1   Stat Mech Results and Methods

Our Return to th stat mech part... with systems A and heat reservoir A' where

$$A \ll A'$$

What is the prob of finding system A in a ny particular microstate r with energy E_r?

$$E_r + E' = E^{(0)}, \implies E' = E^{(0)} - E_r$$

And from the DoS the number of states in A' is

$$\Omega'(E^{(0)} - E_r)$$

or the Multiplicity of A' given E_r. The prob P_r has a proportionality

$$P_r \propto C'\Omega'(E^{(0)} - E_r)$$

Since $A \ll A'$ and $E_r \ll E^{(0)}$ we can take the log and Taylor expand

$$\ln \Omega'(E^{(0)} - E_r) = \ln \Omega'(E^{(0)}) - \left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E^{(0)}} E_r$$

where the derivative is the thermodynamic beta

$$\left.\frac{\partial \ln \Omega'}{\partial E'}\right|_{E^{(0)}} = \frac{1}{kT} = \beta$$

which is independent of E_r. So taking the exponential again...

$$\Omega'(E^{(0)} - E_r) = \Omega'(E^{(0)})e^{-\beta E_r} = Ce^{-\beta E_r}$$

where the $\Omega'(E^{(0)})$ is a constant, i.e.

$$P_r = Ce^{-\beta E_r}$$

This must be normalized by

$$\sum P_r = 1$$

or

$$C = \frac{1}{\sum e^{-\beta E_r}}$$

where the "Partition Function" is

$$Z \equiv \sum_r e^{-\beta E_r}$$

coined by Planck (1920) as "Zustandsumme" or "Sum over all states".

The probability is

$$P_r = \frac{e^{-\beta E_r}}{Z}$$

Where we have a "Boltzmann funtion" $e^{-\beta E_r}$ and P_r is the cannonincal distribution.

The probability of A having energy E is given by

$$P(E) = \frac{\Omega E e^{-\beta E}}{Z}$$

where the partition function Z is incredibly useful for

- Average energy: From P_r, E_r

$$\bar{E} = \sum_r P_r E_r = \frac{\sum_r e^{-\beta E_r} E_r}{Z}, \quad Z = \sum_r e^{-\beta E_r}$$

Using the mathematically useful fact

$$\frac{\partial Z}{\partial \beta} = -\sum_r E_r e^{-\beta E_r}$$

So we can get

$$\bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

which is just equivalent to

$$\boxed{\bar{E} = -\frac{\partial}{\partial \beta}(\ln Z)}$$

The variance of the change in energy is (NOTE: the square is inside because $(\overline{\Delta E})^2 = 0$)

$$\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2$$

where

$$\overline{E^2} = \sum_r P_r E_r^2 = \frac{\sum_r e^{-\beta E_r} E_r^2}{Z}$$

The top part is equivalent to the second derivative of Z

$$\frac{\partial^2 Z}{\partial \beta^2} = \sum_r e^{-\beta E_r} E_r^2$$

So

$$\overline{E^2} = \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2 = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right) + \frac{1}{Z}\left(\frac{\partial Z}{\partial \beta}\right)^2 = -\frac{\partial \bar{E}}{\partial \beta} + \bar{E}^2$$

where we get second part of the variance from above

$$\bar{E}^2 = \frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2$$

Thus

$$\overline{(\Delta E)^2} = -\frac{\partial \bar{E}}{\partial \beta} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

- Change in Work:

$$dW = \frac{\sum e^{beta E_r}\left(\frac{\partial E_r}{\partial x}dx\right)}{Z}$$

$$= \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}dx$$

$$dW = \bar{X}dx, \quad \boxed{\bar{X} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial x}}$$

Example: A spin-$\frac{1}{2}$ particle (or a two-level system) in a magnetic field B with magnetic moment μ so the two states are

- $\mu B \rightarrow |+\rangle$

- $-\mu B \rightarrow |-\rangle$

The partition function is

$$Z = \sum_r e^{-\beta E_r} = e^{\beta \mu B} + e^{-\beta \mu B} = 2\cosh(\beta \mu B)$$

Thus

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\mu B \frac{\sinh(\beta \mu B)}{\cosh(\beta \mu B)} = -\mu B \tanh(\beta \mu B)$$

And the temperature limits

$$T \rightarrow 0, \bar{E} = -\mu B$$
$$T \rightarrow \infty, \bar{E} = 0$$

Example: Harmonic Oscillator

$$E = \left(n + \frac{1}{2}\right)\hbar\omega$$

Thus the partition function is

$$Z = \sum e^{-\beta E_r} = \sum_{n=0}^{\infty} e^{-\beta(n+1/2)\hbar\omega}$$
$$= e^{\frac{1}{2}\beta\hbar\omega}\sum \left(e^{-\beta\hbar\omega}\right)^n$$

We can simplify the summation using a geometric series

$$\sum_n x^2 = 1 + x + x^2 + \cdots = \frac{1}{1-x}$$

Therefore

$$Z = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$$

and

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Looking at the temperature limits

- $T \rightarrow 0, \beta \rightarrow \infty \quad \bar{E} = \frac{1}{2}\hbar\omega$

- $T \rightarrow \infty, \beta \rightarrow 0 \quad \bar{E} \rightarrow \infty$

Example: Particle in a Box: the solution in 1D is

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

where we get this from the Schrödinger equation wavefunction for a infinite well

$$\psi(x) = A\sin\left(\frac{n_x\pi x}{L_x}\right), \quad k_x = \frac{n_x\pi}{L_x}$$

with boundary conditions $\psi(0) = \psi(L) = 0$. For the 3D box we remember

$$\psi = A\sin(k_x x)\sin(k_y y)\sin(k_z z)$$

where the momentum is $p = \hbar k$ and the energy is

$$E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)$$

In k-space the volume of a point (microstate) is

$$k_x k_y k_z = \frac{\pi^3}{L_x L_y L_z} = \frac{\pi^3}{V}$$

We assume the box is large, so in the range $k \to k + dk$. The volume of the "orange peel" in this range divided by the volume in k-space is

$$\Omega(k) = \frac{1}{8}\frac{4\pi k^2 dk}{\pi^3/V} = \frac{V}{2\pi^2}k^2 dk$$

Note: the k-space is spherical since the vector basis is

$$k = \sqrt{k_x^2 + k_y^2 + k_z^2}$$

and we only deal with positive k_i i.e. the positve x, y, z octant in the Cartesian k-space.

The partition function is then

$$Z = \int_0^\infty \Omega(k)e^{-\beta\frac{\hbar^2 k^2}{2m}}\,dk = \frac{V}{2\pi^2}\int_0^\infty k^2 e^{-\beta\frac{\hbar^2 k^2}{2m}}\,dk$$
$$= \frac{V}{2\pi^2}\frac{\sqrt{\pi}}{4}\left(\frac{2m}{\beta\hbar}\right)^{3/2}$$

or

$$\boxed{Z = \left(\frac{2m}{\hbar^2\pi}\right)^{3/2}\beta^{-3/2}V}$$

Multiple Particles: The system

$$A^{(0)} = A + A', \quad \text{For} \quad A^{(0)}, \quad E_{r,s}^{(0)} = E_r + E_s'$$

and

$$A' \text{ has } E_s, \quad Z^{(0)} = \sum_{r,s} e^{-\beta E_{r,s}^{(0)}}$$

The partition function

$$Z^{(0)} = \sum_{r,s} e^{-\beta(E_r + E_s')}$$
$$= \sum_r e^{-\beta E_r}\sum_s e^{-\beta E_s'} = ZZ'$$

So for N particles

$$Z_N = \left[\left(\frac{2m}{\hbar^2 \pi} \right)^{3/2} \beta^{-3/2} V \right]^N$$

The average Energy is now

$$\bar{E} = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{3}{2} NkT$$

Density of States   For average pressure is equivalent to the generalized force so

$$\bar{P} = \frac{1}{\beta} \frac{\partial (\ln Z)}{\partial V} = \frac{1}{\beta} N \frac{1}{V}$$
$$= \frac{NkT}{V}$$

thus

$$\bar{P} V = NkT$$

Connection to Thermo   For $Z(\beta, x)$ the differential is mathematically stated by

$$d \ln Z(\beta, x) = \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial x} dx$$

or

$$d \ln Z = -\bar{E} d\beta + \beta đW$$
$$= (\beta đW - d(\bar{E}\beta)) + \beta d\bar{E}$$
$$d(\ln Z + \bar{E}\beta) = \beta(đW + d\bar{E}) = \beta đQ$$
$$= \frac{1}{k} dS$$

Thus the entropy of an ideal gas system is

$$S = k(\ln Z + \bar{E}\beta)$$

so using $\bar{E} = \frac{3}{2} NkT$ we get

$$S = Nk \left[\frac{3}{2} \ln \left(\frac{2m}{\hbar^2 \pi} \right) - \frac{3}{2} \ln(\beta) + \ln(V) + \frac{3}{2} \right]$$

where

$$\frac{3}{2} \ln \beta = \frac{3}{2} \ln k + \frac{3}{2} \ln T$$

so

$$S = Nk \left(\ln V + \frac{3}{2} \ln T + \sigma_0 \right), \quad \sigma_0 = \frac{3}{2} \ln \left(\frac{2m}{\hbar^2 \pi} \right) + \frac{5}{2}$$

Two Issues:

- The second law is violated: $T \to 0$ which implies $S \to -\infty$

- Gibbs paradox: