Kinetic theory of gases

$f(\vec{r},\vec{p},t)\, d^3r\, d^3p$: # of molecules in $d^3r\, d^3p$.

$$\int f(r,p,t)\, d^3r\, d^3p = N$$

Free gas

$$f(r+v\delta t\,,\ p+F\delta t\,, t+\delta t)\, d^3r'\, d^3p' = f(r,v,t)\, d^3r\, d^3p.$$

$$r_i' = r_i + v_i\delta t = r_i + \frac{p_i}{m}\delta t$$

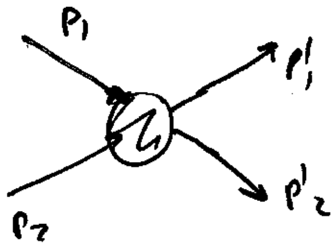
$$p_i' = p_i + F_i\delta t$$

$$\underset{\uparrow\ \text{Jacobian}}{\begin{pmatrix} \frac{\partial r_i'}{\partial r_j} & \frac{\partial r_i'}{\partial p_j} \\ \frac{\partial p_i'}{\partial r_j} & \frac{\partial p_i'}{\partial p_j} \end{pmatrix}} = \underbrace{\begin{pmatrix} \delta_{ij} & \delta_{ij}\,\delta t/m \\ \frac{\partial F_i}{\partial r_j}\delta t & \delta_{ij} \end{pmatrix}}_{\det = 1+O(\delta t^2)}$$

$$\frac{\partial}{\partial t}f + \frac{p}{m}\cdot\frac{\partial f}{\partial \vec{r}} + F\cdot\frac{\partial f}{\partial \vec{p}} = \left(\frac{\partial f}{\partial t}\right)_{coll.}$$

Collisions

$$dN_{12} = \underbrace{F(r,p_1,p_2,t)}_{\simeq\, f(r,p_1,t)\, f(r,p_2,t)}\, d^3r\, d^3p_1\, d^3p_2$$



$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int d^3p_2\, d^3p'_1\, d^3p'_2 \;\; \delta(E'_1+E'_2-E_1-E_2)\, \delta^{(3)}(p'_1+p'_2-p_2-\vec{p})\,\cdot$$

$$\cdot \left(-P_{12\to 1'2'}\, F_{12} + P_{1'2'\to 12}\, F_{1'2'}\right)$$

p_1 in volume

$$P_{12\to 1'2'} = P_{1'2'\to 12} \qquad \left(= |T_{12\to 1'2'}|^2 \right)$$

$$\left(\frac{\partial f}{\partial t}\right)_{coll} = \int d^3p_2\, d^3p'_1\, d^3p'_2 \;\; \delta^{(4)}(p_f-p_i)\, P_{12\to 1'2'} \left(f(p'_1)f(p'_2) - f(p_1)f(p_2)\right)$$

No external force.

indep. of position.

$$\frac{\partial f}{\partial t}(\vec{p}_1, t) = \int d^3p_2\, d^3p'_1\, d^3p'_2 \quad \delta^{(4)}(P_f - P_i)\, P_{12\to 1'2'} \cdot$$

$$\cdot \left(f(p'_1) f(p'_2) - f(p_1) f(p_2) \right)$$

$$H = \int d^3p\, f(p,t) \ln f(p,t)$$

$$\frac{dH}{dt} = \int d^3p \quad \frac{\partial f}{\partial t} \ln f + \int d^3p \quad \frac{\partial f}{\partial t}$$

$$= \int d^3p \quad (1 + \ln f) \frac{\partial f}{\partial t}$$

$$= \int d^3p_1\, d^3p_2\, d^3p'_1\, d^3p'_2 \quad \delta^{(4)}(P_f - P_i) \quad P_{12\to 1'2'} \cdot$$

$$\cdot \left(1 + \ln f(p_1, t)\right) \left(f(p'_1) f(p'_2) - f(p_1) f(p_2) \right)$$

symmetrize p_1, p_2

$$= \frac{1}{2} \int d^3p_1\, d^3p_2\, d^3p'_1\, d^3p'_2\, (2 + \ln f_1 + \ln f_2)\, \delta^{(4)}(P_f - P_i)\, P_{12\to 1'2'}$$

$$(f'_1 f'_2 - f_1 f_2)$$

Symmetrize $12 \leftrightarrow 1'2'$

$$= \frac{1}{4}\int d^3p_1\, d^3p_2\, d^3p_1'\, d^3p_2' \quad (\ln f_1 f_2 - \ln f_1' f_2')(f_1' f_2' - f_1 f_2)\,\cdot$$

$$\cdot\, \delta^{(4)}(P_f - P_i)\; P_{12\to 1'2'}$$

$$(\ln y - \ln x)(x-y) = \underbrace{x}_{>0} \ln(y/x)\,(1 - y/x)$$

$$(\ln\alpha)(1-\alpha) \begin{cases} \alpha<1 & <0 \\ \alpha>1 & <0 \\ \alpha=1 & \to 0. \end{cases}$$

$$\boxed{\frac{dH}{dt} \leq 0}$$

0 only for $\alpha = 1 \Rightarrow \boxed{f_1' f_2' = f_1 f_2}$

Stationary case, $\frac{dH}{dt} = 0 \Rightarrow \underbrace{f_1' f_2' = f_1 f_2}_{\text{equilibrium.}}$

$$\ln f(p_1') + \ln f(p_2') = \ln f(p_1) + \ln f(p_2)$$

if $\quad p_1' + p_2' = p_1 + p_2$

$\quad\quad \varepsilon_1' + \varepsilon_2' = \varepsilon_1 + \varepsilon_2$

•) one possibility.

$$\ln f(p) = \alpha\, \varepsilon(p)$$

or

$$\ln f(p) = \alpha\, \varepsilon(p) + \vec{\beta}\cdot\vec{p}$$

$$= \alpha \frac{\vec{p}^2}{2m} + \vec{\beta}\,\vec{p}$$

$$f(p) = C e^{-A(\vec{p}-\vec{p}_0)^2}$$

$$= \left(\frac{A}{\pi}\right)^{3/2} N \; e^{-A(\vec{p}-\vec{p}_0)^2}$$

$$\langle\vec{p}\rangle = \frac{1}{N}\int d^3\vec{p}\;\; N\left(\frac{A}{\pi}\right)^{3/2}\vec{p}\; e^{-A(\underbrace{\vec{p}-\vec{p}_0}_{\vec{k}})^2}$$

$$= \frac{1}{N}\int d^3\vec{k}\;\; N\left(\frac{A}{\pi}\right)^{3/2}(\vec{k}+\vec{p}_0)\; e^{-A\vec{k}^2} = \vec{p}_0 \; ; \; \overset{\text{take}}{\vec{p}_0 = 0}$$

$$\langle\varepsilon\rangle = \frac{1}{\cancel{N}}\int d^3\vec{p}\;\; \cancel{N}\left(\frac{A}{\pi}\right)^{3/2}\frac{\vec{p}^2}{2m}\; e^{-A\vec{p}^2} =$$

$$\int d^3 p_x \, e^{-A\vec{p}^{\,2}} = \left(\frac{\pi}{A}\right)^{3/2} = \pi^{3/2} A^{-3/2}$$

$$-\frac{\partial}{\partial A} \int d^3 p \, e^{-A\vec{p}^{\,2}} = \int d^3 p \; \vec{p}^{\,2} e^{-A\vec{p}^{\,2}}$$

$$= \frac{3}{2} \pi^{3/2} A^{-5/2}$$

$$\langle \varepsilon \rangle = \left(\frac{A}{\cancel{\pi}}\right)^{3/2} \frac{1}{2m} \frac{3}{2} \frac{\cancel{\pi^{3/2}}}{A^{5/2}} = \frac{3}{4mA}$$

$$A = \frac{3}{4m\varepsilon}$$

$$\boxed{f(p) = \left(\frac{3}{4\pi m\varepsilon}\right)^{3/2} N \, e^{-\frac{3}{4m\varepsilon}\vec{p}^{\,2}}}$$

$$H = -\int d^3p \; f \ln f$$

$$= -\int d^3p \left(\frac{3}{4\pi m\varepsilon}\right)^{3/2} N\, e^{-\frac{3}{4m\varepsilon}\vec{p}^{\,2}} \cdot$$

$$\left(\frac{3}{2}\ln\left(\frac{3}{4\pi m\varepsilon}\right) + \ln N - \frac{3}{4m\varepsilon}\vec{p}^{\,2} \right)$$

$$= -N \left\{ \frac{3}{2}\ln\left(\frac{3}{4\pi m\varepsilon}\right) + \ln N - \frac{3}{2\cancel{\varepsilon}}\cancel{\varepsilon} \right\}$$

$$= \frac{3}{2} N \ln\varepsilon + \underline{\text{indep of } \varepsilon}$$

$S(E,V)$

$$dE = T\,dS - p\,dV$$

$$dS = \frac{1}{T}dE + \frac{p}{T}dV$$

$$ds = \frac{1}{T}d\varepsilon + \frac{p}{T}\frac{dV}{N}$$

add

$$\frac{\partial S}{\partial \varepsilon} = \frac{3}{2\varepsilon} = \frac{1}{T} \qquad \varepsilon = \frac{3}{2} T k_B$$

$$S = -k_B \int d^3p \, f \ln f$$

$$\int d^3r \int d^3p \, f = N$$

$$f = \frac{N}{V}\left(\frac{\cancel{3}}{4\pi m E}\right)^{3/2} e^{-\frac{3}{4mE}\vec{p}^{\,2}}$$

$$f = \frac{N}{V}\left(\frac{\cancel{3}}{2\pi m k_B T}\right)^{3/2} e^{-\frac{1}{k_B T}\frac{\vec{p}^{\,2}}{2m}}$$

$$S = -k_B \int d^3r \int d^3p \; f \ln f$$

$$= -k_B \cancel{V} \int d^3p \; \frac{N}{\cancel{V}}\left(\frac{3}{2\pi m k_B T}\right)^{3/2} e^{-\frac{1}{k_B T}\frac{\vec{p}^{\,2}}{2m}} \cdot$$

$$\left\{ \ln\frac{N}{V} + \frac{3}{2}\ln\left(\frac{\cancel{3}}{2\pi m k_B T}\right) - \frac{1}{k_B T}\frac{\vec{p}^{\,2}}{2m} \right\}$$

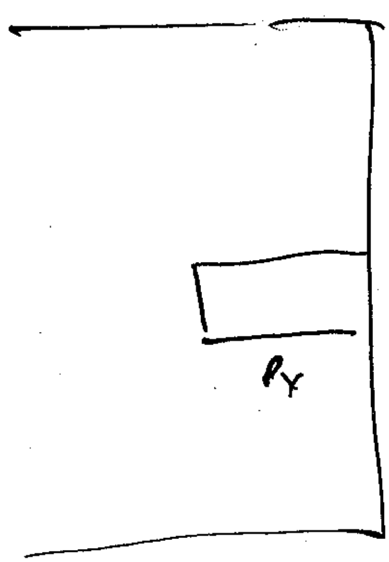
$$= -Nk_B \ln\frac{N}{V} + \frac{3k_B N}{2}\ln(2\pi m k_B T) + \frac{N}{\cancel{V}}\frac{3}{2}k_B \cancel{T}$$

$$S = \frac{3}{2} k_B N - k_B N \ln \frac{N}{V} + \frac{3}{2} k_B N \ln (2\pi m k_B T)$$

$$\frac{P}{T} = \frac{\partial S}{\partial V} = k_B \frac{N}{V}$$

$$\boxed{pV = k_B N T}$$ ideal gas.

<u>check pressure</u>.



$$\delta t : \quad \underbrace{v_x \delta t A \frac{N}{V}}_{\text{\# of molecules in small volume.}} \overbrace{2p_x}^{\Delta p}$$

$$F = \frac{\Delta p}{\Delta t} = 2 \frac{p_x^2}{m} A \frac{N}{V}$$

$$P = \frac{F}{A} = 2 \frac{p_x^2}{m} \frac{N}{V} \rightarrow \frac{\cancel{2}}{m} \frac{N}{V} \langle p_x^2 \rangle$$

pressure

only $p_x > 0 \rightarrow 1/2$

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$$\langle p_x^2 \rangle = \frac{1}{\cancel{N}} \int d^3r \int d^3p \, \frac{\cancel{N}}{\cancel{V}} \, p_x^2 \left(\frac{1}{2\pi m k_B T} \right)^{3/2} e^{-\frac{\vec{p}^2}{2m k_B T}}$$

$$= \int_{-\infty}^{\infty} dp_x \, \frac{p_x^2}{\sqrt{2\pi m k_B T}} \, e^{-\frac{\vec{p}^2}{2m k_B T}}$$

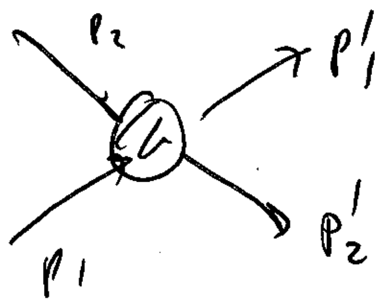
$$\int dx \, x^2 e^{-ax^2} = -\frac{\partial}{\partial a} \sqrt{\frac{\pi}{a}} = \frac{1}{2} \sqrt{\pi} \, a^{-3/2}$$

$$\langle p_x^2 \rangle = \frac{1}{2} \cancel{\sqrt{\pi}} \, \frac{(2m k_B T)^{3/2}}{(2m k_B T)^{1/2} \cancel{\sqrt{\pi}}} = \frac{2m k_B T}{2} = m k_B T$$

$$P = \frac{1}{\cancel{m}} \frac{N}{V} \cancel{m} k_B T \Rightarrow \boxed{pV = N k_B T} \checkmark$$

Conservation laws

Consider a collision



Suppose $\chi(\vec{r}_1, \vec{p}_1)$ is conserved

namely $\chi(\vec{r}_1, \vec{p}_1) + \chi(\vec{r}_2, \vec{p}_2) = \chi(\vec{r}_1, \vec{p}_1') + \chi(\vec{r}_2, \vec{p}_2')$

χ : mass or particle #

$\chi = m v_i = p_i$ momentum (3 components indep.)

$\chi = \varepsilon$: energy. $= \frac{1}{2} m v^2$

↳ we can define "thermal energy"

$$\chi = \frac{1}{2} m (v - u(r,t))^2$$

$$u(r,t) = \langle v \rangle$$

$$\int d^3p\, \chi(r,p) \left(\frac{\partial f}{\partial t}\right)_{coll} = 0.$$

$$= \int d^3p_1\, \chi(p_1)\, d^3p_1'\, d^3p_2\, d^3p_2' \cdot \delta(\varepsilon_1' + \varepsilon_2' - \varepsilon_1 - \varepsilon_2) \,.$$

$$\cdot\, \delta^{(3)}(\vec{p}_1' + \vec{p}_2' - \vec{p}_1 - \vec{p}_2) \, \left(P_{12 \to 1'2'}\right) \left(f_1' f_2' - f_1 f_2\right)$$

$$= \int d^3p_1\, d^3p_2\, d^3p_1'\, d^3p_2' \, \underbrace{\delta_\varepsilon \delta_p \, P_{12 \to 1'2'}}_{\text{antisym } p_1 \leftrightarrow p_1',\ p_2 \leftrightarrow p_2'} \Big[\underbrace{\chi(p_1) + \chi(p_2)}_{\text{sym } p_1 p_2} -$$

$$- \chi(p_1') - \chi(p_2') \Big] \left(f_1' f_2' - f_1 f_2\right)$$

$$= 0$$

$$\Rightarrow \quad \int d^3p \left(\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{r}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} \right) \chi(p) = 0$$

$$\frac{\partial}{\partial t} \int d^3p\, \chi(p) f + \frac{\partial}{\partial x_i} \int d^3p\, \frac{\vec{p}_i}{m} \chi(p) f$$

$$- \int d^3p\, \frac{\vec{p}_i}{m} \frac{\partial \chi}{\partial x_i} f - \int d^3p\, f \frac{\partial F}{\partial \vec{p}} \chi - \int d^3x\, f\, F \frac{\partial \chi}{\partial p} = 0$$

$$f \Rightarrow \rho(\vec{r})\, f(\vec{p})$$

let's say $\partial f/\partial \vec{r} = 0$

$$\frac{\partial}{\partial t}\langle \rho \chi \rangle + \frac{\partial}{\partial x_i}\left\langle \rho \frac{\vec{p}_i}{m} \chi(\vec{p}) \right\rangle -$$

$$- \left\langle \rho \frac{\vec{p}_i}{m} \frac{\partial \chi}{\partial x_i} \right\rangle - \left\langle \rho\, F_i \frac{\partial \chi}{\partial p_i} \right\rangle = 0$$

χ = mass.

$$\frac{\partial(\rho m)}{\partial t} + \frac{\partial}{\partial x_i} \rho \langle m v_i \rangle = 0$$

$$\partial_t \rho_m + \nabla j = 0 \qquad j = \rho m \langle v_i \rangle$$

$\chi = m v_i$ momentum

$$\frac{\partial}{\partial t}\left(\rho_m \langle v_i \rangle\right) + \frac{\partial}{\partial x_j} \rho_m \langle v_j v_i \rangle -$$

$$- \rho F_i = 0$$

$$\langle v_i \rangle = u_i$$

$$\frac{\partial}{\partial t}(\rho_m u_i) - \rho F_i + \frac{\partial}{\partial x_j}\left(\rho_m \langle v_i v_j \rangle\right) = 0$$

$$\underbrace{\langle (v_i - u_i)(v_j - u_j) \rangle}_{P_{ij}/\rho_m} = \langle v_i v_j \rangle - u_i u_j - \cancel{u_i u_j} + \cancel{u_i u_j}$$

$$\frac{\partial}{\partial t}(\rho_m u_i) - \rho F_i + \frac{\partial}{\partial x_j}\left(P_{ij} + \rho_m u_i u_j\right) = 0$$

$$\frac{\partial}{\partial t}(\rho_m u_i) + \frac{\partial}{\partial x_j}(\rho_m u_i u_j) + \frac{\partial}{\partial x_j} P_{ij} - \rho F_i = 0$$

$$\frac{\partial}{\partial x_j}\left((\rho_m u_j) u_i\right) = \frac{\partial(\rho_m u_j)}{\partial x_j} u_i + \rho_m u_j \frac{\partial u_i}{\partial x_j}$$

$$= -u_i \frac{\partial \rho}{\partial t} + \rho_m u_j \frac{\partial u_i}{\partial x_j}$$

$$\rho_m \frac{\partial u_i}{\partial t} + \rho_m u_j \frac{\partial u_i}{\partial x_j} = F_i - \frac{1}{\rho} \frac{\partial}{\partial x_j} P_{ij}$$

$$\frac{\partial u_i}{\partial t} + u_j \frac{\partial u_i}{\partial x_j} = \frac{F_i}{\rho} - \frac{1}{\rho} \frac{\partial P_{ij}'}{\partial x_j}$$