Physics 210B

→ Nonequilibrium Statistical Mechanics
   - near equilibrium
   - dynamic, fluctuating

II.) Kinetic Theory

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

(i) Dynamics + Diluteness → 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 $\rightarrow$ Boltzmann via diluteness + BBGKY hierarchy

\[ \text{diluteness} \quad = \quad n d \] Dimensionless $\# \quad = \quad \text{density} \]

- H theorem

- Implications

$\Rightarrow$ What is a dilute gas?

\[ \text{Physical system } \rightarrow \text{ scales} \]

\( \text{i.} \quad V_{1,2} \rightarrow 2 \text{ body potential} \cdot V(|x_1 - x_2|) \]

i.e. hard sphere ranged.
Contrast Coulomb: \( V = 2 \pi z^2 / \sqrt{z} \)

(iii) \( n^{-1/3} = \text{mean interparticle spacing} \)

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

(iv) \( l_{\text{mfp}} = \text{mean free path} \)

\( l_{\text{mfp}} = \frac{1}{n \sigma} \)

\( \sigma \) is the cross-section for 2-particle collision.

Where from?

\( V_{\text{int}} \approx \pi L_{\text{cyl}} \) → volume of interaction cylinder.

Interaction cylinder for scattering of particle with x-sect. \( \sigma \). Cylindrical has length \( L_{\text{cyl}} \).
Now let \( x \equiv \# \text{ of collisions in cylinder of length } L \)

\[ x = \pi V_{\text{int}} = \pi NTL_{\text{cyl}} \]

so for \( x = 1 \),

\[ L_{\text{cyl}} = \frac{1}{\pi NT} \equiv L_{\text{mp}} \]

\[ L_{\text{mp}} = \frac{r^3}{N} \equiv r (\frac{N}{Ad})^2 \]

Alternatively,

\[ L_{\text{mp}} = \frac{V_{\text{int}}}{V_{\text{coll}}} \]

\( \text{(iv)} \) \( L \rightarrow \text{system size/gradient scale} \)

Usually: gradient scale for thermodynamic quantity

\[ \frac{1}{L} \approx \frac{DT}{F} \frac{\text{m}}{\text{N}} \text{ etc.} \]

\( \frac{1}{L} \) usually \( \ll \) box scale

'Short' mean free path:

\[ L_{\text{mp}} < L \text{ usual collisional regime} \]
Short mean free path regime is described by local fluid equations.

\[ \frac{\lambda_{\text{ms}}} > L \]

\[ \rightarrow \text{Long mean free path regime (kinetic equations)} \]

\[ \rightarrow \text{LDA Vlasov Theory} \]

\[ \kappa = \frac{\lambda_{\text{ms}}}{L} \quad \text{mostly} \quad \kappa < 1 \]

\&

\[ \text{hundsen} \]

Classical dilute gas collisional ordering:

\[ a < \bar{\tau} < \lambda_{\text{ms}} < L \]  \text{key ordering}
Observe:

- $d < \bar{r}$

\[ nd^3 < 1 \]

- Volume of intersection << Volume of mean spacing
- Particles 'usually' free, non-interacting

\[ nd^3 < 1 - \text{diluteness} \]

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

- $\text{mean} > \bar{r} > d$

- $\text{mean} > \bar{r} > d$

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

Collisions more infrequent. (Most of time particles are free)
Should contrast "liquid": \( l \mapsto r \).

**NB:** Beware: liquid.

Fluid equations - also yes.

Related:

\[- \frac{\text{KE}}{\langle v_{\text{cut}} \rangle} \sim \frac{\text{KE}}{\text{Vent} \left( \frac{d^3}{v_N^2} \right)} \gg 1 \]

- contrast: crystal.

(\text{ii}) From Liouville \( \rightarrow \) Boltzmann

- phase space: dofs, translation only.

\[ p, x, \Gamma \]
- phase space distribution:

\[ f(\Gamma) d\Gamma \rightarrow \text{# particles in } d\Gamma \text{ neighborhood of} \]

point \( \Gamma \) on phase space

\[ d\Gamma = d^3x \cdot d^3p \]

- neglect rotation, internal degrees

\[ \rightarrow \]

point molecules: translation dof only

\[ F = f(x, p, t) \]

\[ d\Gamma = d^3x \cdot d^3p \]

Seek equation for \( F(x, p, t) \)

\[ \rightarrow \text{Boltzmann Equation} \]
\[ \frac{df}{dt} + \nabla \cdot df = C(f) \]

\[ C(f) = N \int d\mathbf{y}_2 \, \frac{d}{d\mathbf{y}_2} \cdot \mathbf{y}_2 \left[ f(\mathbf{y}_1, t) f(\mathbf{y}_2, t) \right] \]

\[ \text{collision operator} \]

\[ \text{quadratic, nonlinear} \]

\[ \text{test field particles} \]

\[-C(f) \text{ describes evolution of} \]

\[ f(\mathbf{y}, t) \text{ interaction with ensemble of "field" particles} \]

\[ \text{distribution of} \]

\[ \text{"test" particle} \]

\[ \text{Nonlinear} \rightarrow \text{"test", field} \]

\[ \text{particles same} \]

\[ \text{why?} - 2 \text{body interaction} \]
- BE is evolution equation for $f(x, p, t)$
  something useful

- Fluid equations derived from moments of BE.

N.B. Approximate form B.E.:

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

Knudsen (crook) model $\Rightarrow$ $\nabla \cdot f = -V_0$

$F_0 \sim \text{max}$

⇒ The Problem

- only really know Liouville equation
  for $N$ particle distribution

$N \sim N_a \sim 6.023 \times 10^{23}$ particles.
i.e. \( F_N(x_1, x_2, v_1, v_2; ... - x_0, v_0, t) \)

\[ \sum_{i=1}^{N} \frac{\partial}{\partial x_i} \int d^3x_i F_N + \sum_{i=1}^{N} \frac{1}{2} \frac{\partial^2}{\partial x_i \partial x_j} \int d^3x_i F_N = 0 \]

not useful ... 

How get \( F_N \to f \)

\[ \Delta \text{BGK theory} \]

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

Rests on 3 points/ideas:

1) diluteness: \( \Lambda d^3 \ll 1 \) \( \checkmark \)

2) molecular chaos

\[ \delta \Rightarrow F(1, 2) \to F(1) F(2) \]

(connection to chaos!? )
3.) Detailed Balance — Basic interaction is time reversible

Two new ideas:

a.) Detailed Balance

In statistical equilibrium:

\# collisions \( A, P \rightarrow P', P' \)

\[ = \# \text{ collisions } \quad \text{(field-particle scatterer)} \]

\text{interaction} \quad \text{(test particle)}

\[ = W \]
\# collisions \( \bar{p}, p' \rightarrow p, p' \)

\[ \begin{array}{c}
\bar{p} \\
p' \\
\rightarrow \\
p \\
p' \\
\end{array} \]

I.e.

\[ \# \rightarrow \]

\[ \# < \]

What does \# collisions mean?

Quantitatively,

\[ WC \bar{p}, p; j, k; \bar{p}', p' \rightarrow \text{transition probability} \]

Then \( D, B \neq \)

\[ WC \bar{p}, p; j, k; \bar{p}', p' \rightarrow \frac{F_{j2}(p, \bar{p})}{d^3 p' \cdot d^3 p} \cdot d^3 \bar{p} \cdot d^3 p' \]

\[ = WC \bar{p}, p; j, k; \bar{p}', p' \rightarrow F (p, \bar{p}) \]
\[ \mathcal{F}_{1/2}(p_1, p_1) = 2 \text{ particle distribution} \]

\[ \text{1) at } p_1, \text{ 2) at } p_1 \]

\[ \frac{1}{2} \]

# particles at \( p \) which interact with others at \( p_1 \) is:

\[ \mathcal{F}_{1/2}(p, p_1) d^3p \quad d^3p_1 \]

Aside:

→ Molecular chaos

\[ \mathcal{F}(1, 2) = \mathcal{F}(1) \mathcal{F}(2) \]

Valid if:

- chaos
d.e. one \( \lambda \) > 0

Easy if \( N \gg 1 \) → consider resonant denominators

gas ~ dilute ~ no strong correlations

not crystal build up \( T \rightarrow \langle U(4, 2) \rangle \)
Issue: How low can one go with $N$ and still have molecular chaos?

See: Zaslavsky - billiards problem.

So, on statistical equilibrium:

\[ f(p, p_i) = f(p_i) f(p) \]

\[ f = f_0 = f^{\text{Maxwellian}} \]

(Maxwellian - well known - annihilates collision operator)

\[ f_0 = c \exp \left[ - \frac{(E - p \cdot V)}{T} \right] \]

\[ f(p) f(p_i) \xrightarrow{\text{mech flow}} f(p') f(p_i') \]

Now, on equilibrium.
\[ \exp \left[ - \frac{(E + E_i)}{T} + \frac{(p + p_i) \cdot V}{T} \right] \]

\[ = \exp \left[ - \frac{(E' + E_i')}{T} + \frac{(p' + p_i') \cdot V}{T} \right] \]

but energy, momentum conservation ≠

\[ E + E_i = E_i' + E' \] energy

\[ p + p_i = p_i' + p' \] momentum

\[ f(\mathbf{p}, \mathbf{p}_i) = f(\mathbf{p}', \mathbf{p}_i') = \text{constant} \]

\[ \text{on } \sigma \text{-state eqn.} \]

\[ \rightarrow \text{Back to Detailed Balance} \]

As \[ f(\mathbf{p}, \mathbf{p}_i) = f(\mathbf{p}', \mathbf{p}_i') \]

Then, \# collisions \( p, p_i \rightarrow p', p_i' \)

\[ = \# \text{ collisions } p', p_i' \rightarrow p, p_i' \]
\[ W(\mathbf{P}, \mathbf{A}, \mathbf{A}^\prime) = W(\mathbf{P}^\prime, \mathbf{P}^\prime, \mathbf{P}, \mathbf{P}) \]

The diagram shows a transition from \( \mathbf{P} \) to \( \mathbf{P}^\prime \), which leads to detailed balance as a consequence of time-reversal invariance of basic interaction dynamics.

\[ \because \text{Detailed balance is a consequence of time-reversal invariance of basic interaction dynamics.} \]

\( \because \text{Note the}\)

- \( \varepsilon_j \mathbf{P} \cdot \mathbf{V} \) (invariant under time reversal)

- Requires no stereoisomerism

(All that - new substance under parity inversion of molecular structure.)
Can relate $w$ to $T$ by

$$w(f, f', j, f', f') \, dp' \, dp' = \nu_{ro} \, dt$$

Where From?

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

\[ \nu_{ro} \int \, dt \]