Partition Functions: A recap

- We have described several thermodynamic functions which are useful

$$U \, , \quad F = U - TS \, , \quad H = U + PV \, , \quad G = U + PV - TS$$

Now we will discuss how to compute these systematically using partition functions.

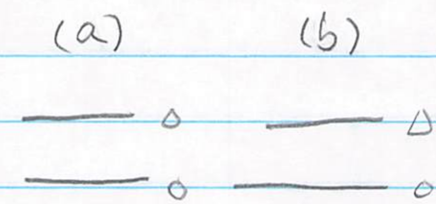
Partition Function when Energy is a sum of energies:

- First consider a system consisting of two atoms, each of which can be in one of two states of energy

atom (a) and atom (b)

$\varepsilon_i^{(a)} = 0, \Delta$ or $\varepsilon_j^{(b)} = 0, \Delta$

$$E_{TOT} = \varepsilon_i^{(a)} + \varepsilon_j^{(b)}$$



- There are four states

$$(0,0), \; (0,\Delta), \; (\Delta,0), \; (\Delta,\Delta)$$

(Technically we are assuming that (a) and (b) are distinguishable) Thus $(0,\Delta)$ and $(\Delta,0)$ are two states, not the same state.

- Now

$$Z_{TOT} = \sum_{i,j=0}^{\Delta} e^{-E_{TOT}/kT}$$

$$= \sum_{i,j} e^{-(\varepsilon_i^{(a)} + \varepsilon_j^{(b)})/kT}$$

$$= \sum_{i,j} e^{-\varepsilon_i^{(a)}/kT} \, e^{-\varepsilon_j^{(b)}/kT}$$

$$= \sum_i e^{-\varepsilon_i^{(a)}/kT} \sum_j e^{-\varepsilon_j^{(b)}/kT} = Z^{(a)} Z^{(b)}$$

- So if the energy breaks up into a sum of energies, the partition function factorizes into a product

$$\boxed{Z_{TOT} = Z^a Z^b}$$

- Now the free energy is

$$F_{TOT} = -k_B T \ln Z_{TOT} \qquad \text{(see home work)}$$

$$F_{TOT} = -k_B T \ln Z^{(a)} - k_B T \ln Z^{(b)}$$

$$F_{TOT} = F^{(a)} + F^{(b)}$$

- If System (a) and (b) have the same energy levels (as in this example) then $F^{(a)} = F^{(b)}$ and

$$F_{TOT} = 2F^{(a)}$$

- Clearly this generalizes to N distinguishable systems. If the energy is a sum of energies (with the same energy level scheme, for simplicity)

$$E = \varepsilon_i^{(1)} + \varepsilon_j^{(2)} + \varepsilon_k^{(3)} + \ldots \ldots \varepsilon^{(N)}$$

$$Z = \sum_{ijk\ldots} e^{-E/kT} = Z_1^N$$

Where

$$Z_1 = \sum_i e^{-\varepsilon_i/kT}$$

- So in this case

$$F_{TOT} = -k_B T \ln Z_{tot} = -k_B T \ln Z_1^N = -N k_B T \ln Z_1$$

$$\boxed{F_{TOT} = N F_1}$$

(for total system of N distinguishable subsystems with the same level scheme)

- We had this in homework. For one harmonic oscillator we had

$$Z_1 = \frac{1}{1 - e^{-\hbar\omega\beta}}$$

The oscillators are separated in space and are distinguishable

- For N harmonic oscillators

$$F_{TOT} = -N k_B T \ln Z_1 = + N \underbrace{k_B T \ln(1 - e^{-\hbar\omega\beta})}_{=F_1}$$

- Then

$$S_{TOT} = -\frac{\partial F_{TOT}}{\partial T} = N\left(-\frac{\partial F_1}{\partial T}\right) = N S_1 \xrightarrow{\text{homework}} = N\left(\frac{\beta\hbar\omega}{e^{\hbar\omega\beta} - 1} - \ln(1 - e^{-\beta\hbar\omega})\right)$$

- Note we have $F_{TOT} = U_{TOT} - T S_{TOT}$ so

$$U_{TOT} = F_{TOT} + T S_{TOT} = N \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} = N U_1$$

So $S_{TOT} = N S_1$ and $U_{TOT} = N U_1$ etc
since $Z_{TOT} = Z_1^N$.