Physics 210B Fall 2022

→ 'Nonequilibrium' Statistical Mechanics
- near equilibrium
- dynamic, fluctuating

I.) Kinetic Theory

Dynamics + Dilueteness → Boltzmann Eqn.
→ H Theorem → Fluid Equations + Transport

ii.) Dynamics + Dilueteness → BBGKY → Boltzmann
→ H Theorem

Goal:- statistical theory of many body system

- focus on **Dilute, Monatomic Gas**

↔ simplest possible system.

To do:

- what is a dilute gas?
- Liouville → Boltzmann via dilueness + BBGKY hierarchy

dilueness dimensionless # $= n d^3$ (d^3 → range of potential; n → density)

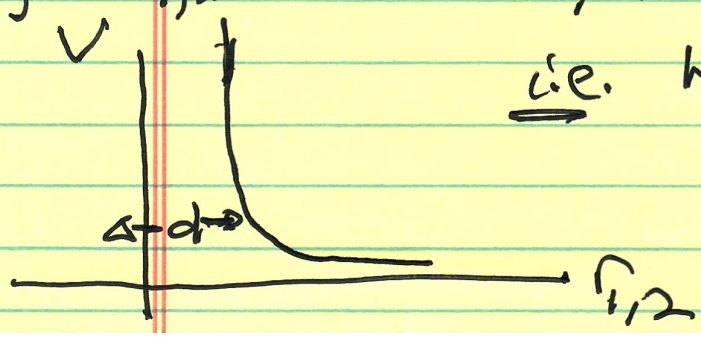
- H theorem
- Implications

→ What is a dilute gas?

Physical system ⇒ scales

i.) $V_{1,2}$ → 2 body potential $V(|r_1 - r_2|)$

i.e. hard spheres assumed.



Contrast Coulomb: $V = q_1 q_2 / r_{12}$

(cc) $n^{-1/3}$ = mean interparticle spacing

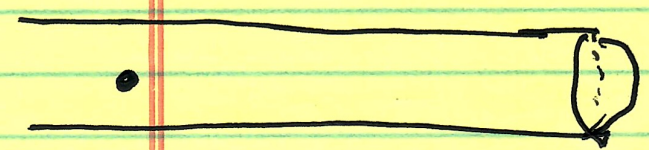
$n^{-1/3} = \bar{r}$

(ccc) ℓ_{mfp} → mean free path.

$\ell_{mfp} = 1/n\sigma$

↓ cross section for 2-particle collision

Where from?



interaction cylinder for scattering of particle with X-sect. σ. Cylinder has length L_{cyl}

$\leftarrow L_{cyl} \rightarrow$

$V_{int} \cong \sigma L_{cyl}$ → volume of interaction cylinder.

↓ volume

Now, let $\alpha \equiv$ # of collisions on cylinder of length L

$$\alpha = n \bar{V}_{int} = n\sigma L_{cyl}$$

so for $\alpha = 1$, $L_{cyl} = 1/n\sigma \equiv \ell_{mfp}$

$$\ell_{mfp} \cong \bar{r}^3/\sigma \cong \bar{r}(\bar{r}/d)^2$$

Alternatively, $\ell_{mfp} = v_{th}/\nu_{coll}$

(v.) $L \rightarrow$ system size / gradient scale

Usually: gradient scale for thermodynamic quantity

$1/L \sim \nabla T/T$ $\nabla n/n$ etc.

usually $L <$ box scale

'short' mean free path: $\ell_{mfp} < L$.

usual collisional regime

Short mean free path regime is described by local fluid equations.

$\ell_{mfp} > L$

↝ Long mean free path regime (kinetic equations)

↳ Vlasov Theory

$Kn = \ell_{mfp}/L$ — mostly here. $Kn < 1$

↓

Knudsen #

So

Classical dilute gas, collisional ordering:

$$d < \bar{r} < \ell_{mfp} < L$$

key ordering

Observe:

- $d \ll \bar{r}$

$\Rightarrow$ $\boxed{n d^3 \ll 1}$

- volume of interaction $\ll$ volume of mean spacing

- particles 'usually' free, non-interacting

$\boxed{n d^3 < 1 \text{ - diluteness}}$

n.b. $d \sim \bar{r}$ $\Rightarrow$ close packing, crystal

- $\ell_{mfp} > \bar{r} > d$

- $\ell_{mfp} > \bar{r} > d$

$\ell_{mfp} / \bar{r} \sim (\bar{r}/d)^2 \gg 1$.

Collisions rare, infrequent.
'Most' of time, (most) particles are free

Should contrast "liquid": $l_{msp} \sim \bar{r}$.

NB: Beware: liquid

Fluid equations – also QES

Related:

active or interacting volume fraction

$$- \quad KE / \langle V_{int} \rangle \sim KE / V_{int}\left(\frac{d^3}{\bar{r}^3}\right) \gg 1$$

– Contrast: crystal.

cc) From Liouville → Boltzmann

– phase space: dof's, translation only.

$$\left.\begin{matrix} p \\ \underline{L} \end{matrix}, \begin{matrix} \underline{V} \\ \underline{x} \end{matrix}\right\} \Gamma$$

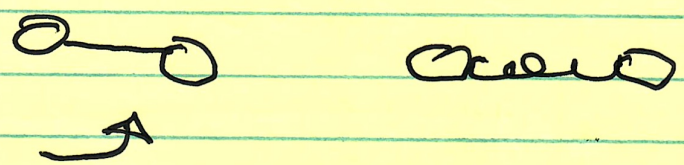
- phase space distribution:

$f(\Gamma)\,d\Gamma \Rightarrow$ # particles in $d\Gamma$ neighborhood of point $\underline{\Gamma}$ in phase space

$\underline{\Gamma} \in d\Gamma$

$d\Gamma = d^3\underline{x}\, d^3\underline{p}$

- neglect rotation, internal dofs



point molecules - translation d-o-f only

$F = f(\underline{x}, \underline{p}, t)$

$d\Gamma = d^3\underline{x}\, d^3\underline{p}$

Seek equation for $F(\underline{x}, \underline{p}, t)$

$\Rightarrow$ **Boltzmann Equation**

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f = C(f)$$

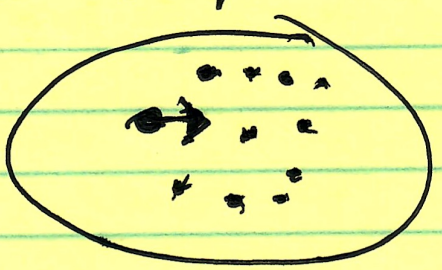
↓ collision operator

$$C(f) = N \int d\Gamma_2 \; \frac{\partial \underline{V}_{12}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}} \left[f(1;t)\, f(2;t) \right]$$

↑ quadratic, nonlinear

↓ test, field particles

- $C(f)$ describes evolution of $f(1;t)$ ↓ distribution of "test" particle interaction with ensemble of "field" particles.



Nonlinear → 'test', 'field' particles same.

why? - 2 body interaction

- BE is evolution equation for $f(\underline{x}, \underline{p}, t)$
  something useful
  ↕
- Fluid equations derived from moments of B.E.

N.B. Approximate form B.E.:

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f = -\nu (f - f_0)$$

Krook (crook) model → ν → relaxation rate

$-\nu_c$

$f_0 \sim f_{max}$.

→ <u>The Problem</u>

- only really know Liouville equation for N particle distribution

$N \sim N_A \sim 6.023 \times 10^{23}$ particles.

i.e. $f_N(\underline{x}_1, \underline{v}_1; \underline{x}_2, \underline{v}_2; \ldots \underline{x}_N, \underline{v}_N, t)$

$\Downarrow$

N particle distribution

$$\partial_t f_N + \sum_{i=1}^{N} \underline{v}_i \cdot \underline{\nabla}_i f_N + \sum_{i=1}^{N} \underline{\dot{p}}_i \cdot \frac{\partial f_N}{\partial \underline{p}_i} = C$$

not useful ....

How get $f_N \to f$

$\Rightarrow$ BBGKY Theory

i.e. exploit weak correlations and aspects of basic interactions to simplify!

Rests on 3 points/ideas:

1.) diluteness: $n d^3 \ll 1$ ✓

2.) molecular chaos (connection to chaos!?)

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

3.) Detailed Balance — Basic interaction is time reversible

Two new ideas:

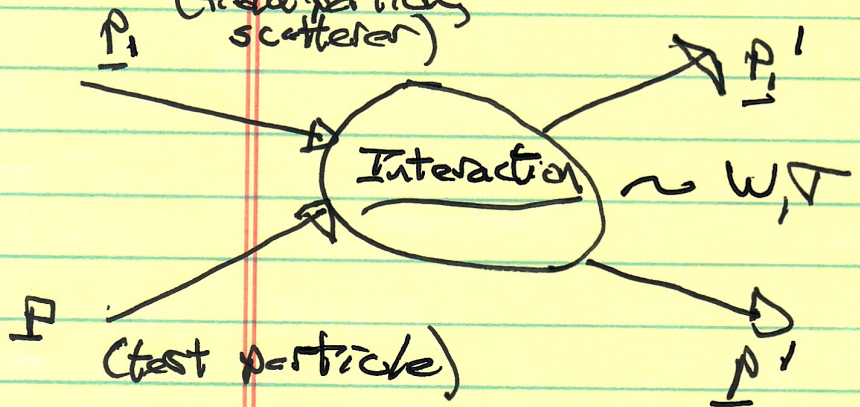
a.) Detailed Balance

In statistical equilibrium:

collisions $\underline{P}_1, \underline{P} \rightarrow \underline{P}_1', \underline{P}'$

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

i.e. interaction $\underline{P}_1, \underline{P} \rightarrow \underline{P}_1', \underline{P}'$



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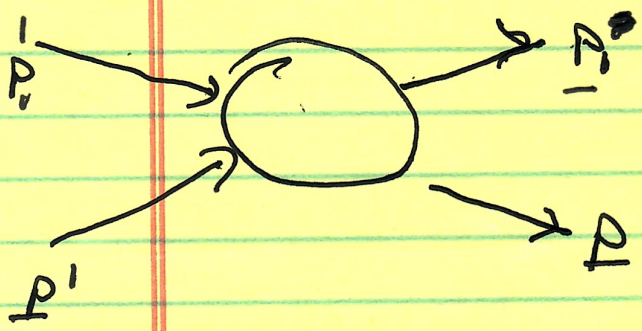
collisions $p_1', p_1' \to p_1, p_1$



i.e. # $\longrightarrow$ = # $\longleftarrow$

What does # collisions mean?

Quantitatively,

$W(p, p_1; p', p_1')$ = transition probability

Then D.B $\Rightarrow$

$W(p, p_1; p', p_1') f_{1,2}(p, p_1) d^3p\, d^3p_1\, d^3p'\, d^3p_1'$

$= W(p', p_1'; p, p_1) f(p', p_1')$ " " " "

$f_{1,2}(\underline{p}, \underline{p}_1)$ = 2 particle distribution
① at $\underline{p}$, ② at $\underline{p}_1$

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

$f_{1,2}(\underline{p}, \underline{p}_1)\, d^3p\, d^3p_1$

Aside:

→ Molecular chaos

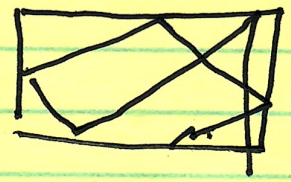
$f(1,2) = f(1) f(2)$

Valid if: ~ chaos
i.e. one $\lambda_L > 0$

easy if $N \gg 1$ ⇒ consider resonant denominators

~ dilute – no strong correlations
gas
not crystal
build-up $T \gg \langle U(1,2) \rangle$

Issue: How low can one go with N and still have molecular chaos?

see —  Zaslavsky — "billiards" problem

so, in statistical equilibrium:

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

$f = f_0 = f_{\text{Maxwellian}}$ (Maxwellian — will show — annihilates collision operator) ⇒ macro flow

$$f_0 = C \exp\left[- \frac{(\epsilon - \underline{p} \cdot \underline{V})}{T} \right]$$

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

Now, in equilibrium,

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

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

but energy, momentum conservation $\Rightarrow$

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

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

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

[redacted] on stat eqbm.

So

→ Back to Detailed Balance

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

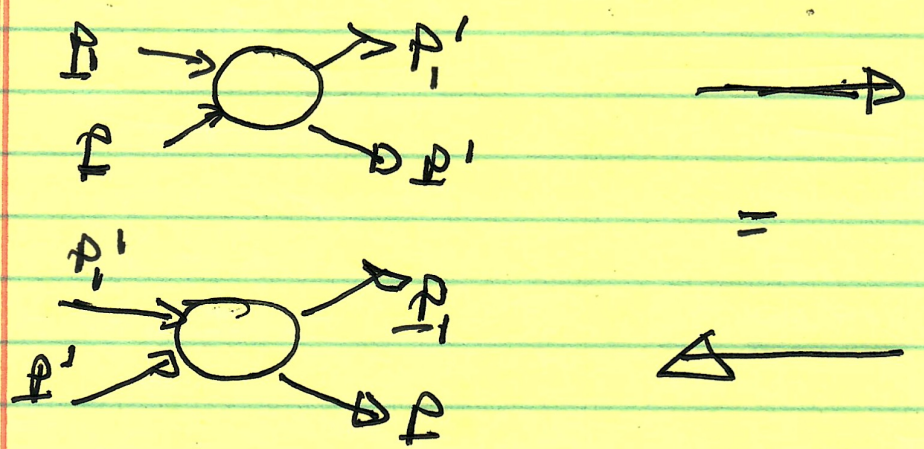
Then, # collisions $\underline{p},\underline{p}_1\to\underline{p}',\underline{p}_1'$

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

If:

$$W(\underline{P}, \underline{P}_1; \underline{P}', \underline{P}_1') = W(\underline{P}', \underline{P}_1'; \underline{P}, \underline{P}_1)$$

Trans Prob



∴ Detailed balance is a consequence of time-reversal invariance of basic interaction dynamics.

n.b.:

- ∈ $\underline{P} \cdot \underline{V}$ invariant under time reversal
- requires no stereoisomerism

(latter → new substance under parity inversion of molecular structure).

→ Can relate W to τ by

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

Where from?

$\frac{d}{dt}$ (Interaction Volume) = transition prob.