

Boltzmann's H-theorem

Consider one single species, with no space gradients, no external forces and constant volume, so that,

$$\frac{\partial f}{\partial t} = \int \left(f' f'_1 - f f_1 \right) g \sigma d\Omega d^3 w_1$$

and define $H = n \langle \ln f \rangle = \int f \ln f d^3 w$. The function $f(\vec{w})$ may be evolving in time due to collisions, so let us calculate the rate of change of H .

$$\frac{\partial H}{\partial t} = \frac{dH}{dt} = \int (1 + \ln f) \frac{\partial f}{\partial t} d^3 w = \frac{\partial}{\partial t} \overbrace{\int f d^3 w}^{n = \frac{N}{V}} + \int \ln f \frac{\partial f}{\partial t} d^3 w$$

$$\frac{\partial H}{\partial t} = \int \int \int \ln f \left(f' f'_1 - f f_1 \right) g \sigma d\Omega d^3 w_1 d^3 w \quad \otimes$$

Now, we integrate over both \vec{w} and \vec{w}_1 , so they are interchangeable

$$\frac{\partial H}{\partial t} = \iiint \ln f_1 \left(f'_1 f' - f_1 f \right) g \sigma d\Omega d^3 w d^3 w_1 \quad \otimes \otimes$$

since g and σ do not change under this interchange; only $\ln f_1$ is different. We can then write,

$$\frac{\partial H}{\partial t} = \frac{1}{2} (\otimes + \otimes \otimes) = \frac{\partial H}{\partial t} = \frac{1}{2} \iiint \ln(f f_1) (f' f'_1 - f f_1) g \sigma d\Omega d^3 w d^3 w_1 \quad \oplus$$

Again, since each collision has one and only one inverse collision, and we are summing over all possible collisions, primed and unprimed variables can be interchanged (this does not affect g or σ either:

$$\frac{\partial H}{\partial t} = \frac{1}{2} \int \int \int \ln(f' f'_1) (f f_1 - f' f'_1) g \sigma d\Omega \overbrace{d^3 w' d^3 w'_1}^{=d^3 w d^3 w_1} \quad \oplus \oplus$$

we then have,

$$\frac{\partial H}{\partial t} = \frac{1}{2} (\oplus + \oplus \oplus) = \frac{1}{4} \int \int \int \underbrace{\ln \frac{f' f'_1}{f f_1} (f f_1 - f' f'_1)}_{\leq 0} g \sigma d\Omega d^3 w d^3 w_1 \leq 0$$

Hence we have found that H can only decrease in time: an irreversible macroscopic behavior built up from reversible microscopic interactions. The explanation, for this paradox lies in the “molecular chaos” assumption, i.e., in each collision all impact parameters are equally likely because they do not interact (the collisions) with each other. This cannot be strictly true, but the net effect appears to cancel out as the number of particles increases. We suspect

that the irreversible quantity H must be connected with the entropy of the system, and will prove this later.

Relationship between H and Entropy S

We had defined $H = n\langle \ln f \rangle = \int f \ln f d^3w$, and when f is equilibrated,

$$f = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mw^2}{2kT}}, \quad \ln f = \ln \left[n \left(\frac{m}{2\pi kT} \right)^{3/2} \right] - \frac{mw^2}{2kT}$$

$$H = n \left\{ \ln \left[n \left(\frac{m}{2\pi kT} \right)^{3/2} \right] - \underbrace{\left\langle \frac{\frac{1}{2}mw^2}{kT} \right\rangle}_{\frac{3}{2}} \right\} \quad \boxed{H = n \left\{ \ln \left[n \left(\frac{m}{2\pi kT} \right)^{3/2} \right] - \frac{3}{2} \right\}}$$

The natural variables for entropy S_{tot} are energy $E = N\frac{3}{2}kT$, number of molecules N and volume $V = \frac{N}{n}$. Changing H to these variables, and using $H_{tot} = HV$ (H was per unit volume),

$$\boxed{H_{tot} = N \left\{ \ln \left[\left(\frac{m}{\frac{4}{3}\pi} \right)^{\frac{3}{2}} \frac{N^{\frac{5}{2}}}{VE^{\frac{3}{2}}} \right] - \frac{3}{2} \right\}}$$

We have no closed form for S_{tot} , but its partial derivatives can be calculated from,

$$dE = TdS_{tot} - PdV + \mu dN$$

where μ is the chemical potential.

We then find,

$$dS_{tot} = \frac{dE}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN = \frac{1}{T}dE + k\frac{N}{V}dV - \frac{\mu}{T}dN$$

and so:

$$\left(\frac{\partial S_{tot}}{\partial E} \right)_{N,V} = \frac{1}{T} \quad ; \quad \left(\frac{\partial S_{tot}}{\partial V} \right)_{N,E} = \frac{kN}{V} = nk \quad ; \quad \left(\frac{\partial S_{tot}}{\partial N} \right)_{E,V} = -\frac{\mu}{T}$$

Now, from the definition of H_{tot} above,

$$\left(\frac{\partial H_{tot}}{\partial E} \right)_{N,V} = -\frac{3N}{2E} = -\frac{1}{kT}$$

$$\left(\frac{\partial H_{tot}}{\partial V} \right)_{N,E} = -\frac{N}{V} = -n$$

$$\left(\frac{\partial H_{tot}}{\partial N} \right)_{E,V} = \ln \left[\left(\frac{m}{4\pi} \right)^{\frac{3}{2}} \frac{N^{\frac{5}{2}}}{VE^{\frac{3}{2}}} \right] - \frac{3}{2} + \mathcal{N} \frac{5}{2} \frac{1}{\mathcal{N}} = 1 + \ln \left[n \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \right]$$

Comparing the first two derivatives of S_{tot} and H_{tot} , we see that

$$S = -kH + f(N)$$

Without invoking the Third Law of Thermodynamics (the entropy tends to zero at $T = 0$), which cannot apply directly to a gas, because condensation and crystallization must occur as $T \rightarrow 0$, the function of $f(N)$ is indeterminate. When comparing changes of entropy of a fixed amount of gas (fixed N) this does not matter, and we can provisionally identify,

$$S = -kH$$

which does have the proper evolution during approach to equilibrium.

The derivatives $(\frac{\partial H}{\partial N}, \frac{\partial S}{\partial N})$ can be used to evaluate the chemical potential of the substance, but now the function $f(N)$ does matter, and it must be obtained from other data. We do not pursue this here.

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