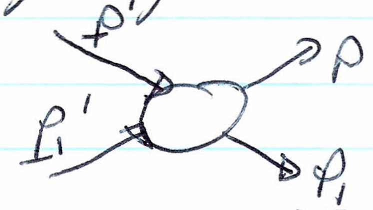
3.) Boltzmannia and H-Theorem

Now, can also write B.E. in terms collision operator based on scattering into + out of state:

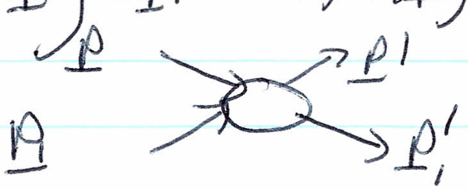
$$\frac{d f(\underline{p})}{dt} = \text{rate of change of } f, \text{ due collisions}$$

$$= \text{rate } \underset{\sim}{\text{in}} - \text{rate } \underset{\sim}{\text{out}}$$

$$\text{in} = \int d\underline{p}' \int d\underline{p}_1' \int d\underline{p}' \; f(\underline{p}')\, f(\underline{p}_1')\, w(\underline{p}', \underline{p}_1'; \underline{p}, \underline{p}_1)$$



$$\text{out} = \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \; f(\underline{p})\, f(\underline{p}')\, w(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1')$$



so

$$\frac{df(\underline{p})}{dt} = \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \; W(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1') \Big(f(\underline{p}')\, f(\underline{p}_1') - f(\underline{p}_1)\, f(\underline{p}) \Big)$$

$\Rightarrow$ B.E.

note: $\rightsquigarrow \underline{p} + \underline{p}_1 = \underline{p}' + \underline{p}_1'$

$\Rightarrow w = w^T$

Observe:

- $C(f) = 0$ for $f = f_0$

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

due conservation of energy and momentum

- will show Maxwellian renders $dS/dt = 0$.

This brings us to:

<u>H-Theorem</u>

- a gas left alone will evolve to an equilibrium of maximal entropy
- evolution accompanied by entropy production

i.e. $\frac{dS}{dt} \geq 0$

- evolution is to uniform Maxwellian

- $dS/dt \geq 0$

  for ideal gas

$$S = \int d\underline{x} \int d\underline{p} \; f \ln(e/f)$$

$$\cong \int dx \int dp \left[-f \ln f \right]$$

see notes on entropy, next lecture.

Will show $dS/dt \geq 0$.

$$\frac{dS}{dt} = -\int d\Gamma \left[\frac{df}{dt} \ln f + f \frac{1}{f} \frac{df}{dt} \right]$$

$$= -\int d\Gamma \left[C(f) \ln(f) + C(f) \right]$$

$$= -\int d\underline{x} \int d\underline{p} \; \ln(f)\, C(f).$$

→ entropy production due explicitly to collisions

$$= -\int dx \int d\underline{p} \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \; \ln f \; w \left(f(\underline{p}') f(\underline{p}_1') - f(\underline{p}) f(\underline{p}_1) \right)$$

Lemma

$$\int \varphi(p)\, C(p)\, dp = \frac{1}{2}\int d^4p\, (\varphi + \varphi_1 - \varphi' - \varphi_1')\, w f' f_1'$$

where notational shorthand ∋

$$d^4p = dp\, dp_1\, dp_1'\, dp'$$

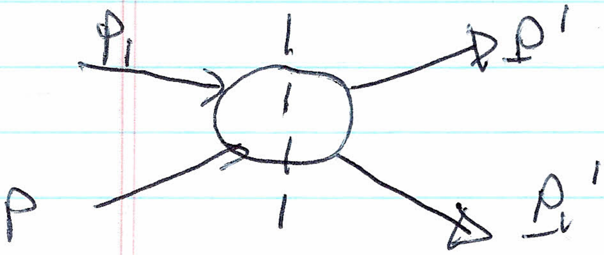
Now, explicitly:

$$\int dp\, \varphi(p)\, C(f) = \int \varphi\, w(p, p_1; p', p_1')\, f' f_1'\, d^4p \quad ①$$

$$- \int \varphi\, w(p', p_1'; p, p_1)\, f f_1 \quad ②$$

now, in ②:

→ interchange $p, p_1 \leftrightarrow p', p_1'$



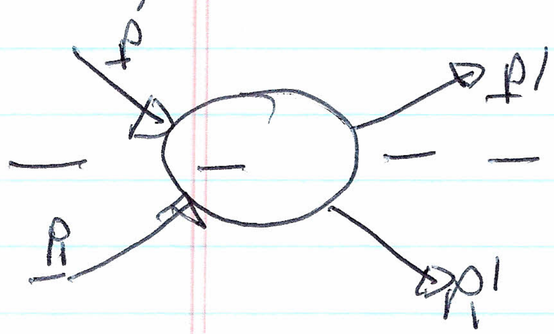
flip / rotate } about !

use T symmetry.

so

$$\int d\underline{p}\, \varphi\, C(f) = \int d^4\underline{p} \left\{ \left(\varphi(\underline{p}) - \varphi(\underline{p}')\right) w(\underline{p},\underline{p}_1;\underline{p}',\underline{p}_1') \times f' f_1' \right\}$$

Now, consider:



and interchange about - - -

i.e. $\underline{p}, \underline{p}'$ with $\underline{p}_1, \underline{p}_1'$

n.b. up-down symmetry equivalent

so

$$\int d\underline{p}\, C(f)\, \varphi = \text{[illegible]}$$

$$= \frac{1}{2} \int d^4\underline{p} \left\{ \left(\varphi(\underline{p}) - \varphi(\underline{p}') + \varphi(\underline{p}_1) - \varphi(\underline{p}_1')\right) \times w f' f_1' \right\}$$

this proves Lemma!

Now, let $\varphi = \ln f$,

so Lemma $\Rightarrow$

$$\frac{dS}{dt} = -\frac{1}{2}\int d\underline{x} \int d^4\underline{p} \left(\ln f + \ln f_1 - \ln f' - \ln f_1'\right) * w \; f' f_1'$$

$$= \frac{1}{2}\int d\underline{x} \int d^4\underline{p} \; w f' f_1' \ln\left(f' f_1' / f f_1\right)$$

$x \equiv f' f_1' / f f_1$

$$\boxed{\frac{dS}{dt} = \frac{1}{2}\int d\underline{x} \int d^4\underline{p} \; w f f_1 \, x \ln x}$$

Now since $\int c(f)\, d\Gamma = 0$

have $\int w f f_1 (x-1) d^4\underline{p}\, d\underline{x} = 0$

i.e. write zero in complex way.

so adding:

$$\frac{dS}{dt} = \frac{1}{2}\int d^4p \int dx \; w f f_1 \left[x \ln x - x + 1 \right]$$

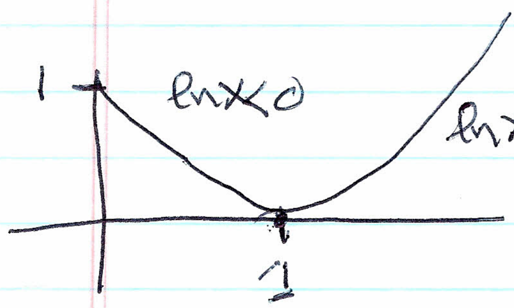
gives entropy production rate.

$F(x) = x \ln x - x + 1$

$F' = 1 + \ln x - 1$

$F(0) = 1$
$F(1) = 0$

so



so

$$dS/dt \geq 0$$

Boltzman H-thm!

– $dS/dt = 0$ for $x = 1$

$f f_1 = f' f_1'$

$\ln f + \ln f_1 = \ln f' + \ln f_1'$

$\Rightarrow$ $\ln f + \ln f_1 = \text{const.}$

sum of logs conserved in collision

$\Rightarrow \ln f = c + \underline{\beta} \cdot \underline{V} + \alpha E$ { see next lecture

$\alpha < 0$

$\frac{dS}{dt} = 0$ determines Maxwellian

→ keys: → detailed balance ⇔ ω symmetry

→ molec. chaos
$f(1,2) = f(1) f(2)$

→ $dS/dt \geq 0$

$dS/dt = 0$ corresponds $C(f) = 0$

collisions drive system to equilibrium

→ $d\underline{x}$ irrelevant!!

entropy produced <u>locally</u>

i.e. relaxation to local Maxwellian.

→ Essence of H-thm. is:

macroscopic irreversibility from microscopically reversible dynamics + molec. chaos (micro-chaos)