The H Theorem and Irreversibility

Thm: If $f_1(\vec{p}, \vec{q}, t)$ satisfies the Boltzmann equation, then $\frac{dH}{dt} \le 0$, where

$$\boxed{H(t) \equiv \int d^3p\, d^3q\, f_1(\vec{p}, \vec{q}, t) \ln f_1(\vec{p}, \vec{q}, t)}$$

Proof: $$\frac{dH}{dt} = \int d^3p_1\, d^3q_1\, \frac{\partial f_1}{\partial t}(\ln f_1 + 1)$$

$$= \int d^3p_1\, d^3q_1\, \frac{\partial f_1}{\partial t} \ln f_1 + \frac{d}{dt}\underbrace{\int d^3p_1\, d^3q_1\, f_1}_{N}$$

$$= \int d^3p_1\, d^3q_1\, \frac{\partial f_1}{\partial t} \ln f_1$$

Use Boltzmann Eq:

$$\frac{dH}{dt} = \int d^3p_1\, d^3q_1\, \ln f_1 \left[\left(\frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1} - \frac{\vec{p}_1}{m} \cdot \frac{\partial f_1}{\partial \vec{q}_1}\right)\right]$$

$$- \int d^3p_1\, d^3q_1\, d^3p_2\, d^2\sigma\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1, \vec{q}_1) f_1(\vec{p}_2, \vec{q}_2) - f_1(\vec{p}_1{}', \vec{q}_1) f_1(\vec{p}_2{}', \vec{q}_1)\right] \ln f_1(\vec{p}_1, \vec{q}_1)$$

Top line: $\int d^3p_1\, d^3q_1\, \ln f_1 \frac{\partial U}{\partial \vec{q}_1} \cdot \frac{\partial f_1}{\partial \vec{p}_1}$

$\overset{\vec{p}_1 \text{ by parts}}{=} - \int d^3p_1\, d^3q_1\, \cancel{f_1} \frac{\partial U}{\partial \vec{q}_1} \frac{1}{\cancel{f_1}} \frac{\partial f_1}{\partial \vec{p}_1}$

$\overset{\vec{p}_1 \text{ by parts}}{=} 0$

Similarly, $-\int d^3p_1\, d^3q_1\, (\ln f_1)\, \frac{\vec{p}_1}{m} \cdot \frac{\partial f_1}{\partial \vec{q}_1}$

$\vec{q}_1$ by parts $\int d^3p_1\, d^3q_1\, \frac{1}{\cancel{f_1}}\, \frac{\vec{p}_1}{m} \cdot \frac{\partial f_1}{\partial \vec{q}_1} \cdot \cancel{f_1}$

$\vec{q}_1$ by parts 0

So, the streaming terms in $\frac{dH}{dt}$ vanish.

Collision terms: Average over expressions with dummy variables $(\vec{p}_1, \vec{p}_2)$ and $(\vec{p}_2, \vec{p}_1)$ (interchanged)

(1) $\rightarrow$ $$\frac{dH}{dt} = -\frac{1}{2}\int d^3q\, d^3p_1\, d^3p_2\, \underbrace{d^2b}_{= d^2\sigma}\, |\vec{v}_1 - \vec{v}_2| \Big[f_1(\vec{p}_1, \vec{q}_1)\, f_1(\vec{p}_2, \vec{q}_1)$$
$$- f_1(\vec{p}_1{}', \vec{q}_1) f_1(\vec{p}_2{}', \vec{q}_1)\Big] \underbrace{\ln\left(f_1(\vec{p}_1, \vec{q}_1)\, f_1(\vec{p}_2, \vec{q}_1)\right)}_{= \ln f_1(\vec{p}_1) + \ln f_1(\vec{p}_2)}$$

Change variables: $(\vec{p}_1, \vec{p}_2, \vec{b}) \rightarrow (\vec{p}_1{}', \vec{p}_2{}', \vec{b}{}')$

Jacobian $= 1$ by time reversal invariance

(can reverse sign of final momenta $\rightarrow$ collision w/ original momenta)

suppressing dependence on $\vec{q}_1$

$$\frac{dH}{dt} = -\frac{1}{2}\int d^3q\, d^3p_1{}'\, d^3p_2{}'\, d^2b'\, |\vec{v}_1 - \vec{v}_2| \Big[f_1(\vec{p}_1)\, f_1(\vec{p}_2)$$
$$- f_1(\vec{p}_1{}')\, f_1(\vec{p}_2{}')\Big] \ln\left(f_1(\vec{p}_1)\, f_1(\vec{p}_2)\right)$$

For elastic collisions, $|\vec{v}_1 - \vec{v}_2| = |\vec{v}_1{}' - \vec{v}_2{}'|$

$\rightarrow$ Can remove primes on dummy variables $\vec{p}_1{}', \vec{p}_2{}'$

$(\vec{p}_1{}', \vec{p}_2{}') \leftrightarrow (\vec{p}_1, \vec{p}_2)$ – same functional dependence

② $$\frac{dH}{dt} = -\frac{1}{2}\int d^3q\, d^3p_1\, d^3p_2\, d^2b\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1')f_1(\vec{p}_2') - f_1(\vec{p}_1)f_1(\vec{p}_2) \right] \ln\left(f_1(\vec{p}_1')f_1(\vec{p}_2')\right)$$

Average ① and ②

$$\Rightarrow \frac{dH}{dt} = -\frac{1}{4}\int d^3q\, d^3p_1\, d^3p_2\, d^2b\, |\vec{v}_1 - \vec{v}_2| \left[f_1(\vec{p}_1)f_1(\vec{p}_2) - f_1(\vec{p}_1')f_1(\vec{p}_2') \right] \left[\ln\left(f_1(\vec{p}_1)f_1(\vec{p}_2)\right) - \ln\left(f_1(\vec{p}_1')f_1(\vec{p}_2')\right) \right]$$

The integrand (with the $-1/4$ factored out) is always positive.

Hence, $\boxed{\frac{dH}{dt} \leq 0}$ — the H Theorem.

Time Irreversibility

We wrote $\left.\frac{df_1}{dt}\right|_{coll}$ as a function of the 2-particle distribution function $f_2(\vec{p}_1^{(1)}, \vec{x}_1, \vec{p}_2^{(1)}, \vec{b}, - ; t)$ before the collision,

we then assumed the colliding particles were independent before the collision: $f_2 = f_1 \cdot f_1$. (molecular chaos)

After the collision, subtle correlations then arise. So, the assumption of molecular chaos distinguishes the past and present.

It is a statement about the state of the system at early times which is distinct from the state of the system at later times.

Equilibrium

$\frac{dH}{dt}=0 \rightarrow f_1(\vec{p}_1,\vec{q}_1)\,f_1(\vec{p}_2,\vec{q}_1) - f_1(\vec{p}_1{}',\vec{q}_1)\,f_1(\vec{p}_2{}',\vec{q}_1) = 0$

$$\rightarrow \underbrace{\ln f_1(\vec{p}_1,\vec{q}) + \ln f_1(\vec{p}_2,\vec{q})}_{\text{Before collision}} = \underbrace{\ln f_1(\vec{p}_1{}',\vec{q}) + \ln f_1(\vec{p}_2{}',\vec{q})}_{\text{After collision}} \quad \forall \vec{q}.$$

Any additive conserved quantity will satisfy this relation

$\ln f_1 = a(\vec{q}) - \vec{\alpha}(\vec{q})\cdot\vec{p} - \beta(\vec{q})\left(\frac{\vec{p}^{\,2}}{2m}\right)$, which we can

$$= \left(a(\vec{q}) + \beta(\vec{q})U(\vec{q})\right) - \vec{\alpha}(\vec{q})\cdot\vec{p} - \beta(\vec{q})\left(\frac{p^2}{2m} + U(\vec{q})\right)$$

$$\boxed{f_1(\vec{p},\vec{q}) = N(\vec{q})\exp\left[-\vec{\alpha}(\vec{q})\cdot\vec{p} - \beta(\vec{q})\left(\frac{p^2}{2m} + U(\vec{q})\right)\right]}$$

- local equilibrium ($\forall \vec{q}$)

Away from collisions, f_1 evolves unless $\{H_1, f_1\} = 0$

$\rightarrow f_1 = f_1(H_1, \underset{\text{(by } H_1)}{\text{other conserved}} \text{ quantities})$

$$\Rightarrow f_1(\vec{p},\vec{q}) = N\exp\left[-\vec{\alpha}\cdot\vec{p} - \beta\left(\frac{p^2}{2m} + U(\vec{q})\right)\right]$$

Normalization: $\int d^3p\, d^3q\, f_1(\vec{p},\vec{q}) = N$

particle in a box, $U(\vec{q})=0$

$$\rightarrow \boxed{f_1(\vec{p},\vec{q}) = \frac{N}{V}\left(\frac{\beta}{2\pi m}\right)^{3/2}\exp\left[\frac{-\beta(\vec{p}-\vec{p}_0)^2}{2m}\right]}$$

$$\boxed{\vec{p}_0 = \langle\vec{p}\rangle = \frac{m\vec{\alpha}}{\beta}}, \quad \boxed{\langle p^2\rangle = \langle p_x^2 + p_y^2 + p_z^2\rangle = \frac{3m}{\beta}}$$

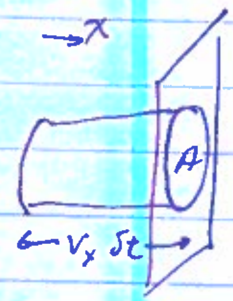
By considering equilibrium between two gases, we can argue that for the two gases in equilibrium

$$\left\langle \frac{p_a^2}{2m_a} \right\rangle = \left\langle \frac{p_b^2}{2m_b} \right\rangle = \frac{3}{2\beta}$$

$\rightarrow$ β (or $\frac{1}{\beta}$) plays the role of an empirical temperature describing equilibrium of gases.

Equation of state

Force on wall from gas $= \dfrac{\text{impulse on wall}}{\text{unit time.}}$



particles hitting wall in area A w/ momentum bet. $[\vec{p}, \vec{p}+d\vec{p}]$ in time δt:

$$dN(\vec{p}) = \left(f_1(\vec{p})\, d^3p\right)\left(A v_x \delta t\right)$$

$$\text{Force } F = \frac{1}{\delta t} \int_{-\infty}^{0} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z\, f_1(\vec{p}) \Big(A \underbrace{\frac{p_x}{m}}_{v_x} \delta t\Big) \underbrace{(2p_x)}_{\text{impulse}}$$

Pressure $P = \frac{F}{A} = \int d^3p\, f_1(\vec{p})\, \frac{p_x^2}{m}$

$$= \frac{1}{m} \int d^3p\; p_x^2\, \frac{N}{V} \left(\frac{\beta}{2\pi m}\right) e^{-\beta \frac{p^2}{2m}}$$

$$= \frac{1}{\beta}\left(\frac{N}{V}\right)$$

Compare with ideal gas law: $PV = N k_B T$

$\rightarrow$ identify $\boxed{\beta = \frac{1}{k_B T}}$

Other properties of ideal gases can be derived, as well.