partial f^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{x}_1} f^{(1)} = \underbrace{(N-1)}_{\#\text{ binary pairs}} \int d\Gamma_2 \underbrace{\frac{\partial V_{1,2}}{\partial \underline{x}_1}}_{\text{2 part. dist}} \cdot \underbrace{\frac{\partial f^{(2)}}{\partial \underline{p}_1}}_{\text{2 part. int.}}$$

→ RHS accounts for (1) evolution via all possible binaries.

→ now have:

$$\frac{\partial}{\partial t} f^{(1)} = (\;)\, f^{(2)}$$

hierarchy problem → how truncate ?!

→ form eqn. for $f^{(2)}$
⇒ integrating out 3 on...

$$\frac{\partial}{\partial t} f^{(2)} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{x}_1} f^{(2)} + \underline{v}_2 \cdot \frac{\partial}{\partial \underline{x}_2} f^{(2)}$$

$$- \frac{\partial V_{1,2}}{\partial \underline{x}_1} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_1} - \frac{\partial V_{1,2}}{\partial \underline{x}_2} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_2}$$

$$= (N-2) \int d\Gamma_3 \left[\frac{\partial f^{(3)}}{\partial \underline{p}_1} \cdot \frac{\partial V_{1,3}}{\partial \underline{r}_1} + \frac{\partial f^{(3)}}{\partial \underline{p}_2} \cdot \frac{\partial V_{2,3}}{\partial \underline{r}_2} \right]$$

note:

→ $N-2$ from # re-labelings

$\sim N$, as $N \gg 1$.

→ hierarchy, $\frac{\partial f^{(2)}}{\partial t} \sim f^{(3)}$

Now, examine RHS of $f^{(2)}$ equation:

$$\text{RHS}' \sim N \int d\underline{p}_3 \int d\underline{x}_3 \; \frac{\partial f^{(3)}}{\partial \underline{p}} \cdot \frac{\partial V}{\partial \underline{r}}$$

$$\int d\underline{p}_3 \, f^{(3)} \sim \frac{f^{(2)}}{V}$$ → volume factor, $\int d^3x$ norm.

RHS $\sim N$ [redacted] $\int d^3x \; \frac{\partial V}{\partial r} \frac{\partial f^{(2)}}{V \partial p}$

↓

$$\sim N \; \frac{\partial V}{\partial r} \; \frac{d^3}{V} \; \frac{\partial f^{(2)}}{\partial p}.$$

$d \ll \bar{r}$

i.e. interaction only active in fraction d^3/V of total volume! → /mote V, f overlap.

Now,

$$\text{RHS} \sim \frac{\cancel{V}}{\bar{r}^3}\,\frac{\partial V}{\partial r}\,\frac{d^3}{\cancel{V}}\,\frac{\partial f^{(2)}}{\partial p}$$

$$\sim \frac{d^3}{\bar{r}^3}\,\frac{\partial V}{\partial r}\,\frac{\partial f^{(2)}}{\partial p}$$

$\therefore$

$$\text{RHS}/\text{LHS} \sim d^3/\bar{r}^3 \ll 1 .$$

so

$$\boxed{\frac{d}{dt} f^{(2)}(t, \Gamma_1, \Gamma_2) = 0 .}$$

- constitutes truncation of BBGKY hierarchy for dilute gas.
- key is $d^3 < \bar{r}^3$ ordering.

Now:

- $df^{(2)}/dt = 0$ is ~ mechanical (no thought, for dilute)
- if posit statistical independence of colliding

particles, a's' Molecular Chaos

i.e. $f(t,1,2) = f(t,1)\, f(t,2)$

then

- $f(t, \Gamma_1, \Gamma_2)\big|_{t_0} = f(t, \Gamma_1)\, f(t, \Gamma_2)$

serves as initial condition for
$\frac{d f^{(2)}}{dt} = 0.$

- ensures/consistent with "freely moving particles, interacting only within $d \ll \bar{r}$".

Then, for Boltzmann Eqn.:

- consider 1 particle distribution fctn.

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \frac{\partial f}{\partial \underline{x}} = N \int d\Gamma_2\, \frac{\partial V_{1,2}}{\partial \underline{r}_1} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_1}$$

$$= N \int d\Gamma_2\, \frac{\partial V_{1,2}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} \left[f(1,t)\, f(2,t) \right]$$

$\Rightarrow$

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f = C(f) \quad \to \text{B.E.}$$

collision operator.

$$C(f) = \int d\Gamma_2 \, \frac{\partial V_{1,2}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} \left[f(1,t) \, f(2,t) \right]$$

- have absorbed norm factor
- note $C(f)$ nonlinear $\to$ 2 body collision

Alternatively,

$$\frac{df}{dt} = C(f) \; ,$$

f const. along phase space trajectories, up to collisions.