Boltzmann's H-theorem [tln40]

Boltzmann's H-function: $H(t) \equiv \int d^3v_1\, f(\vec{v}_1,t)\ln f(\vec{v}_1,t)$.

$$\Rightarrow \frac{dH}{dt} = \int d^3v_1 \left[\frac{\partial f(\vec{v}_1,t)}{\partial t}\ln f(\vec{v}_1,t) + \frac{\partial f(\vec{v}_1,t)}{\partial t}\right].$$

Use $\int d^3v_1 \frac{\partial f(\vec{v}_1,t)}{\partial t} = \frac{d}{dt}\int d^3v_1\, f(\vec{v}_1,t) = 0$ and use Boltzmann equation.

$$\begin{aligned}\Rightarrow \frac{dH}{dt} = -&\int d^3v_1 \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1,\vec{v}_2;\vec{v}_1',\vec{v}_2') \\ &\times \ln f(\vec{v}_1,t)\left[f(\vec{v}_1,t)f(\vec{v}_2,t) - f(\vec{v}_1',t)f(\vec{v}_2',t)\right].\end{aligned}$$

Likewise:

$$\begin{aligned} dH/dt &= \cdots\{\vec{v}_1 \leftrightarrow \vec{v}_2\},\ \{\vec{v}_1' \leftrightarrow \vec{v}_2'\}, \\ dH/dt &= \cdots\{\vec{v}_1 \leftrightarrow \vec{v}_1'\},\ \{\vec{v}_2 \leftrightarrow \vec{v}_2'\}, \\ dH/dt &= \cdots\{\vec{v}_1 \leftrightarrow \vec{v}_2'\},\ \{\vec{v}_2 \leftrightarrow \vec{v}_1'\}.\end{aligned}$$

$$\begin{aligned}\Rightarrow 4\frac{dH}{dt} = -&\int d^3v_1 \int d^3v_2 \int d^3v_1' \int d^3v_2'\, \sigma(\vec{v}_1,\vec{v}_2;\vec{v}_1',\vec{v}_2') \\ &\times \left[f(\vec{v}_1,t)f(\vec{v}_2,t) - f(\vec{v}_1',t)f(\vec{v}_2',t)\right] \\ &\times \left\{\ln\left[f(\vec{v}_1,t)f(\vec{v}_2,t)\right] - \ln\left[f(\vec{v}_1',t)f(\vec{v}_2',t)\right]\right\}.\end{aligned}$$

The function $h(x,y) \equiv (x-y)(\ln x - \ln y)$ is non-negative for $x,y>0$ and is equal to zero if $x=y$.

Properties of $H(t)$: $\frac{dH}{dt} \leq 0$ and $\frac{dH}{dt} = 0$ if $f(\vec{v}_1,t)f(\vec{v}_2,t) = f(\vec{v}_1',t)f(\vec{v}_2',t)$.

The (stationary) velocity distribution which makes H stationary is the Maxwell distribution (Boltzmann's derivation).

Boltzmann's H-function is related to the uncertainty in our knowledge of the particle velocities as contained in the distribution $f(\vec{v}_1,t)$: $H(t) = -\Sigma_f$.

The stationary H-function is related to the entropy of an ideal gas at equilibrium: $S = -Nk_BH(\infty)$. Here the uncertainty in our knowledge of particle velocities is a maximum.