

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...

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

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

$$P_r = C e^{-\beta E_r}$$

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 cannonical 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:

$$\begin{aligned} dW &= \frac{\sum e^{\beta E_r} \left(\frac{\partial E_r}{\partial x} dx \right)}{Z} \\ &= \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} dx \\ dW &= \bar{X} dx, \quad \boxed{\bar{X} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial x}} \end{aligned}$$

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

$$\begin{aligned} T \rightarrow 0, \bar{E} &= -\mu B \\ T \rightarrow \infty, \bar{E} &= 0 \end{aligned}$$

Example: Harmonic Oscillator

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

Thus the partition function is

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

We can simplify the summation using a geometric series

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

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

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

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 $k \rightarrow k + dk$. 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 positive x, y, z octant in the Cartesian k -space.

The partition function is then

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

or

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

Multiple Particles: The system

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

and

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

The partition function

$$\begin{aligned} Z^{(0)} &= \sum_{r,s} e^{-\beta(E_r + E'_s)} \\ &= \sum_r e^{-\beta E_r} \sum_s e^{-\beta E'_s} = Z Z' \end{aligned}$$

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

$$\bar{E} = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{3}{2} N k T$$

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

$$\begin{aligned} \bar{P} &= \frac{1}{\beta} \frac{\partial (\ln Z)}{\partial V} = \frac{1}{\beta} N \frac{1}{V} \\ &= \frac{N k T}{V} \end{aligned}$$

thus

$$\bar{P} V = N k T$$

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

$$\begin{aligned} d \ln Z &= -\bar{E} d\beta + \beta dW \\ &= (\beta dW - d(\bar{E}\beta)) + \beta d\bar{E} \\ d(\ln Z + \bar{E}\beta) &= \beta(dW + d\bar{E}) = \beta dQ \\ &= \frac{1}{k} dS \end{aligned}$$

Thus the entropy of an ideal gas system is

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

so using $\bar{E} = \frac{3}{2} N k T$ we get

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

where

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

so

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

Two Issues:

- The second law is violated: $T \rightarrow 0$ which implies $S \rightarrow -\infty$
- Gibbs paradox: $S > S' + S''$