Physics 210b

→ 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

To do:

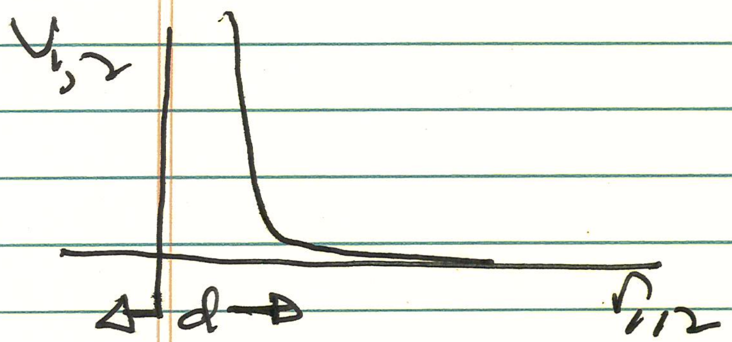
- basic ideas, assumptions
- Liouville → Boltzmann via BBGKY hierarchy
- H-Theorem
- Implications

i.) Basics

Ideal monatomic gas:

<u>Scales:</u>

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



i.e. hard sphere, range d.

N.B. Contrast Coulomb!

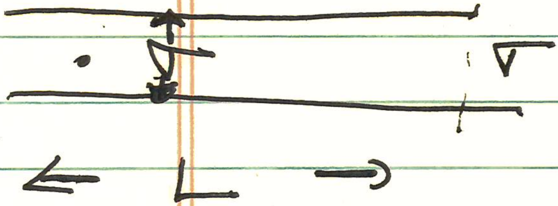
ii.) $n^{-1/3} \rightarrow$ mean interparticle spacing:

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

iii.) $l_{mfp} \rightarrow$ mean free path

$$l_{mfp} = 1/n\,\underset{\substack{\downarrow \\ \text{cross section} \\ \text{for 2 particle collision.}}}{\sigma}$$

Where from?



interaction cylinder for particle with σ, length L

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

if α = # collisions in cylinder of length L

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

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

Alternatively,

$$\ell_{mfp} = v_{Th} / \nu_{coll}.$$

(iv.) $\underline{L}$ → system size

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

→ 'usual' collisional regime (local fluid eqns.)

$\ell_{mfp} > L$

→ Long mean free pat (kinetic equations)

$K = l_{mfp}/L$ — will re-visit.

$\downarrow$

Knudsen #.

Classical dilute gas, collisional ordering:

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

Observe:

- $d < \bar{r}$

$\Rightarrow nd^3 < 1$

~ volume of interaction << mean spacing volume

~ particles usually "free", non-interacting.

$\Rightarrow$ diluteness *

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

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

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

  → collisions rare, interaction infrequent

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

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

→ diluteness!

$\Leftrightarrow$ $T / \left(V_{int}(d^3/\bar{r}^3)\right) \gg 1$

contrast: crystal

→ How Exploit Basic Assumptions?

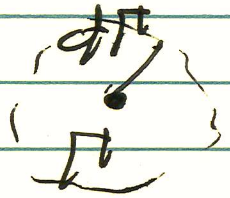
- phase space: dof's, translational only.

$$\left\{ \begin{array}{ll} \underline{p}, & \underline{v} \\ \underline{x}, & \underline{x} \end{array} \right.$$

- 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 dof's

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

$$C(f) \Big\downarrow$$

collision operator

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

↑ quadratic, NL.

Why? – 2-body interaction (collisions).

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

The problem:

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

i.e.

$$f(x_1, v_1; x_2, v_2; \ldots x_N, v_N, t)$$

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

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: $\underline{nd^3 \ll 1}$ ✓

2.) molecular chaos

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

why?

3.) detailed balance

(basic interaction is time reversible)

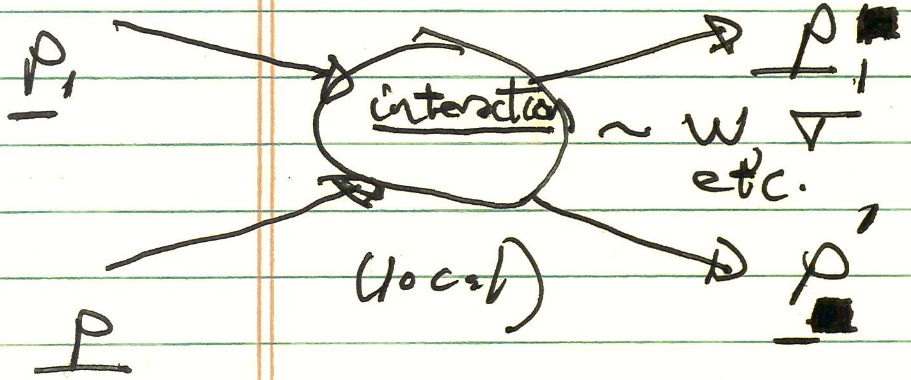
Two new ideas:

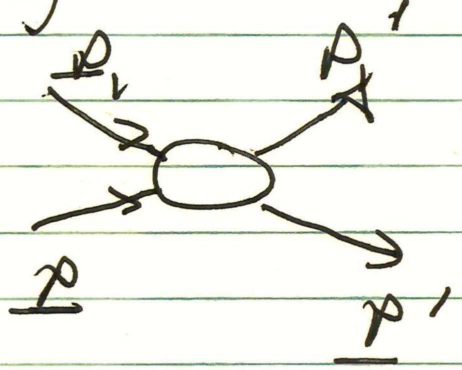
a.) Detailed Balance

D.B. ⇒ In statistical equilibrium,

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

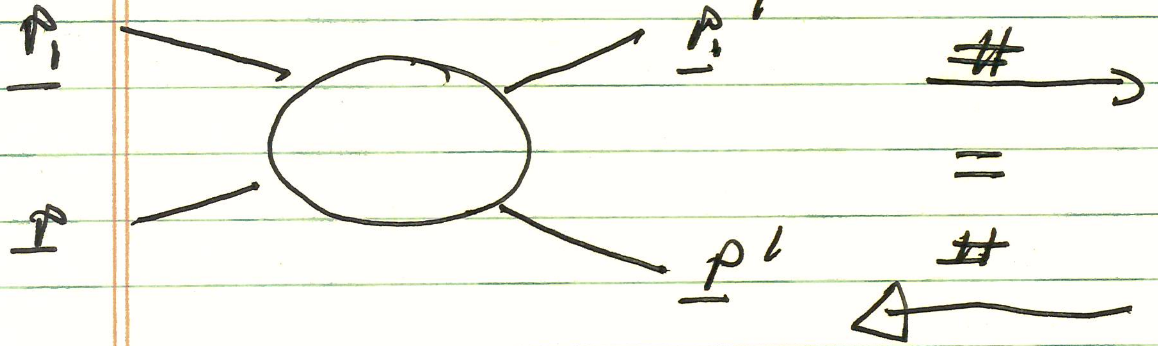
(field particle – scatterer ensemble)





(test particle) ⇒ B.E. dist usually, for T.P.

= \# 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.:

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

$f_{1,2}(\underline{p}, \underline{p}_1)$ = 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:

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

→ Molecular Chaos

In statistical equilibrium:

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

and.

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

$$f_0(p) = c\,\exp\left[-\frac{(\epsilon \;\text{[illegible]}\; \underline{p}\cdot \overset{\text{macro flow}}{\underline{V}})}{T}\right]$$

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

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

in eqb'm:

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

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

energy/momentum conservation in collision $\Rightarrow$

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

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

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:

$$\# \text{ colns } \underline{p}, \underline{p}_1 \rightarrow \underline{p}', \underline{p}_1'$$

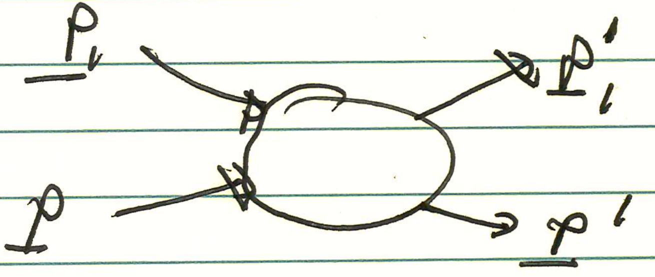
$$= \# \text{ colns } \underline{p}', \underline{p}_1' \rightarrow \underline{p}, \underline{p}_1$$

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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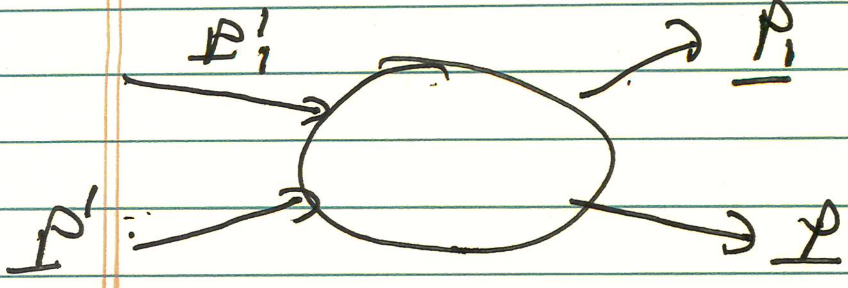


prob.

⇒ **Detailed Balance** is a consequence of time-reversal invariance of basic interaction dynamics!

i.e.

$$\boxed{W(\underline{p}, \underline{p}_1 ; \underline{p}_1', \underline{p}') = \underbrace{W(\underline{p}', \underline{p}_1' ; \underline{p}, \underline{p}_1)^T}_{\text{parity inversion}}}$$

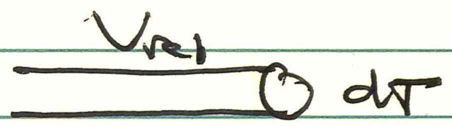
n.b.:

- 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?:

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



b.) Molecular Chaos

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

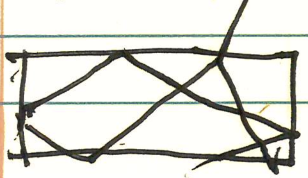
valid if: ~ chaos (one $\lambda_L > 0$)
(easy if $N \gg 1$)
~ dilute (no strong correlations build up)

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

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:

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

→ N particle distribution.

This satisfies full Liouville Equation

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

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

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

from familiar Liouville Thm ⇒ phase space flow of Hamiltonian system is incompressible.

Now, f^N → exact, but useless

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

↓

optimal

approach: integrate out additional particles
reduce description

catch: basic interaction is 2 body!

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

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

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: $\underline{x}$ and $\underline{p}$ integrating out!

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

→ 1 particle distribution

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

→ <u>2</u> particle distribution

So for $N=1$

surface term.
kills $N \neq \underline{1}$ by ~~St~~.

$$\int d\Gamma_2\, d\Gamma_3 \ldots d\Gamma_N \left(\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \frac{\partial}{\partial x_i} (\underline{v}_i f^N) + \sum_{i=1}^{N} \frac{\partial}{\partial p_i} \left(\underbrace{\left(-\sum_{j<i} \frac{\partial V_{ij}}{\partial x_i} \right)}_{\text{depends on particle 2}} f^N \right) \right) = 0$$

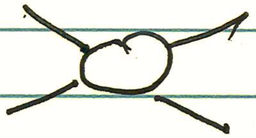
$\Rightarrow$

Boltzmann.

$$\frac{df}{dt} = \underset{\substack{\downarrow \\ \underline{\text{operator}}}}{C(f)}$$

f not cons. locally

in-out in phase space.



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

⟺ but:

$$\frac{\partial n}{\partial t} + \nabla\cdot(n\underline{v}) = 0$$

n conserved.

- Liouville
- $f^{(1)}$
- $f^{(1,2)}$

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

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

→ now have:

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

↳ classic problem in stat. mech

hierarchy problem → how truncate ?

so → form eqn. for $\underline{f}^{(2)}$:

→ integrating out 3 on ....

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

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

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

Consider:

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

$$+ \left(1 \Leftrightarrow 2 \right)$$

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

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

$(N \gg 1)$

$$f^{(3)} \sim \underbrace{\overset{p}{\frac{1}{(\Delta p)^3}} \; \overset{x}{\frac{1}{V}}}_{\text{normalizations}} f^{(2)}$$

so doing p integral:

$$② \sim N \int d\underline{x}_3 \; \frac{\partial f^{(2)}}{\partial \underline{p}_2} \cdot \frac{\partial V_{23}}{\partial r_2} \; \frac{1}{V}$$

$$\sim n \int d\underline{x}_3 \; \frac{\partial V_{2,3}}{\partial r_2} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_2}$$

- Volume integral ≠ 0 where product
  ≠ 0 so
- only at interaction sphere, volume d^3

$$② \sim n d^3 \; \frac{\partial V_{23}}{\partial r_2} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_2}$$

so

$$\frac{②}{①} \sim n d^3 \sim \left(d/\bar{r}\right)^3 \lll 1$$

so $② \to 0$.

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:

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

$$\int d\underline{p}_3 \, f^{(3)} \sim \frac{f^{(2)}}{V}$$

→ volume factor, $\int d^3x$ norm. → normalization in space ($\int d^3x \, f^{(1)} = 1$)

$$RHS \sim N \, [redacted] \int d^3x_3 \, \frac{\partial V}{\partial r} \frac{\partial f^{(2)}}{V \partial p}$$

(2 particle active $\sim d^3$)

$$\downarrow$$

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

$d \ll \bar{r}$

i.e. interaction only active in fraction d^3/V of total volume!

→ limits $\frac{V_2 f}{\partial r \partial p}$.

active volume ratio [redacted] $\frac{d^3}{V}$,, $\sim$ [redacted] d^3/V → $\frac{\text{active volume}}{\text{Total}}$.

Now,

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

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

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

so

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

$f^{(2)}$ const.

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

Now:

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

particles, à la Molecular Chaos

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

then

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

serves as initial condition for

$$\frac{df^{(2)}}{dt} = 0.$$

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

$f^{(2)}_{\text{coll}}$

Then, for Boltzmann Eqn.:

- consider 1 particle distribution fctn.

$$\boxed{\begin{aligned} \frac{\partial f}{\partial t} + \underline{v}\cdot\frac{\partial f}{\partial \underline{x}} &= N\int d\Gamma_2\, \frac{\partial V_{1,2}}{\partial \underline{r}_1}\cdot\frac{\partial f^{(2)}}{\partial \underline{p}_1} \xrightarrow{} t \\ &= N\int d\Gamma_2\, \frac{\partial V_{1,2}}{\partial \underline{r}_1}\cdot\frac{\partial}{\partial \underline{p}_1}\left[f^{(1)}(1,t)\, f^{(1)}(2,t)\right] \end{aligned}}$$

Boltzmann Eqn.

$$\Rightarrow \boxed{\begin{aligned} &\frac{\partial f}{\partial t} + \underline{v}\cdot\underline{\nabla} f = \underbrace{C(f)}_{\text{collision operator}} \quad \rightarrow \text{B.E.} \\ &C(f) = \int d\Gamma_2 \, \frac{\partial V_{1,2}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} \left[f(1,t)\, f(2,t) \right] \end{aligned}}$$

- have absorbed norm factor

- note C(f) nonlinear → 2 body collision

Alternatively,

$$\frac{df}{dt} = C(f)$$, f const. along phase space trajectories, up to collisions.