Define $f = -kT \ln Z$

$$\frac{df}{dT} = \frac{f-U}{T} \qquad \frac{dF}{dT} = \frac{F-U}{T}$$

At $T=0$,

$$F = U - TS = U = \langle E \rangle$$

ground state has $E=0$ $\qquad P_s = \frac{e^{-\beta E_s}}{Z} \qquad P_{gnd} = \frac{1}{Z}$

$$P_{other} = \frac{e^{-E_s/kT}}{Z}$$

$$Z = 1 + \sum_{excited} e^{-E_s/kT}$$

0 at $T=0$

$Z = 1 \qquad P_{gnd} = 100\% \qquad P_{excited} = 0\%$

$$F = \langle E \rangle = E_{gnd} = 0$$

$$f = -kT \ln Z = -kT \ln 1 = 0.$$

F & f obey same 1st-order diff. eq.

& same boundary condition $T=0$

$$\therefore \quad \boxed{F = -kT \ln Z} \qquad Z = e^{-F/kT}$$

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{\partial}{\partial N}\left(-kT \ln Z\right) = -kT \frac{\partial \ln Z}{\partial N}$$

Composite Systems

Consider 2-particle system, distinguishable particles

Let S be state of both combined

e.g. 2 coins $S \in \{HH, HT, TH, TT\}$

$$Z = \sum_S e^{-\beta E_S}$$

if particles don't interact, $E_S = E_{S_1} + E_{S_2}$

$$Z = \sum_{S_1} \sum_{S_2} e^{-\beta E_{S_1}} e^{-\beta E_{S_2}} = \left(\sum_{S_1} e^{-\beta E_{S_1}}\right)\left(\sum_{S_2} e^{-\beta E_{S_2}}\right)$$

$$Z = Z_1 Z_2$$

if particles are indistinguishable

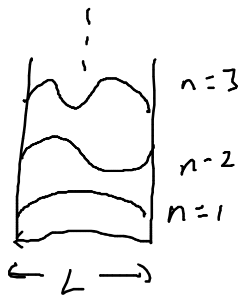
$Z_2 = Z_1$ $$Z = \frac{1}{2!} Z_1^2$$ or else I will overcount (just as with Ω)

For N indistinguishable particles

$$\boxed{Z = \frac{1}{N!} Z_1^N}$$

One Particle of an Ideal Gas

in a 1D box of length L



$$\lambda_n = \frac{2L}{n}$$

deBroglie

$$p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}$$

$$E_n = \frac{p_n^2}{2m} = \frac{h^2}{8mL^2} n^2$$

$$Z = \sum_{n=1}^{\infty} e^{-\beta \frac{h^2}{8mL^2} n^2} \xrightarrow{L,T \text{ big}} \int_0^\infty e^{-\frac{h^2}{8mL^2kT} n^2} \, dn$$

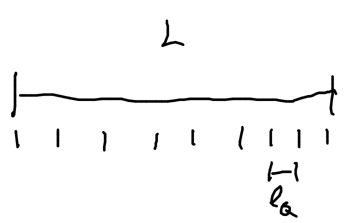
$$Z = \frac{L}{\ell_Q}$$

quantum length

$$\ell_Q = \frac{h}{\sqrt{2\pi m kT}}$$

"pixel size"

$$Z \propto T^{1/2}$$



$$Z = 8$$

For small pixels, integration is allowed

$$Z = \frac{L}{\ell_Q} \quad \text{if} \quad \ell_Q \ll L$$

e.g. N_2 has $\ell_Q = 2\times10^{-11}\,m$ @ 300K

but $\ell_Q \propto \frac{1}{\sqrt{T}}$, so colder $T \rightarrow$ larger pixels

in 3D,

$$Z = Z_x Z_y Z_z = \frac{V}{V_Q} \qquad V_Q = \ell_Q^3 = \frac{h^3}{(2\pi m kT)^{3/2}}$$

$$Z = C\,T^{3/2} = C'\,\beta^{-3/2}$$

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\left(\frac{\partial}{\partial \beta}\left(-\frac{3}{2}\ln \beta\right)\right) = \frac{3}{2}\frac{1}{\beta} = \frac{3}{2}kT.$$

More generally,

$$Z_1 = \frac{V}{V_Q} Z_{int}$$

partition function for internal degrees of freedom (rotation, vibration)

ideal gas of N particles

$$\boxed{Z = \frac{1}{N!}\left(\frac{V Z_{int}}{V_Q}\right)^N} \qquad V_Q = \frac{h}{(2\pi m)^{3/2}} \beta^{3/2}$$