L26: review

Constant E: $P_j = \frac{1}{W}$; W is the number of microstates accessible at energy E

constant T: $P_j = \frac{W_j e^{-E_j/RT}}{Z}$; Z indicates the # of microstates accessible at temperature T

$Z = e^{-\frac{F}{RT}}$; $F = E - TS$

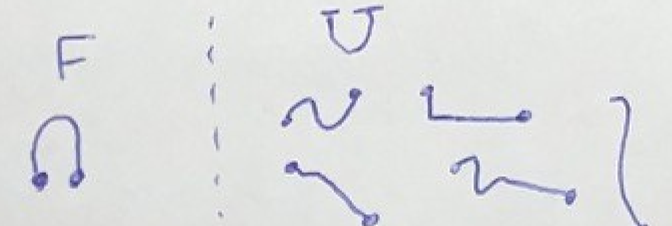
$Z = \sum W_j e^{-E_j/RT}$

(sometimes β is used instead of $\frac{1}{RT}$:

$Z = e^{-\beta F}$)

Example: protein hairpin folding

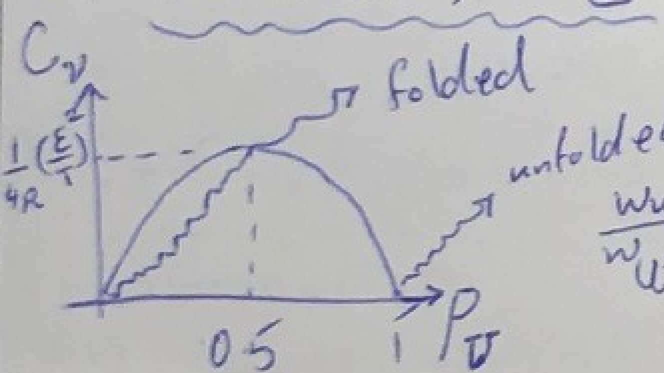
1) System info:

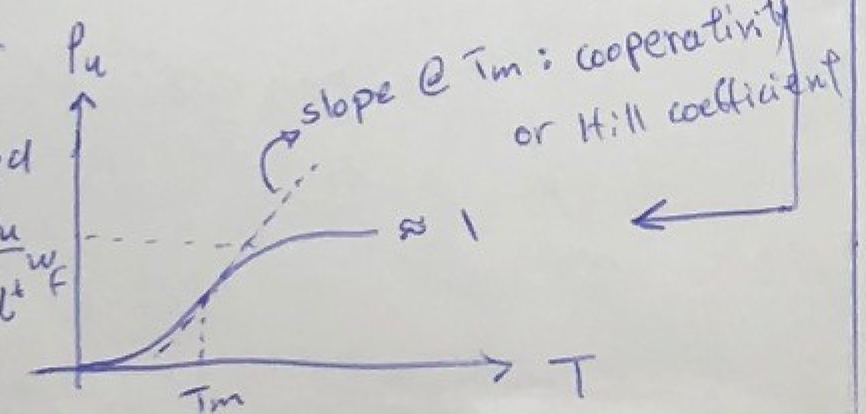


$W_F < W_U$

$E_F < E_U$

2) Postulates, Z





Today: two more systems, this time getting system info from QM

ex #1: energy & heat capacity of an ideal gas (or solution) at constant temperature

use result from homework S4.2:

$\beta \equiv \frac{1}{k_B T}$: $Z = e^{-\beta F} = e^{-\beta E + \frac{S}{k_B}}$

$\Rightarrow -\frac{\partial Z}{\partial \beta} = E\, e^{-\beta E + \frac{S}{k_B}} = E \cdot Z$

$\Rightarrow \boxed{E = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}}$ → true for any system at constant T

info about the system:

"Particle in a box" is just a particle moving around in a box of length L.

$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$

* note that in stat mech we only care about E and we can ignore the wavefunction ψ!

$$Z = \sum_{n_x, n_y, n_z = 1}^{\infty} 1 \cdot e^{-\beta \{\frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)\}}$$

$$\approx \int_1^{\infty} dn_x \int_1^{\infty} dn_y \int_1^{\infty} dn_z \, e^{-\beta \frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)}$$

$$\approx \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \, e^{-\beta \frac{h^2}{8mL^2}(n_x^2+n_y^2+n_z^2)}$$

$$= \int_0^{\infty} dn_x \int_0^{\infty} dn_y \int_0^{\infty} dn_z \left(e^{-\beta \frac{h^2}{8mL^2} n_x^2}\right)\left(e^{-\beta \frac{h^2}{8mL^2} n_y^2}\right)\left(e^{-\beta \frac{h^2}{8mL^2} n_z^2}\right)$$

$$\Rightarrow Z \approx \left(\int_0^{\infty} dn_x \, e^{-\beta \frac{h^2}{8mL^2} n_x^2}\right)\left(\int_0^{\infty} dn_y \, e^{-\beta \frac{h^2}{8mL^2} n_y^2}\right) \cdot \left(\int_0^{\infty} dn_z \, e^{-\beta \frac{h^2}{8mL^2} n_z^2}\right) = \left(\int_0^{\infty} dx \, e^{-\beta \frac{h^2}{8mL^2} x^2}\right)^3$$

$$= \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V, \quad V \equiv L^3$$

* note that in deriving line 2 from line 1, the summation has been approximated by an integral; this is valid because the exponents of the function are small

$$\Rightarrow E_1 = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} =$$

one particle

$$= -\left(\frac{\beta h^2}{2\pi m}\right)^{3/2} \cdot \frac{1}{V} \cdot \left(\frac{2\pi m}{h^2}\right)^{3/2} \cdot V \cdot \left(-\frac{3}{2}\right)\beta^{-5/2}$$

$$= \frac{3}{2}\beta^{-1}$$

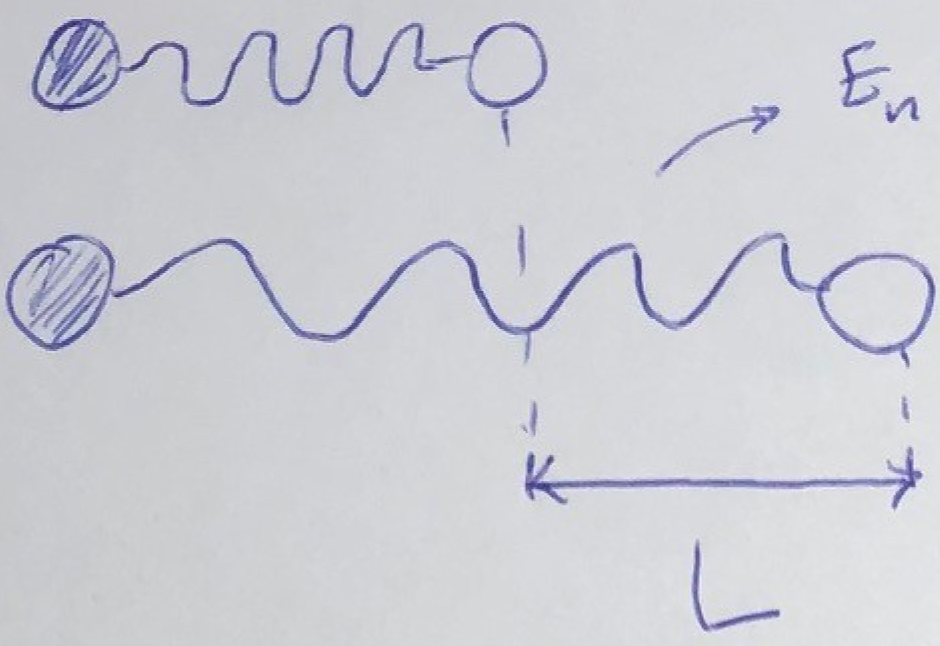
For N particles: $E \to N E_1$

$$\Rightarrow E = \frac{3}{2} N \beta^{-1} \Rightarrow E = \frac{3}{2} N k_B T = \frac{3}{2} nRT$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} nR$$

↳ this system has 3 degrees of freedom, so "per degree of freedom, the system has energy $\frac{1}{2} k_B T$"
("Equipartition theorem")
↳ this only holds at high T (so we can approximate the summation by an integral in the previous page)

ex #2: spring at constant temperature T that is randomly bouncing



$E_n = \hbar\omega(n+\frac{1}{2}) = h\nu(n+\frac{1}{2})$

: Stored potential energy $= \frac{1}{2} k_B T$

Spring moves $\Rightarrow$ kinetic energy $= \frac{1}{2} k_B T$

what is Z for the spring

$$Z = \sum_{n=0}^{\infty} 1 \cdot e^{-\frac{\hbar\omega n}{k_B T}} = \sum_{n=0}^{\infty} \left(e^{-\frac{\hbar\omega}{k_B T}}\right)^n$$

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}, \quad x<1$$

$$\Rightarrow Z = \frac{1}{1-e^{-\frac{\hbar\omega}{k_B T}}}$$