11.C.3. Boltzmann's H Theorem

Boltzmann's H function is defined as

$$H(t) = \int d\,\boldsymbol{r} \int d\,\boldsymbol{p}\;\; f(\boldsymbol{r},\boldsymbol{p},t)\ln f(\boldsymbol{r},\boldsymbol{p},t)$$

(11.75)

which should be compared to the (equilibrium) Gibb's entropy [see (7.2) of §7.A]

$$S = -k_B \int d\,\boldsymbol{q}^N \int d\,\boldsymbol{p}^N \rho(\boldsymbol{q}^N,\boldsymbol{p}^N)\ln\left[\,C_N\,\rho(\boldsymbol{q}^N,\boldsymbol{p}^N)\right]$$

(11.75a)

Aside from the hydrodynamic 1-particle approximation inherent in the replacement of ρ with f, $H(t)$ can be taken as the generalization of the entropy to the non-equilibrium case, namely,

$$S(t) = -k_B\,H(t)$$

(11.84)

Now, the 2nd law of thermodynamics states that

$$\Delta S > 0 \qquad\qquad \text{for all spontaneous processes}$$

It would be interesting to see how $H(t)$ behaves under similar circumstances.

Taking the time derivative of (11.75) gives

$$\frac{d\,H}{d\,t} = \int d\,\boldsymbol{r} \int d\,\boldsymbol{p}\;\; \frac{\partial f}{\partial\,t}\left(\ln\,f + 1\right)$$

(11.76)

where

$$f = f(\boldsymbol{r},\boldsymbol{p},t)$$

Using (11.74) to replace $\frac{\partial f}{\partial\,t}$, we have

$$\frac{d\,H}{d\,t} = \int d\,\boldsymbol{r} \int d\,\boldsymbol{p}\left[-\dot{\boldsymbol{r}}\cdot\frac{\partial\,f}{\partial\,\boldsymbol{r}} + \int d\,\boldsymbol{p}' \int d\,\Omega\;\, v\,\sigma(b,v)\left(f_f\,f_f' - f\,f'\right)\right]\left(\ln\,f + 1\right)$$

(11.77)

where

$$\overline{\boldsymbol{p}} = \boldsymbol{p}' - \boldsymbol{p} \qquad f_f = f(\boldsymbol{r},\boldsymbol{p}_f,t) \qquad f' = f(\boldsymbol{r},\boldsymbol{p}',t) \qquad f_f' = f\,(\boldsymbol{r},\boldsymbol{p}_f',t)$$

Now,

$$\begin{aligned}\int d\,\boldsymbol{r}\,\dot{\boldsymbol{r}}\cdot\frac{\partial\,f}{\partial\,\boldsymbol{r}}\left(\ln\,f + 1\right) &= \int d\,\boldsymbol{r}\,\dot{\boldsymbol{r}}\cdot\frac{\partial}{\partial\,\boldsymbol{r}}\left(\,f\ln f\right)\\ &= \int d\,\boldsymbol{r}\,\frac{\partial}{\partial\,\boldsymbol{r}}\cdot\left(\dot{\boldsymbol{r}}\,f\ln f\right) \qquad\qquad \left[\;\frac{\partial\,\dot{\boldsymbol{r}}}{\partial\,\boldsymbol{r}} = 0\;\right]\\ &= \dot{\boldsymbol{r}}\,f\ln f\,\Big|_S \qquad\qquad [\;S = \text{surface at infinity.}\;]\\ &= 0\end{aligned}$$

Therefore, (11.77) simplifies to

$$\frac{d\,H}{d\,t} = \int d\,\boldsymbol{r} \int d\,\boldsymbol{p} \int d\,\boldsymbol{p}' \int d\,\Omega\;\, v\,\sigma(b,v)\left(f_f\,f_f' - f\,f'\right)\left(\ln f + 1\right)$$

(11.78)

$$= \int d\boldsymbol{r} \int d\boldsymbol{p}' \int d\boldsymbol{p} \int d\Omega\; v\,\sigma(b, v)\left(f_f' f_f - f' f\right)\left(\ln f' + 1\right) \qquad [\,\boldsymbol{p} \leftrightarrow \boldsymbol{p}'\,]$$

$$= \frac{1}{2} \int d\boldsymbol{r} \int d\boldsymbol{p} \int d\boldsymbol{p}' \int d\Omega\; v\,\sigma(b, v)\left(f_f f_f' - f f'\right)\left(\ln f + \ln f' + 2\right)$$

(11.80)

$$= \frac{1}{2} \int d\boldsymbol{r} \int d\boldsymbol{p} \int d\boldsymbol{p}' \int d\Omega\; v\,\sigma(b, v)\left(f_f f_f' - f f'\right)\left[\ln(f f') + 2\right]$$

(11.80a)

$$= \frac{1}{2} \int d\boldsymbol{r} \int d\boldsymbol{p}_f \int d\boldsymbol{p}_f' \int d\Omega\; v\,\sigma(b, v)\left(f f' - f_f f_f'\right)\left[\ln(f_f f_f') + 2\right] \qquad [\,\boldsymbol{p} \leftrightarrow \boldsymbol{p}_f,\;\; \boldsymbol{p}' \leftrightarrow \boldsymbol{p}_f'\,]$$

$$= \frac{1}{2} \int d\boldsymbol{r} \int d\boldsymbol{p} \int d\boldsymbol{p}' \int d\Omega\; v\,\sigma(b, v)\left(f_f f_f' - f f'\right)\left[-\ln(f_f f_f') - 2\right] \qquad [\, d\boldsymbol{p}_f\, d\boldsymbol{p}_f' = d\boldsymbol{p}\, d\boldsymbol{p}'\,]$$

$$= \frac{1}{4} \int d\boldsymbol{r} \int d\boldsymbol{p} \int d\boldsymbol{p}' \int d\Omega\; v\,\sigma(b, v)\left(f_f f_f' - f f'\right) \ln\left(\frac{f f'}{f_f f_f'}\right) \qquad \text{[Combined with}$$

(11.80a).]

$$\leq 0$$

(11.81)

where we have used $\overline{p}$, μ, $\sigma_{CM} > 0$ and

$(x - y)(\ln x - \ln y) \geq 0$ [$\ln x$ is monotonically increasing with x.]

(11.81a)

(11.81) is known as the Boltzmann’s H theorem. The 2nd law is thus proved microscopically, albeit only for ideal gas like systems for which the Boltzmann transport equation is applicable.

Since

$(x - y)(\ln x - \ln y) = 0 \quad \Leftrightarrow \quad x = y$

we have

$$\frac{dH}{dt} = 0 \quad \Leftrightarrow \quad f_f f_f' = f f' \quad \text{for all collisions.} \qquad (11.81b)$$

$$\text{or} \quad \ln f_f + \ln f_f' = \ln f + \ln f' \qquad (11.82)$$

In other words, equilibrium is achieved if and only if the detailed balance condition is satisfied.

At equilibrium,

$f(\boldsymbol{r}, \boldsymbol{p}, t) = f_{eq}(\boldsymbol{p}) \qquad \forall\; \boldsymbol{r},\; t$

Since the only 1-particle quantities that are conserved under elastic collisions are the total momentum, kinetic energy & particle number. We have

$$\ln f_{eq}(\boldsymbol{p}) = A + \boldsymbol{B}\cdot\boldsymbol{p} + C\,\frac{p^2}{2m}$$

(11.83)

where A, $\boldsymbol{B}$ & C are constants. Thus,

$$f_{eq}(\boldsymbol{p}) = \exp\left(A + \boldsymbol{B}\cdot\boldsymbol{p} + C\,\frac{p^2}{2m}\right)$$

(11.83a)

which is a generalization of the Maxwell-Boltzmann distribution to the case $\langle \boldsymbol{p} \rangle \neq 0$.