Physics 210B 12a

→ Nonequilibrium Statistical Mechanics

→ Notes 1: Boltzmannia, Fluids and Transport

Section 1: BBGKY → Boltzmann and H Theorem

Kinetic Theory

Goal: statistical theory of many body system.

"Laboratory Animal" – Dilute Monatomic Gas, simplest possible....

To do:

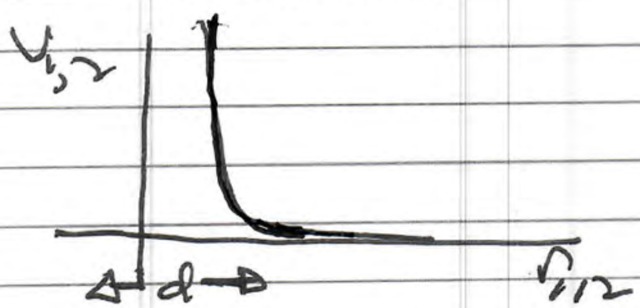
- basic ideas, assumptions
- Liouville → Boltzmann via BBGKY hierarchy
- H- Theorem
- Implications

i.) Basics

Ideal monatomic gas:

$\boxed{\text{Scales}}$:

i) $\underline{d}$ → range of inter-molecular interaction



i.e. hard sphere, range d.

N.B. Contrast Coulomb!

ii.) $n^{-1/3}$ → mean interparticle spacing:

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

iii.) l_{mfp} → mean free path

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

σ ↓ cross section for 2 particle collision.

Where from?

$\leftarrow L \rightarrow$

interaction cylinder for particle with σ, length L

$V_{int} = \sigma L$

if α = # collisions in cylinder of length L

$\alpha = n V_{int} = n \sigma L$

$\alpha = 1 \Rightarrow L \equiv l_{mfp} = 1/n\sigma$
$= \bar{r}(\bar{r}/d)^2$

Alternatively,

$l_{mfp} = V_{th} / \nu_{coll}.$ $\qquad 1/L \sim \frac{\nabla T}{T}$

(iv.) $\underline{L}$ → system size / gradient scale

short mean free path: $l_{mfp} < L$
→ 'usual' collisional regime
(local fluid eqns.)

$l_{mfp} > L$
→ Long mean free path
(kinetic equations)

$$\boxed{K = l_{mfp}/L}$$

Knudsen #.

— will re-visit

mostly $K \ll 1$ here.

Classical dilute gas collisional ordering:

$$\boxed{d < \bar{r} < l_{mfp} < L}$$

→ key

Observe:

— $d < \bar{r}$

⇒ $nd^3 < 1$

~ Volume of interaction << mean spacing volume

~ particles usually "free", non-interacting.

⇒ diluteness *

· $d \sim \bar{r}$ → close packing, crystal.

opposite limit

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

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

→ collisions rare, interaction infrequent

→ contrast liquid : $l_{mfp} \sim \bar{r}$

Related : → $T / \langle V_{int} \rangle \gg 1$

→ diluteness !

[active/interacting volume fraction]

⇔ $T / V_{int}(d^3/\bar{r}^3) \gg 1$

contrast : crystal N.B. Plasma ?

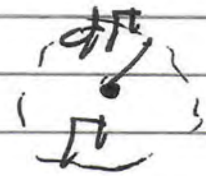
→ How Exploit Basic Assumptions ?

- phase space: dof's, translational only. $\left\{ \begin{matrix} \underline{p}, & \underline{v} \\ \underline{x}, & \underline{x} \end{matrix} \right.$ Γ

- Phase space distribution :

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

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



— neglect rotation, internal d.o.f.'s

⇒ point molecules → translation d-o-f, only.

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

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

⇒ Boltzmann Equation

i.e. $$\frac{\partial f}{\partial t} + \underline{v}\cdot\nabla f = \underbrace{C(f)}_{\text{collision operator}}$$

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

quadratic, NL.

BE is nonlinear
→ test, field particles

$\boxed{\text{Why? — 2-body interaction (collisions).}}$

- B.E. is evolution equation for $f(x, p, t)$ *

- Fluid equations derived from moments of B.E.] ~~useful~~ useful

The problem:

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

i.e.

$$f(x_1, v_1; x_2, v_2; \text{---} \; x_N, v_N, t)$$

$$\partial_t f_N + \sum_{i=1}^{N} \underline{v}_i \cdot \underline{\nabla}_i f_N + \sum_{i=1}^{N} \dot{p}_i \cdot \frac{\partial f_N}{\partial p_i} = 0$$

not useful.

How get:

$$f_N \rightarrow f \; ?$$

Bogoliubov, Born, Green, Kirkwood, Yvon

— 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. $f(1,2) \to f(1)\,f(2)$

'hidden' correction to chaos. why?

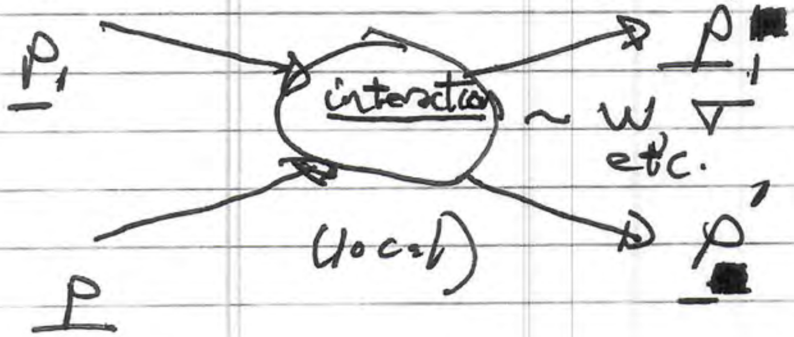
3.) detailed balance

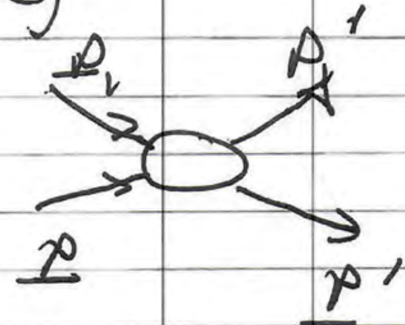
(basic interaction is time reversible)

Two new ideas:

a.) Detailed Balance

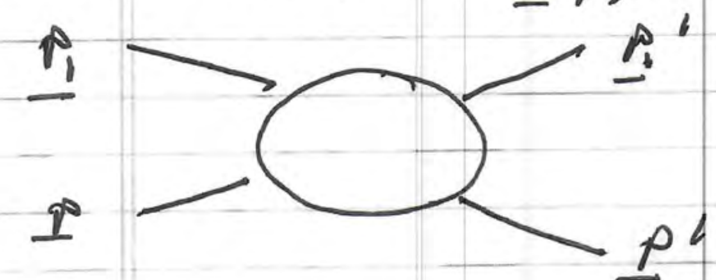
D.B. $\Rightarrow$ In statistical equilibrium,
can speak of
$\#$ collisions $\underline{p}, \underline{p}_1 \rightarrow \underline{p}', \underline{p}_1'$
(field particle – scatterer ensemble)

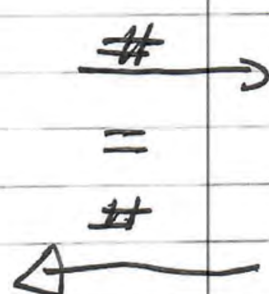




(test particle) $\rightarrow$ B.E. usually for T.P. dist

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





Quantitatively,

$W(\underline{p}, \underline{p}_1 ; \underline{p}', \underline{p}_1') =$ transition probability

Then D.B.:

$$\left[\begin{array}{l} W(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1') f_{1,2}(\underline{p}, \underline{p}_1) d^3\underline{p}_1 d^3\underline{p} d^3\underline{p}_1' d^3\underline{p}' \\ = W(\underline{p}', \underline{p}_1'; \underline{p}, \underline{p}_1) f_{1,2}(\underline{p}', \underline{p}_1') d^3\underline{p}' d^3\underline{p}_1' * \\ \qquad d^3\underline{p}_1 d^3\underline{p} \end{array}\right.$$

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

so

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

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

→ Molecular Chaos

In statistical equilibrium:

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

and:

will derive

$f = f_0$ (Maxwellian, to be shown)

macro flow

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

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

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

in eqbrm:

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

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

energy/momentum conservation in collision $\Rightarrow$

$$\epsilon + \epsilon_1 = \epsilon_1' + \epsilon' \qquad \checkmark \quad \underline{\text{energy}} \text{ conservation}$$

$$\underline{p} + \underline{p}_1 = \underline{p}' + \underline{p}_1' \qquad \checkmark \quad \text{momentum conservation}$$

so since:

$$f_0(\underline{p})\, f_0(\underline{p}_1) = f_0(\underline{p}')\, f_0(\underline{p}_1')$$

$$f(\underline{p}, \underline{p}_1) = f(\underline{p}', \underline{p}_1')$$ ✓ in stat. equilibrium

thus:

$\#$ colns $\underline{p}, \underline{p}_1 \to \underline{p}', \underline{p}_1'$

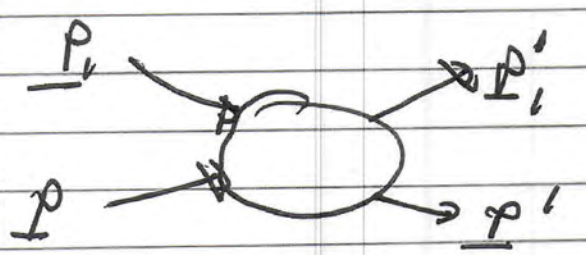
$= \#$ colns $\underline{p}', \underline{p}_1' \to \underline{p}, \underline{p}_1$

if

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

i.e.

prob.



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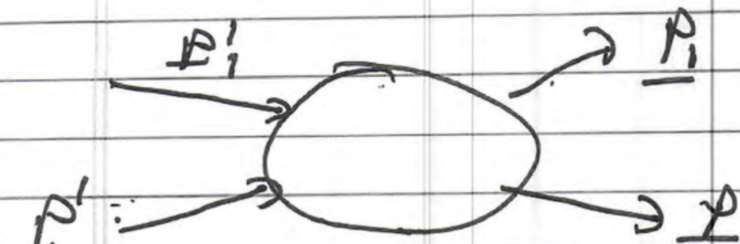

≡ prob.

B.

$\Rightarrow$ $\boxed{\text{Detailed Balance is a consequence of time-reversal invariance of basic interaction dynamics!}}$

i.e. $$\boxed{w(\underline{p}, \underline{p}_1 ; \underline{p}_1', \underline{p}') = w(\underline{p}', \underline{p}_1' ; \underline{p}, \underline{p}_1)^{T}}$$

parity inversion ?

n.b.:

- ϵ, $\underline{p}\cdot\underline{V}$ invariant under T.
- requires no stereoisomerism (i.e. latter gives a new substance upon parity inversion of molecular structure)
- can relate w to σ by:

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

Where from? :

$$\frac{d}{dt}\,(\text{Interaction Volume}) = \text{transition probability}$$

V_{rel}

$d\tau$

b.) Molecular Chaos

$$f(1,2) = f(1)\, f(2) \qquad (\text{general})$$

valid if: ~ chaos (one $\lambda > 0$)
(easy if $N \gg 1$)

~ dilute (no strong correlations build up)

$$T \gg \langle V(1,2) \rangle$$

gas, not crystal.

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

see Zaslavsky → "billiards" problem

etc

→ BBGKY to Boltzmann.

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

system described by:

$f(t, \underline{x}_1, \underline{p}_1; \underline{x}_2, \underline{p}_2; \cdots \underline{x}_N, \underline{p}_N)$

→ N particle distribution.

This satisfies full Liouville Equation

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

$$\underline{\nabla} \cdot \underline{V}_{\Gamma} = 0$$

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

Liouville Thm: f^N conserved along N particle orbits

$f^N \to$ exact, useless $\quad N \sim 10^{23}$

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

$f(\underline{x}, \underline{v}, t) \Rightarrow$ phase space density

approach: integrate out additional particles $\Leftrightarrow$ reduce description

catch: basic interaction is 2 body !

$$\dot{\underline{x}}_i = \underline{v}_i$$

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

so

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

Define: $\underline{\text{1-particle distribution}}$

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

$\underline{x}, \underline{p}$

integrate out other dependencies

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

$\rightarrow$ $\underline{\text{2 particle distribution}}$

so, for $N = 1$

total deriv

$$\int d\Gamma_2 \, d\Gamma_3 \ldots d\Gamma_N \left(\frac{\partial}{\partial t} f^N + \sum_{i=1}^{N} \frac{\partial}{\partial \underline{x}_i} \cdot (\underline{v}_i f^N) \right.$$

$N \neq 1$ killed by surface term

$$\left. + \sum_{i=1}^{N} \frac{\partial}{\partial p_i} \cdot \left(\sum_{j<i} \left(\frac{\partial V_{ij}}{\partial x_i} \right) f_N \right) \right) = 0$$

$\rightarrow$ 2 particle interaction.

V_{ij} is 2-particle interaction $\Rightarrow$ necessarily enters with f_2.

Need treat all possible pairs $\Rightarrow$

$$\frac{\partial f^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{x}_1} f^{(1)}$$

$$= \underbrace{(N-1)}_{\substack{\#\ \text{binary pairs} \\ N \text{ particles}}} \int d\Gamma_2 \underbrace{\frac{\partial V_{1,2}}{\partial \underline{x}_1}}_{\substack{\text{2 particle} \\ \text{interaction}}} \cdot \underbrace{\frac{\partial f^{(2)}}{\partial \underline{p}_1}}_{\substack{\text{2 body} \\ \text{distribution}}}$$

N.B.: $\partial_t f^{(1)} = \int (\,)\, f^{(2)}$

→ hierarchy problem
– how un-couple. ?

Need $f^{(2)}$ eqn. !

→ how? – integrate out from 3, on.

$\Rightarrow$

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

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

1, 2 are particles 'in' $f(1,2)$

$$= \underset{\substack{\uparrow \\ \#\ \text{triplets}}}{(N-2)} \int d\Gamma_3 \left[\frac{\partial f^{(3)}}{\partial \underline{p}_1} \cdot \frac{\partial V_{1,3}}{\partial r_1} + \frac{\partial f^{(3)}}{\partial \underline{p}_2} \cdot \frac{\partial V_{2,3}}{\partial r_2} \right]$$

Can we simplify this?

$$\frac{\partial f^{(2)}}{\partial t} + \underline{v}_1 \cdot \nabla_1 f^{(2)} - \underset{①}{\frac{\partial V_{1,2}}{\partial \underline{x}_1} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_1}} + (1 \leftrightarrow 2)$$

$$= \underset{②}{(N-2) \int d\Gamma_3 \left[\frac{\partial f^{(3)}}{\partial \underline{p}_1} \cdot \frac{\partial V_{1,3}}{\partial r_1} + \frac{\partial f^{(3)}}{\partial \underline{p}_2} \cdot \frac{\partial V_{2,3}}{\partial r_2} \right]}$$

Look at ② / ①

$\rightarrow$ exploit low volume filling of interaction $-$ $n d^3 \ll 1$.

$$② \sim N \int d\underline{x}_3 \int d\underline{p}_3 \, \frac{\partial f^{(3)}}{\partial \underline{p}_2} \cdot \frac{\partial V_{2,3}}{\partial \underline{r}_2}$$

ign $N-2$ → large N

$$f^{(3)} \sim \underbrace{\frac{1}{(\Delta p)^3} \frac{1}{\text{Vol.}}}_{\text{normalizations}} f^{(2)}$$

$$② \quad N \int d\underline{x}_3 \cancel{\int d\underline{p}_3} \, \frac{1}{\cancel{(\Delta p)^3}\, \text{Vol.}} \frac{\partial f^{(2)}}{\partial \underline{p}_2} \frac{\partial V_{2,3}}{\partial \underline{r}_2}$$

→ $\int dp_3$ cancels $1/\Delta p^3$ normalization

$$\sim \int dx_3 \, \frac{\partial f^{(2)}}{\partial \underline{p}_2} \frac{\partial V_{2,3}}{\partial r_2} \, \frac{N}{\text{Vol}}$$

V fills d^3 volume

$$② \sim d^3 \, \frac{N}{\text{Vol.}} \left(\frac{\partial}{\partial \underline{r}_2} V_{2,3} \right) \left(\frac{\partial f^{(2)}}{\partial p_2} \right)$$

$$\sim n d^3 \left(\frac{\partial V_{2,3}}{\partial \underline{r}_2} \right) \left(\frac{\partial f}{\partial \underline{p}_2} \right)$$

so

$$\boxed{②/① \sim n d^3 \ll 1}$$

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

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

- constitutes truncation of BBGKY Hierarchy, for dilute gas
- key is $d^3/\bar{r}^3 \ll 1$

  $\Rightarrow$ basic scale ordering.

$\rightarrow \frac{df^{(2)}}{dt} = 0$ is straightforward for dilute.

$\Rightarrow$ if posit statistical independence of colliding particles, ala'

Molecular Chaos.

$$f(t, 1; 2) = f(t, 1)\, f(t, 2)$$

then,

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

serves as i.c. for $\frac{df^{(2)}}{dt} = 0$

so

$\frac{df^{(2)}}{dt} = 0$, so $f^{(2)}$ always factorizes

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

- so $f^{(2)} \cong f(1)\, f(1)$ and

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

$\rightsquigarrow$ Boltzmann Equation.

Boltzmann Eqn.

$$\boxed{\begin{aligned} &\frac{\partial f}{\partial t} + \underline{v}\cdot\nabla f = C(f) \\ &C(f) = \int d\Gamma_2 \, \frac{\partial V_{1,2}}{\partial r_1}\cdot\frac{\partial}{\partial p_1}\left[f(1,t)\, f(2,t)\right] \end{aligned}}$$

- absorbed normalization
- $C(f) \equiv$ collision operator (integral)
- $C(f)$ nonlinear $\Rightarrow$ 2 body collision
- have "test particle" ($f(1)$) scattered by other "field particles" but "test", "field" the same.

  $\Rightarrow$ nonlinearity

- $C(f) \sim \nu_{coll}$.

  $C(f) \cong -\nu\left[f - f_{eq}\right]$ (Krook)

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

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

- what if $C(f) \to 0$

have:

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f + \frac{\underline{F}}{m} \cdot \frac{\partial f}{\partial \underline{v}} = 0$$

$$\underline{F} = q \underline{E}$$

$$\partial_x E = 4\pi n_0 q \int f \, dv$$

$\left.\frac{\text{Vlasov}}{\text{Jeans}}\right\rangle$ Eqn.

continuity eqn. for incompressible flow of phase space fluid.

- Plasma: $\boxed{\bar{r} < \lambda_D < l_{mfp} < L}$

Long range / glancing $\Rightarrow$ Fokker Planck.