H-theorem :

$$H(t) := \int d^3\vec{r}\, d^3\vec{p} \quad f_1(\vec{r},\vec{p},t)\, \ln\left(f_1(\vec{r},\vec{p},t)\right)$$

$$S = -k_B\, \rho \ln \rho \quad , \quad S = -k_B H$$

theorem (1872) : $\dfrac{dH}{dt} \leq 0$

Proof :

$$\frac{dH}{dt} = \int d^3\vec{r}\, d^3\vec{p} \left(\frac{\partial f_1}{\partial t} \ln f_1 + f_1 \frac{1}{f_1} \frac{\partial f_1}{\partial t} \right)$$

$$= \int d^3\vec{r}\, d^3\vec{p}\, (\ln f_1 + 1) \frac{\partial f_1}{\partial t}$$

$$\int d^3\vec{r}\, d^3\vec{p}\, \frac{\partial f_1}{\partial t} = \frac{\partial}{\partial t} \underbrace{\int d^3\vec{r}\, d^3\vec{p}\, f_1}_{N} = 0$$

$$= \int d^3\vec{r}\, d^3\vec{p}\, \ln f_1 \frac{\partial f_1}{\partial t}$$

"1'st BBGky" : $\dfrac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\dfrac{\partial f_1}{\partial t}\right)_{coll.} = \dfrac{\partial V}{\partial \vec{r}} \cdot \dfrac{\partial f_1}{\partial \vec{p}} - \dfrac{\vec{p}}{m} \cdot \dfrac{\partial f_1}{\partial \vec{r}} + \left(\dfrac{\partial f_1}{\partial t}\right)_{coll.}$

$$H_1 = \frac{p^2}{2m} + V(\vec{r})$$

$$\frac{dH}{dt} = \int d^3\vec{r}\, d^3\vec{p}\, \ln f_1 \left(\frac{\partial V}{\partial \vec{r}} \cdot \frac{\partial f_1}{\partial \vec{p}} - \frac{\vec{p}}{m} \cdot \frac{\partial f_1}{\partial \vec{r}} + \left(\frac{\partial f_1}{\partial t}\right)_{coll.} \right)$$

$$\int d^3\vec{p}\, \frac{\vec{p}}{m} \cdot \int d^3\vec{r}\, \underbrace{\ln f_1 \frac{\partial f_1}{\partial \vec{r}}} = 0 \qquad \int d^3\vec{r}\, \frac{\partial V}{\partial \vec{r}} \cdot \int d^3\vec{p}\, \ln f_1 \frac{\partial f_1}{\partial \vec{p}} = 0$$

$$\frac{\partial}{\partial \vec{r}}(f_1 \ln f_1) - \underbrace{f_1 \frac{\partial}{\partial \vec{r}} \ln f_1}$$

$$f_1 \frac{1}{f_1} \frac{\partial f_1}{\partial \vec{r}} = \frac{\partial f_1}{\partial \vec{r}}$$

$$\frac{dH}{dt} = \int d^3\vec{r}\, d^3\vec{p}\, \ln f_1 \left(\frac{\partial f_1}{\partial t}\right)_{coll.}$$

"Boltzmann equation".

$$\left(\frac{\partial f_1}{\partial t}\right)_{coll.} = \int d^3\vec{P}_2\, d^3\vec{P}_1'\, d^3\vec{P}_2'\ \omega(\vec{P},\vec{P}_2|\vec{P}_1',\vec{P}_2')\left[f_1(\vec{r},\vec{P}_1')f_1(\vec{r},\vec{P}_2') - f_1(\vec{r},\vec{P})f_1(\vec{r},\vec{P}_2)\right]$$

$$d\Gamma \equiv d^3\vec{P}_1\, d^3\vec{P}_2\, d^3\vec{P}_1'\, d^3\vec{P}_2'\, d^3\vec{r}$$

$$\frac{dH}{dt} = \int d\Gamma\ \omega(\vec{P}_1,\vec{P}_2|\vec{P}_1',\vec{P}_2')\ln f_1(\vec{P}_1)\left[f_1(\vec{P}_1')f_1(\vec{P}_2') - f_1(\vec{P}_1)f_1(\vec{P}_2)\right]$$

$1 \leftrightarrow 2$

$$\frac{dH}{dt} = \int d\Gamma\ \omega(\vec{P}_1,\vec{P}_2|\vec{P}_1',\vec{P}_2')\ \ln f_1(\vec{P}_2)\left[f_1(\vec{P}_1')f_1(\vec{P}_2') - f_1(\vec{P}_1)f_1(\vec{P}_2)\right]$$

$$\frac{dH}{dt} = \frac{1}{2}\int d\Gamma\ \omega(\vec{P}_1,\vec{P}_2|\vec{P}_1',\vec{P}_2')\ \underbrace{\left(\ln f_1(\vec{P}_1) + \ln f_1(\vec{P}_2)\right)}_{\ln\left(f_1(\vec{P}_1)f_1(\vec{P}_2)\right)}\left[f_1(\vec{P}_1')f_1(\vec{P}_2') - f_1(\vec{P}_1)f_1(\vec{P}_2)\right]$$

$P \leftrightarrow P'$

$$\frac{dH}{dt} = -\frac{1}{2}\int d\Gamma\ \omega(\vec{P}_1,\vec{P}_2|\vec{P}_1',\vec{P}_2')\ \ln\left(f_1(\vec{P}_1')f_1(\vec{P}_2')\right)\left[f_1(\vec{P}_1')f_1(\vec{P}_2') - f_1(\vec{P}_1)f_1(\vec{P}_2)\right]$$

$$\frac{dH}{dt} = -\frac{1}{4}\int d\Gamma\ \omega(\vec{P}_1,\vec{P}_2|\vec{P}_1',\vec{P}_2')\ \underbrace{\left(\ln(\underbrace{f_1(\vec{P}_1')f_1(\vec{P}_2')}_{X}) - \ln(\underbrace{f_1(\vec{P}_1)f_1(\vec{P}_2)}_{Y})\right)\left[f_1(\vec{P}_1')f_1(\vec{P}_2') - f_1(\vec{P}_1)f_1(\vec{P}_2)\right]}_{(\ln X - \ln Y)(X - Y)\ \geq 0}$$

$X > Y \iff \ln X > \ln Y$

$*$ if Rate $\propto f_2(\vec{P}_1',\vec{P}_2')$: $\frac{dH}{dt} \geq 0$ $*$

$$\boxed{\frac{dH}{dt} \leq 0} \xrightarrow{?} \frac{dS}{dt} \geq 0$$

E.T. Jaynes $\longrightarrow$ "Violation of Boltzmann's H-theorem in Real Gases"
Phys. Rev. A, Vol. 4, num. 2 (1971)

Detailed Balance : $f_1(\vec{P}_1) f_1(\vec{P}_2) = f_1(\vec{P}_1') f_1(\vec{P}_2') \Longrightarrow \frac{dH}{dt} = 0$

Fluid Dynamics :

Thermodynamics $\longrightarrow$ Properties of Equilibrium

Fluid Dynamics $\longrightarrow$ low energy - long wavelength excitations

Relevant dynamical variables :

- density : $\rho(\vec{r},t) = m\, n(\vec{r},t)$
- Temperature : $T(\vec{r},t)$
- Velocity field : $\vec{u}(\vec{r},t)$

Why ?

$$A(\vec{r},\vec{P}) \rightarrow \langle A \rangle (\vec{r},t) := \frac{\int A(\vec{r},\vec{P}) f_1(\vec{r},\vec{P},t)\, d^3\vec{P}}{\underbrace{\int f_1(\vec{r},\vec{P},t)\, d^3\vec{P}}_{\rightarrow\, n(\vec{r},t)}}$$

$$f_1(\vec{r}_1,\vec{P}_1) = N \int \prod_{i=2}^{N} d^3\vec{r}_i\, d^3\vec{P}_i\, f$$

$n(\vec{r}) \langle A \rangle = \langle n(\vec{r}) A \rangle$

$$\langle A \rangle (\vec{r},t) = \frac{1}{n(\vec{r},t)} \int A(\vec{r},\vec{P}) f_1(\vec{r},\vec{P},t)\, d^3\vec{P}$$

evolution of $\langle A \rangle$: Streaming term + $\underset{\text{Rapid variation}}{\underline{\text{Collision term}}}$

$$\left(\frac{\partial \langle A \rangle}{\partial t}\right)_{coll.} = \frac{1}{n(\vec{r},t)} \int A(\vec{r},\vec{P}) \left(\frac{\partial f_1}{\partial t}\right)_{coll.} d^3\vec{P} = 0$$

$$\int d\Gamma\, \omega(\vec{P}_1,\vec{P}_2|\vec{P}_1',\vec{P}_2') \left(f_1(\vec{P}_1') f_1(\vec{P}_2') - f_1(\vec{P}_1) f_1(\vec{P}_2)\right) \left(A(\vec{r},\vec{P}_1) + A(\vec{r},\vec{P}_2) - A(\vec{r},\vec{P}_1') - A(\vec{r},\vec{P}_2')\right) = 0$$

$$\boxed{A(\vec{r},\vec{P}_1) + A(\vec{r},\vec{P}_2) = A(\vec{r},\vec{P}_1') + A(\vec{r},\vec{P}_2')}$$

Collisional invariants $\longrightarrow$ Energy , momentum , $A = 1$

$$\frac{\partial f_1}{\partial t} = \{H_1, f_1\} + \left(\frac{\partial f_1}{\partial t}\right)_{coll.} \quad ; \quad H_1 = \frac{p^2}{2m} + V \qquad -\frac{\partial V}{\partial \vec{r}} = \vec{F}(\vec{r})$$

$$\longrightarrow \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\cdot\frac{\partial}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial}{\partial \vec{p}}\right) f_1 = \left(\frac{\partial f_1}{\partial t}\right)_{coll.}$$

$$\int d^3\vec{p}\; A\left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\cdot\frac{\partial}{\partial \vec{r}} + \vec{F}\cdot\frac{\partial}{\partial \vec{p}}\right) f_1 = 0 \; ; \qquad A\frac{\partial f_1}{\partial \vec{r}} = \frac{\partial}{\partial \vec{r}}(A f_1) - f_1 \frac{\partial A}{\partial \vec{r}}$$

$$\frac{\partial}{\partial t}\left(\int d^3\vec{p}\, A f_1\right) + \frac{\partial}{\partial \vec{r}}\cdot\left(\int \frac{\vec{p}}{m} A f_1\, d^3\vec{p}\right) - \int d^3\vec{p}\, \frac{\vec{p}}{m}\cdot\frac{\partial A}{\partial \vec{r}} f_1$$

$$- \int d^3\vec{p}\, \vec{F}\cdot\frac{\partial A}{\partial \vec{p}} f_1 = 0$$

$$\boxed{\frac{\partial}{\partial t}\langle nA\rangle + \frac{\partial}{\partial \vec{r}}\cdot\langle n\vec{v}A\rangle - \left\langle n\vec{v}\cdot\frac{\partial A}{\partial \vec{r}}\right\rangle - n\left\langle \vec{F}\cdot\frac{\partial A}{\partial \vec{p}}\right\rangle = 0}$$

Master Equation