Physics 210B

Non-equilibrium Statistical Mechanics

Notes 1: Boltzmann, Fluids and Transport

Section 1: BBGKY \rightarrow\text{ Boltzmann and} \quad \nabla^4 \text{ Theorem}

Kinetic Theory

Goal: Statistical theory of many body system.

(Laboratory Animal) \rightarrow \text{ Dilute Monatomic Gas}

To do:

- Basic ideas
  - Assumptions
  - Liouville \rightarrow Boltzmann via BBGKY
  - H-Theorem
  - Implications
i.) Basics

Ideal monatomic gas:

Scenes:

ii.) $d \rightarrow$ range of inter-molecular interaction

\[ \frac{1}{r} \]

$\frac{1}{N}$ e. hard sphere, range $d$.

\[ \frac{1}{N} \]

N.B. Contrast Coulomb!

iii.) $n \rightarrow$ mean inter-particle spacing

\[ n^{-1} = \frac{1}{n} \]

iv.) $\text{mean} \rightarrow$ mean free path

\[ \text{mean} = \frac{1}{N} \frac{1}{r} \text{cross section for 2 particle collision} \]
Where from?

\[ \int_{x}^{L} \]

\[ V_{int} = \frac{\sqrt{L}}{2} \]

if \( x = \# \text{ collisions in cylinder of length } L \)

\[ x = \pi \Rightarrow L = \ell_{\text{max}} = \frac{\sqrt{\pi}}{\sqrt{\pi}} \]

Alternatively,

\[ \ell_{\text{max}} = \frac{V_{th}}{V_{\text{coll}}} \]

(iii) \( L \rightarrow \text{system size} / \text{radial scale} \)

short mean free path: \( \ell_{\text{max}} < L \)

no "usual" collisions again (local fluid eqs.)

\[ \ell_{\text{max}} > L \]

-> long mean free path (kinetic equations)
\[ N = \frac{\text{m}_\text{rep}}{L} \]

\( \text{Knudsen \#} \)

Collisional

Classical dilute gas ordering:

\[ d < \bar{r} < \frac{\text{m}_\text{rep}}{L} \]

Observe:

\[ d < \bar{r} \]

\[ nd^3 < 1 \]

\~ Volume of interaction \ll \text{mean spacing volume} \]

\~ Particles usually "free", non-interacting

\[ \Rightarrow \text{diluteness} \]

\[ d < \bar{r} \rightarrow \text{close packing} \]

\[ \Rightarrow \text{crystal} \]
\[ \text{Related: } \frac{T}{V_{\text{int}}(d^3)/\bar{r}^3} \gg 1 \]

\[ \Rightarrow \frac{T}{V_{\text{int}}(d^3)/\bar{r}^3} \gg 1 \]

\[ \Rightarrow \text{Contrast: crystal} \quad \text{U.B. Plasma?} \]

\[ \Rightarrow \text{How Explicit Basic Assumptions?} \]

- Phase space: do F's, only translations, \( \{ x, x' \} \)

- Phase space distribution:

\[ F(r) \text{ or } \Gamma \Rightarrow \text{# particle in a } n \text{ neighborhood of point } \Gamma \text{ in phase space} \]
\[ d\Gamma = d^3xD^3P \]

-neglect rotation, axial term \( d\Gamma \)

- point molecules \( \leftrightarrow \) translation \( d\Gamma \rightarrow \Gamma \) only.

\[
\Gamma = \Gamma(x, y, t)
\]

\[ d\Gamma = d^3xD^3P \]

Seek equation for \( \Gamma(x, y, t) \)

\[ \Rightarrow \text{Boltzmann Equation} \]

\[ \frac{\partial \Gamma}{\partial t} + v \cdot \nabla \Gamma = \mathcal{L} \]

\[ \mathcal{L} \text{ collision operator} \]

\[ \mathcal{L} \Gamma = N \int dV_{i} \frac{d^3P_{i}}{d^3V_{i}} \left[ \gamma \Gamma(x, y, t) \right] \]

\[ \text{BE is} \]

- nonlinear

\[ \rightarrow \text{test field particles} \]
why? 2-body interaction (collisions).

- B.E. is evolution equation for $f(x,v,t)$.
- Fluid equations derived from moments of B.E.

The problem:
- only really know Liouville Eqn. for $N$ ($N \approx 6.023 \times 10^{23}$) particles.

i.e.

\[ F(x_1, v_1, x_2, v_2, \ldots, x_N, v_N, t) \]

\[ \frac{d}{dt} F_N + \sum_{i=1}^{N} v_i \cdot \frac{\partial}{\partial x_i} F_N + \sum_{i=1}^{N} p_i \cdot \frac{\partial}{\partial v_i} F_N = 0 \]

How get:

$F_N \rightarrow F$ ?
- **answer:** BBGKY Hierarchy
  
  - i.e. exploit weak correlations and aspects of basic interactions to simplify description

- Rests on 3 points/ideas=

  1) diluteness: \( nD^3 \ll 1 \)  

  2) molecular chaos
     
     i.e. \( P_{ij2} \rightarrow P_{i1}P_{j2} \)

  3) detailed balance
     
     (basic interaction is time reversible)

Two new ideas:

a) Detailed Balance
D.B. $\Rightarrow$ In statistical equilibrium,

<table>
<thead>
<tr>
<th># collisions $p', p' \rightarrow p, p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Field particle - scatterer ensemble</td>
</tr>
</tbody>
</table>

Interaction $\sim w, v$ etc.

| Test particle $\Rightarrow$ B.E. usually for T.P. |
| Dist |

$= \# \text{collisions} p', p' \rightarrow p, p$

Quantitatively

$w(p, p', p', p') = \text{transition probability}$
Then D.B.:

\[
\int W(p, p', E, E') \, \mathcal{F}_{i,j}(p, p') \, \frac{d^3p}{d^3p'} \, \frac{d^3p}{d^3p'} \, \frac{d^3p}{d^3p'} \, \frac{d^3p}{d^3p'}
\]

\[
= W(p, p', E, E') \, \mathcal{F}_{i,j}(p, p') \, \frac{d^3p}{d^3p'} \, \frac{d^3p}{d^3p'} + \frac{d^3p}{d^3p'}
\]

\[
\mathcal{F}_{i,j}(p, p') = \text{two particle distribution at } P_j \text{ and } P_i
\]

\[
\Rightarrow \quad \text{number of particles at } P \text{ which interact with others at } P_i \text{ is:}
\]

\[
\mathcal{F}_{i,j}(p, p') \, d^3p \, d^3p'
\]

→ Molecular Chaos

In statistical equilibrium:

\[
P(p, p') = f(p) \, f(p')
\]
\[ F = F_0 \quad \text{(Maxwellian, to be shown)} \]

\[ F_0(p) = c \exp \left[ -\frac{(e - p \cdot V)}{T} \right] \]

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

\[ F(p) F(p') = \frac{T}{\hbar^2} F(p') F(p') \]

can equate:

\[ \exp \left[ -\frac{(e + e_1) + (e + p_1 \cdot V)}{T} \right] = \exp \left[ -\frac{(e' + e_1') + (p' + p_1 \cdot V)}{T} \right] \]

Energy/momentum conservation in collision ⇒

\[ e + e_1 = e_1' + e_1' \quad \text{→ energy conservation} \]

\[ p + p_1 = p_1' + p_1' \quad \text{→ momentum conservation} \]
So since:

\[ F_0 (x) F_0 (y) = F_0 (x') F_0 (y') \]

\[ F(x, y) = F(x', y') \] in stat equilibrium.

Thus:

\[ \text{# cols} x, y \rightarrow x', y' \]

\[ = \text{# cols} x', y' \rightarrow x, y \]

\[ \left[ \text{wcf}_x(x', y', x, y) = \text{wcf}_x(x, y', x', y) \right] \]

\[ \begin{array}{c}
\text{let} \\
\text{prob} \\
\text{prob}
\end{array} \]
Detailed Balance is a consequence of time-reversal invariance of basic interaction dynamics.

\[ W(\mathbf{p}, \mathbf{p}', \mathbf{j}, \mathbf{j}') = W(\mathbf{p}', \mathbf{p}, \mathbf{j}', \mathbf{j}) \]

\[ \text{ parity inversion } \]

\text{Note:}

- $\mathbf{p} \cdot \mathbf{V}$ is invariant under $T$.

- requires no stereochemistry,

  (i.e. letter gives a new substance upon parity inversion of molecular structure)

- can relate $W$ to $\nabla$ by:

\[ W(\mathbf{p}, \mathbf{p}', \mathbf{j}, \mathbf{j}') \, dp' \, dp' = \nu_{\mathbf{p}} \, d\nabla \]
Where from?

\[ \frac{d}{dt} (\text{Interaction Volume}) = \text{transient probability} \]
\[ \frac{\text{Var}}{\text{dt}} \]

b.) Molecular Chaos

\[ f(1, 2) = f(1) f(2) \quad \text{(general)} \]

Valid if: ~ chaos (one \( A > 0 \))

~ dilute (no strong correlations build up)

\[ T \gg \langle V_{A, 2} \rangle \]

gas, not crystal.

Issue: How can one go with \( N \) and still have molecular chaos?

see Zastrowsky \( \rightarrow \) "billiards" problem

etc.
- BBGKY to Boltzmann.

- $N$ particle Hamiltonian, $N \gg 1$

  system described by:

  $F(t, x_i, p_i; x_j, p_j \ldots x_k, p_k)$

  $\rightarrow N$ particle distribution

This satisfies Full Liouville Equation
\[
\frac{df^N}{dt} + \sum_{i=1}^{N} \left( \mathbf{x}_i \cdot \frac{dP_i^N}{dt} \right) + \sum_{i=1}^{N} \left( \mathbf{x}_i \cdot \frac{d}{dt} \mathbf{v}_i \right) = 0
\]

\[
\mathbf{v} \cdot \mathbf{v} = \mathbf{a}
\]

\[
\frac{d}{dt} \sum_{i=1}^{N} \left( \mathbf{x}_i \cdot \frac{dP_i^N}{dt} + \mathbf{a}_i \cdot \frac{d\mathbf{x}_i}{dt} \right) = 0
\]

**Lovelock Thm:** \( F^N \) conserved along \( N \) particle orbits

\( F^N \rightarrow \) exact, useless \( \rightarrow N \rightarrow \frac{d}{dt} \)

**Seek:** \( F^G \), \( F^A \rightarrow \) self for a particle

\( F(\mathbf{x}, \mathbf{v}, t) \rightarrow \) phase space density

approach: integrate out additional particles \( \rightarrow \) reduce description

**Catch:** basic interaction is 2-body\! 

\[
\dot{x}_i = v_i
\]

\[
\dot{v}_i = -a \sum_{j \neq i} V_{ij} v_j / \mathbf{v}_j \cdot \mathbf{x}_j
\]
\[ \frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \left( v_i \cdot \frac{\partial f^N}{\partial x_i} - \frac{\partial f^N}{\partial x_i} \cdot \sum_{j \neq i} \frac{\partial V_{ij}}{\partial x_j} \right) = 0 \]

Define: **1-particle distribution**

\[ F(t, x_1, A) = \int_{A_1} dA_1 \ldots dA_N f^N \]

Integrate out other dependencies

\[ F(t, x_1, x_2, x_3, x_4) = \int dA_5 \ldots dA_{10} f^N \]

\[ \Rightarrow 2 \text{ particle distribution} \]

So for \( N = 1 \)

\[ \int dA_2 dA_3 \ldots dA_{10} \left( \frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \frac{\partial}{\partial x_i} \left( v_i f^N \right) \right) \]

\[ + \sum_{i=1}^{N} a_i \left( \sum_{j \neq i} \frac{\partial V_{ij}}{\partial x_j} \right) f^N \right) = 0 \]

\( \Rightarrow 2 \text{ particle interaction} \)
$V_{ij}$ is 2-particle interaction → necessarily enters with $f_i$.

Need treat all possible pairs $\Rightarrow$

$$\frac{\partial f_i}{\partial x} + \nu_i \cdot \frac{\partial f_i}{\partial \epsilon_i}$$

$$= (N-1) \int \frac{d^3p_2}{(2\pi)^3} \frac{\partial U_{ij}}{\partial x_i} \cdot \frac{\partial f_j}{\partial \epsilon_j}$$

$N$ being binary pairs

$N$ particles → 2-particle interaction

2-body distribution

M.B.: $f_i f_j = \langle \cdot \rangle f_i$ (1) $f_j$

→ hierarchy problem
- how to couple? ?

Need FAQ eqn. ?

→ how? - integrate out from 3, on.
\[ \begin{align*}
\frac{df_1}{dt} + \mathbf{U}_1 \cdot \frac{df_1}{d\mathbf{x}_1} + \mathbf{U}_2 \cdot \frac{df_2}{d\mathbf{x}_2} \\
- \frac{dV_{l_2}}{dx_1} \cdot \frac{df_2}{dA} - \frac{dV_{l_2}}{dx_2} \cdot \frac{df_2}{dA} \\
= (N-2) \sqrt{4 \pi^3} \left[ \frac{df_{\mathcal{G}}}{d\mathbf{r}_{\mathcal{G}}} \cdot \frac{dV_{l_3}}{d\eta_1} + \frac{df_{\mathcal{G}}}{d\mathbf{r}_{\mathcal{G}}} \cdot \frac{dV_{l_3}}{d\eta_2} \right]
\end{align*} \]

Can we simplify this?

1. \[ \frac{df_1}{dt} + \mathbf{U}_2 \cdot \frac{df_2}{d\mathbf{x}_2} \]

2. \[ \frac{df_2}{dt} + \mathbf{U}_1 \cdot \frac{df_2}{d\mathbf{x}_1} \]

\[ (N-2) \sqrt{4 \pi^3} \left[ \frac{df_{\mathcal{G}}}{d\mathbf{r}_{\mathcal{G}}} \cdot \frac{dV_{l_3}}{d\eta_1} + \frac{df_{\mathcal{G}}}{d\mathbf{r}_{\mathcal{G}}} \cdot \frac{dV_{l_3}}{d\eta_2} \right] \]

Look at \( 2/1 \)

\( \rightarrow \) exploit low volume filling of interaction - \( N d^3 \ll 1 \).
\( N \int dx_3 \int dA \quad \frac{A_p}{\sqrt{\text{Vol.}}} \cdot \frac{dV}{\partial x_3} \)

\( \frac{1}{(AP)^3 \cdot \text{Vol.}} \)

Normalization

\( \int dp_0 \) cancels \( \sqrt{AP^3} \) normalization

\( N \int dx_3 \frac{d f}{\partial A^2} \frac{dV}{\partial x_3} \quad \frac{N}{\text{Vol.}} \)

\( V \) fills \( d^3 \) volume

\( \frac{d^3 N}{\text{Vol.}} \left( \frac{A_{p1}}{\sqrt{\text{Vol.}}} \right) \left( \frac{d f}{d p_2} \right) \)

\( \sim \quad n d^3 \left( \frac{A_{p1}}{\sqrt{\text{Vol.}}} \right) \left( \frac{d f}{d p_2} \right) \)
\[ \frac{d}{dt} \sum_{i=1}^{\infty} \frac{1}{r_i^3} \ll 1 \]

\[ \frac{\text{RHS}}{\text{LHS}} \sim \frac{d^3}{r^3} \ll 1. \]

\[ \frac{d}{dt} \left( \sum_{i=1}^{\infty} \frac{e_i}{r_i^3} \right) = 0 \]

- constitutes truncation of Buckingham hierarchy, for dilute gas
- key is \( d^3 / r^3 \ll 1 \)
- same scale ordering.

\[ \Rightarrow \frac{df}{dt} = 0 \text{ is straightforward for dilute.} \]

\[ \Rightarrow \text{if point statistical independence of colliding particles, aka, molecular chaos.} \]
\[ f(t, 1; 2) = f(t, 1) f(t, 2) \]

then,

\[ F(t, r_1, r_2) = f(t, r_1) f(t, r_2) \]

serves as c. c. for \( \frac{df}{dt} = 0 \)

so \( \frac{df}{dt} = 0 \), so \( f(t) \) always factorizes

- consistent with "freely moving particles, interacting only within \( \mathcal{E} \),"

- so \( f(t) = f(t, r_1) f(t, r_2) \) and

\[
\mathcal{H} + \mathbf{v} \cdot \mathbf{F} = N \int dr_3 \frac{\partial}{\partial r_3} \left[ V_2 \cdot \mathbf{F} \right] \left( \frac{f(t^3) f(t, r_3)}{\sqrt{2 \pi \sigma}} \right)
\]

\[ \sim \text{ Boltzmann Equation} \]
Boltzmann Eqn.

\[ \frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f = c\mathcal{C}(\mathcal{F}) \]

\[ c\mathcal{C}(\mathcal{F}) = \int d\mathbf{v}_2 \frac{\partial f(\mathbf{v}_1, \mathbf{v}_2, t)}{\partial \mathbf{v}_1} \left[ f(\mathbf{v}_1^+, t) - f(\mathbf{v}_1^-, t) \right] \]

- Absorbed normalization
- \( c\mathcal{C}(\mathcal{F}) \equiv \text{collision operator (integral)} \)
- \( c\mathcal{C}(\mathcal{F}) \text{ nonlinear} \Rightarrow 2 \text{ body collision} \)

- Have "test particle" (\( f(\mathcal{F}) \)) scattered by other "field particles" but "test" "field" the same.

\( \Rightarrow \text{nonlinearity} \)

- \( c\mathcal{C}(\mathcal{F}) \sim \mathcal{V}_{\text{coll}} \)

\[ c(\mathcal{F}) \equiv -\mathcal{V} \left[ f - f_{\text{eq}} \right] \] (Grad)
- \frac{df}{dt} = c(R)

Phase space density conserved along particle orbits, up to collisions.

- what if \( c(R) \to 0 \)

have:

\[
\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla f + \frac{F}{m} \cdot \nabla f = 0
\]

\[
F = 2E
\]

\[
2\pi E = \int p d\mathbf{v}
\]

\[
\frac{\nu \pi}{\text{Jeans}} \rightarrow \text{Eqn.}
\]

Continuity eqn. for incompressible flow of phase space fluid.

- Plasma:

\[
\frac{\text{Far}}{\text{low}} < \lambda_0 < \text{Lmp} < \frac{\text{L}}{\text{Far}}
\]

has source/generation \( \equiv \text{Fokker-Planck} \).