Basic relations:

$$\langle E \rangle = -\left(\frac{\partial \ln Z}{\partial b}\right)_{N,V} = -\frac{1}{Z}\frac{\partial Z}{\partial b}$$

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$\langle S \rangle = -k_B \sum_i p_i \ln p_i$$

Helmholtz:

$$\langle F \rangle = -k_B T \ln Z \qquad\qquad F = E - TS$$

Note:

$$\begin{aligned} dF &= dE - TdS - SdT + mdN \\ &= -pdV - SdT + mdN \end{aligned}$$

Thus:

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad m = \left(\frac{\partial F}{\partial N}\right)_{V,T}$$

The *N*-particle partition function for *distinguishable* particles is:

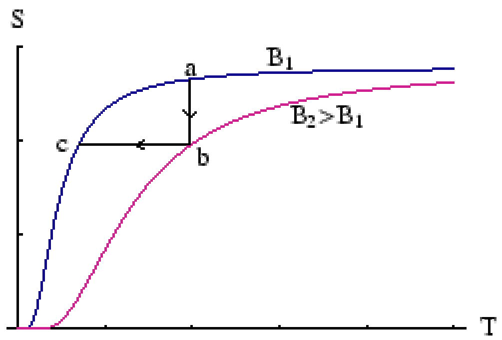
$$Z_N = (Z_1)^N$$

Notice:

$$\begin{aligned} \langle F \rangle &= -k_B T \ln Z_N \\ &= -k_B T \ln Z_1^N \\ &= -N k_B T \ln Z_1 \end{aligned}$$

Thus F is an extensive quantity

Adiabatic demagnetisation:



Basically, increase mag.field…at a constant temp. Thus the entropy will decrease.

Then decrease the mag.field, keeping the entropy constant… hence the temp lowers. Repeat!

3rd Law of Thermodynamics:

In a finite number of steps, absolute zero is unobtainable.

Vibrational energy states:

$$e_n = \left(n + \frac{1}{2}\right)\hbar w$$

Thus, the partition function is:

$$Z_1 = \sum_{n=0}^{\infty} e^{-e_n b} = \ldots = \frac{1}{2\sinh\left[\frac{1}{2}\hbar w b\right]}$$

And the energy is:

$$\langle E\rangle = -\frac{\partial \ln Z_1}{\partial b} = \tfrac{1}{2}\hbar w \coth\left(\tfrac{1}{2}\hbar w b\right)$$

Now, looking at limits:

$$\lim_{b\to\infty}\{\coth b\} = 1 \qquad [\Rightarrow T \to 0]$$

$$\lim_{b\to 0}\{\coth b\} = \frac{1}{b} \qquad [\Rightarrow T \to \infty]$$

Hence:

$$\lim_{T\to 0}\langle E\rangle = \tfrac{1}{2}\hbar w$$

$$\lim_{T\to\infty}\langle E\rangle = k_B T \qquad \approx T > 1000K$$

Rotation energy states:

$$e_\ell = \frac{\ell(\ell+1)\hbar^2}{2I} \qquad g(e_\ell) = 2\ell + 1$$

Thus, the one-body partition function can be written, using the degeneracy of rotation energy level:

$$Z_1 = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-\frac{\ell(\ell+1)\hbar^2 b}{2I}}$$

$$\lim_{T\to\infty} Z_1 = \int_0^\infty (2\ell+1) e^{-\frac{\ell(\ell+1)\hbar^2 b}{2I}} d\ell$$

$$= \frac{2I}{\hbar^2 b} = \frac{2Ik_B T}{\hbar^2}$$

$$\lim_{T\to\infty} \langle E \rangle = k_B T$$

These high-T limits are for:

$$k_B T >> \frac{\hbar^2}{2I}$$

Translational energy states:

$$e = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \qquad \left[T = \frac{p^2}{2m} \,\&\, p = \hbar k \right]$$

Where:

$$k^2 = k_x^2 + k_y^2 + k_z^2 \qquad k_i^2 = \left(\frac{n_i p}{L} \right)^2$$

Hence:

$$Z_1 = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-eb}$$

Will end up with defining the *Density of States*:

$$D(k) \equiv \frac{Vk^2}{2m}$$

$$Z_1 = \int_0^\infty D(k) e^{-be(k)} dk \qquad e(k) = \frac{\hbar^2 k^2}{2m}$$

End up being able to show that:

$\langle E \rangle$ due to translational motion, with 3 degrees of freedom = $\frac{3}{2} k_B T$

Equipartition Theorem:

For each degree of freedom of a system with an energy which is quadratic in either the relevant coordinate or momentum, the average energy is $\frac{1}{2} k_B T$.

e.g.:

2dof:	$E_{vib} = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}kx^2$	$\lim_{T\to\infty} = k_B T$
2dof:	$E_{rot} = \frac{1}{2}I_1\dot{q}_1^2 + \frac{1}{2}I_2\dot{q}_2^2$	$\lim_{T\to\infty} = k_B T$
3dof:	$E_{trans} = \frac{1}{2}m\left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2\right)$	$\lim_{T\to\infty} = \frac{3}{2}k_B T$

Where the high T limits are as follows:

Vib:	$T >> \frac{\hbar w}{k_B}$	$\sim 10^3 K$
Rot:	$T >> \frac{\hbar^2}{Ik_B}$	$\sim 10 - 100K$
Trans:	$T >> \frac{\hbar^2}{mV^{\frac{2}{3}}k_B}$	$\sim 10^{-14} K$

Indistinguishable particles:

e.g. system of 2 particles, with energy levels e_1 & e_2.

The partition function for such a system is:

$$Z_2 = e^{-2e_1 b} + e^{-(e_1+e_2)b} + e^{-2e_2 b}$$

If the system has many more accessible energy levels than it has particles (i.e. NOT in the above case), the following approximation may be used:

$$Z_N \approx \frac{Z_1^N}{N!}$$