Statistical mechanics postulates

First postulate: Equal a priori probability.

In a closed statistical system, with fixed energy, all accessible states are equally likely.

Second postulate:

$$S(E,V,N) = K_B \ln(E,V,N)$$

\# of microstates.

Volume in the phase space.

$$\left.\begin{array}{l} E,V,N \longrightarrow \infty \\ u = \dfrac{E}{N}\ ,\ v = \dfrac{V}{N} \quad \text{constants} \end{array}\right\} \text{Thermodynamic limit.}$$

$C_p, C_v, K_T, \ldots,$ are quantities per mole!

$$s(u,v) = \lim_{\substack{E,V,N\to\infty \\ u,v \text{ constants.}}} \frac{1}{N} S(E,V,N) = \lim_{\substack{E,V,N\to\infty \\ u,v \text{ constants.}}} \frac{1}{N} K_B \ln \Omega(E,V,N)$$

Example: (paramagnet) spin $\frac{1}{2}$

$$\mathcal{H} = -\mu_0 H \sum_{j=1}^{N} \sigma_i$$

$$\Omega(E,N) = \frac{N!}{N_1!\,N_2!} = \frac{N!}{\left[\frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\right]!\left[\frac{1}{2}\left(N + \frac{E}{\mu_0 H}\right)\right]!}$$

$$\ln(\Omega(E,N)) = \ln(N!) - \ln\left(\left[\frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\right]!\right) - \ln\left(\left[\frac{1}{2}\left(N + \frac{E}{\mu_0 H}\right)\right]!\right)$$

$$= N\ln(N) - \frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\ln\left(\left[\frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\right]\right)$$

$$- \frac{1}{2}\left(N + \frac{E}{\mu_0 H}\right)\ln\left(\left[\frac{1}{2}\left(N + \frac{E}{\mu_0 H}\right)\right]\right) - N + \frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right) + \frac{1}{2}\left(N + \frac{E}{\mu_0 H}\right)$$

$$= N\ln(N) - \frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\left[\ln\left(\frac{N}{2}\right) + \ln\left(1 - \frac{u}{\mu_0 H}\right)\right]$$

$$-\frac{1}{2}\left(N - \frac{E}{\mu_0 H}\right)\left[\ln\left(\frac{N}{2}\right) + \ln\left(1 + \frac{u}{\mu_0 H}\right)\right]$$

$$= N\ln(N) - \frac{N}{2}\ln(N) + \frac{N}{2}\ln(2) - \frac{N}{2}\ln(N) + \frac{N}{2}\ln(2) + \frac{Nu}{2\mu_0 H}\ln\left(\frac{N}{2}\right)$$

$$-\frac{Nu}{2\mu_0 H}\ln\left(\frac{N}{2}\right) - \frac{N}{2}\left(1 - \frac{u}{\mu_0 H}\right)\ln\left(1 - \frac{u}{\mu_0 H}\right)$$

$$-\frac{N}{2}\left(1 + \frac{u}{\mu_0 H}\right)\ln\left(1 + \frac{u}{\mu_0 H}\right)$$

$$= N\ln(2) - \frac{N}{2}\left(1 - \frac{u}{\mu_0 H}\right)\ln\left(1 - \frac{u}{\mu_0 H}\right) - \frac{N}{2}\left(1 + \frac{u}{\mu_0 H}\right)\ln\left(1 + \frac{u}{\mu_0 H}\right)$$

Then,

$$\lim_{\substack{E,N\to\infty \\ \frac{E}{N}=u}} \frac{1}{N}\ln(\Omega(E,N) = \ln(2) - \frac{1}{2}\left(1 - \frac{u}{\mu_0 H}\right)\ln\left(1 - \frac{u}{\mu_0 H}\right)$$

$$-\frac{1}{2}\left(1 + \frac{u}{\mu_0 H}\right)\ln\left(1 + \frac{u}{\mu_0 H}\right)$$

$$s(u) = k_B\ln(2) - \frac{1}{2}k_B\left(1 - \frac{u}{\mu_0 H}\right)\ln\left(1 - \frac{u}{\mu_0 H}\right)$$

$$-\frac{1}{2}k_B\left(1 + \frac{u}{\mu_0 H}\right)\ln\left(1 + \frac{u}{\mu_0 H}\right)$$

By the other hand,

$$\frac{1}{T} = \frac{\partial s}{\partial u} = -\frac{k_B}{2}\left(-\frac{1}{\mu_0 H}\right) - \frac{k_B}{2}\left(\frac{1}{\mu_0 H}\right)$$

$$+\frac{k_B}{2\mu_0 H}\ln\left(1 - \frac{u}{\mu_0 H}\right) - \frac{k_B}{2\mu_0 H}\ln\left(1 + \frac{u}{\mu_0 H}\right)$$

then

$$\exp\left(\frac{2\mu_0 H}{k_B T}\right) = \frac{1 - \frac{u}{\mu_0 H}}{1 + \frac{u}{\mu_0 H}} \longrightarrow \frac{u}{\mu_0 H} = \frac{1 - \exp\left(\frac{2\mu_0 H}{k_B T}\right)}{1 + \exp\left(\frac{2\mu_0 H}{k_B T}\right)}$$

$$= \frac{\exp\left(\frac{-\mu_0 H}{K_B T}\right) - \exp\left(\frac{\mu_0 H}{K_B T}\right)}{\exp\left(\frac{-\mu_0 H}{K_B T}\right) + \exp\left(\frac{\mu_0 H}{K_B T}\right)}$$

$$= - \tanh\left(\frac{\mu_0 H}{K_B T}\right)$$

Therefore,

$$u = -\mu_0 H \tanh\left(\frac{\mu_0 H}{K_B T}\right)$$

$$\frac{E}{N} = \frac{-\mu_0 H N_1 + \mu_0 H N_2}{N} \qquad N_1 \rightarrow \uparrow \qquad N_2 \rightarrow \downarrow$$

$$\rightarrow \quad u = -\frac{H}{N}(\mu_0 N_1 - \mu_0 N_2) = -Hm$$

$$\rightarrow \quad m = \mu_0 \tanh\left(\frac{\mu_0 H}{K_B T}\right) = m(T, H)$$

If $K_B T \gg \mu_0 H$, then $m = \frac{CH}{T}$, $C := \frac{\mu_0^2}{K_B}$.