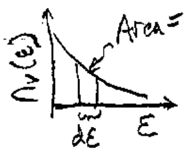
Statistical Mechanics in 75 minutes SM.1

Recall from lecture 3: $n_v(\varepsilon) = \underbrace{n_0}_{\text{Normalizer}} \underbrace{e^{-\varepsilon/k_BT}}_{\text{Boltzmann factor}}$ ← Boltzmann constant

$n_v(\varepsilon)$ is the "number density" distribution function defined so:



$$n_v(\varepsilon)d\varepsilon = \#\ \text{particles}/_V \text{ w/ energy } \varepsilon$$

Thus: $\dfrac{\cancel{n_0} e^{-\varepsilon_1/k_BT}}{\cancel{n_0} e^{-\varepsilon_2/k_BT}} = \dfrac{P(\varepsilon_1)}{P(\varepsilon_2)}$, where $P(\varepsilon_i)$ is the probability of being in the state with ε_i energy

This is the central result of Stat. Mech. for <u>closed</u> systems.

Can we find a similar ratio for <u>open</u> systems by using μ?

First let's define $Z(T)$, the partition function: $Z = \sum_i e^{-\varepsilon/k_BT}$
such that $P(\varepsilon_i) = e^{-\varepsilon_i/k_BT}/Z$

Now we do like we did to get $\underset{\text{average velocity}}{\langle v\rangle} = \int_0^\infty \underset{\text{velocity ("observable")}}{v}\, \overbrace{F(v)}^{\text{probability ("distribution")}} dv$ (see reading for lecture 3)
i.e.: multiply an "observable" by a "distribution" and sum (or integrate)

Do this for ε as the "observable": $U = \langle\varepsilon\rangle = \sum_i \varepsilon_i P(\varepsilon_i) = \dfrac{\sum \varepsilon_i e^{-\varepsilon_i/k_BT}}{Z}$

if we write out the last expression as: $\dfrac{\sum_i \varepsilon_i e^{-\varepsilon_i/k_BT}}{\sum_i e^{-\varepsilon_i/k_BT}}$ we see

this is the same as $\dfrac{(k_BT)^2}{\sum_i e^{-\varepsilon_i/k_BT}} \cdot \dfrac{d\sum e^{-\varepsilon_i/k_BT}}{dT}$ $\left(\dfrac{d\left(\frac{-\varepsilon_i}{k_BT}\right)}{dT} \text{ gives the } {+\varepsilon_i}/(k_BT)^2\right)$

From our Clausius-Clapeyron derivation we know $\dfrac{1}{P}\dfrac{dP}{dT} = \dfrac{d\ln P}{dT}$
So we use this same trick to get $U = (k_BT)^2 \dfrac{d\ln Z}{dT}$

$$\int_0^\infty e^{-x^2}dx = \frac{\pi^{1/2}}{2}$$

SM.2

We can use this result to show $U_{\text{ideal gas}} = \frac{3}{2}k_B T$

but first let's consider the ideal gas as N "$\underbrace{\text{particles-in-a-box}}_{\text{P-in-a-B}}$"

we know (or will learn) that the P-in-a-B energy levels are:

Planck's → $h/2\pi$ →

$$E_n = \underbrace{\frac{\hbar^2}{2M}\left(\frac{\pi}{L}\right)^2}_{\alpha}(n_x^2+n_y^2+n_z^2) \quad \text{for } n\text{'s } 1, 2, \ldots$$

where M is particle mass and L is the Box's length

$$\text{So } Z_{1\,\text{particle}} = \sum_{n's} e^{-\left(\frac{\alpha(n_x^2+n_y^2+n_z^2)}{k_B T}\right)} \approx \int_0^\infty e^{-\frac{\alpha(n_x^2-n_y^2-n_z^2)}{k_B T}} \underset{\text{all } n's}{dN}$$

we can look up this integral for n_x and cube the result

$$Z \to \left(\frac{\pi}{8}^{3/2}\right)\cdot\left(\frac{\hbar^2\pi^2}{2ML^2}\right)^{3/2}\cdot\left(\frac{1}{k_B T}\right)^{3/2} = \frac{V}{(2\pi\hbar^2/Mk_B T)^{3/2}} = V\cdot n_Q$$

where $V = L^3$ and $n_Q \equiv (Mk_B T/2\pi\hbar^2)^{3/2}$ ← quantum conc.

This "quantum concentration" tells us at what conc. we have to start dealing with non-classical effects; (for He, $n_Q = 13{,}300\,M$)

$$\text{Since } \ln Z = -\frac{3}{2}\ln\frac{1}{k_B T} + \underset{\text{terms}}{T\text{ indep.}} \to U = (k_B T)^2\frac{d\ln Z}{dT} = +\frac{3}{2k_B}\,\frac{1}{T}\,(k_B T)^2 = \boxed{\frac{3}{2}k_B T}$$

So, what have we accomplished? We started with the Boltzmann distribution law that tells us the "distribution" and used it to find the average value of an "observable," in this case energy $\langle\varepsilon\rangle$ or U, and showed it $= (k_B T)^2\frac{d\ln Z}{dT}$ where Z is the partition function that normalizes the distribution. Finally, we found the particular form of Z for an ideal gas (particle-in-a-box) and used this Z to show $\langle\varepsilon\rangle = \frac{3}{2}k_B T = U$

For N_A particles $Z_N = \frac{1}{N!}\cdot Z_{1\,\text{particle}}^{N_A}$ and $\langle\varepsilon\rangle = \frac{3}{2}N_A k_B T = \boxed{\frac{3}{2}RT}$

It's great we get $U_{\text{ideal gas}} = \frac{3}{2}RT$ from Stat. Mech, can we also get $PV = NRT$? Yes!

Start with the definition of Helmholtz Free Energy:

(closed system) $\boxed{F = U - TS}$ and $dF = -PdV - SdT$

so $\left(\frac{\partial F}{\partial T}\right)_V = -S$ and $F = U + T\left(\frac{\partial F}{\partial T}\right)_V \rightarrow -\frac{U}{(k_BT)^2} = -\frac{F}{(k_BT)^2} + \left(\frac{\partial F}{\partial T}\right)\frac{1}{T k_B{}^2}$

by the same trick we used in the Gibbs-Helmholtz: $-\frac{U}{(k_BT)^2} = \frac{\partial\left(\frac{F}{k_BT}\right)}{\partial T}$

if we let $\frac{F}{k_BT} = -\ln Z$ we get $\frac{-U}{(k_BT)^2} = \frac{-d\ln Z}{dT}$ or $U = (k_BT)^2\frac{d\ln Z}{dT}$

since this is our U from before $\frac{F}{k_BT}$ must really be $-\ln Z$ or $F = -k_BT\ln Z_N$ for N particles.

Substitute in $Z_N = \frac{1}{N!}Z_{1\,\text{particle}}^N$ and use Stirling's approx.

$$F = -k_BTN\underbrace{\ln Z_{1\,\text{part.}}}_{(\ln V + \ln n_Q)} + k_BTN\ln N - k_BTN \quad \text{and since} \left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$-P = -k_BTN\left(\frac{1}{V}\right) \quad \text{i.e.} \quad PV = k_BNT \rightarrow \text{if } N \text{ is moles} \rightarrow = NRT$$

What have we accomplished now? We used macroscopic-thermo-like manipulations to relate U and F and used the micro-thermo (i.e. stat. mech.) result that U can be expressed as a function of Z to relate F and Z. Then using the macroscopic-thermo result, $\left(\frac{\partial F}{\partial V}\right)_T = -P$ we reduced $dF(Z)/dV$ to the $\boxed{\text{ideal gas eqn}}$, which is similar to how we will get μ (next...)

Our original question was: can we find a $\frac{P(\varepsilon_1)}{P(\varepsilon_2)}$ like ratio for open systems?
→ we now have the tools we need to do this.

In the end we want $\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = \frac{e^{(\text{something})}}{e^{(\text{something})}}$, so what's "something"

we know this ratio $= \frac{\Omega(N_1,\varepsilon_1)}{\Omega(N_2,\varepsilon_2)}$ where Ω is "# of ways" and
$S = k_B \ln \Omega$, so $\hookrightarrow = e^{\frac{S(N_1,\varepsilon_1)}{k_B}} / e^{\frac{S(N_2,\varepsilon_2)}{k_B}} = e^{-\Delta S/k_B}$

we don't know the exact form of $S(N,\varepsilon)$ but we can approximate it by: $S(N_0,\varepsilon_0) - S(N,\varepsilon) = S(N_0,\varepsilon_0) - N\left(\frac{\partial S}{\partial N_0}\right)_{U_0} - \varepsilon\left(\frac{\partial S}{\partial U_0}\right)_{N_0}$

$$\text{So } \Delta S = \left[\cancel{S(N_0,\varepsilon_0)} - N_1\left(\frac{\partial S}{\partial N_0}\right)_{U_0} - \varepsilon_1\left(\frac{\partial S}{\partial U_0}\right)_{N_0}\right] - \left[\cancel{S(N_0,\varepsilon_0)} - N_2\left(\frac{\partial S}{\partial N_0}\right)_{U_0} - \varepsilon_2\left(\frac{\partial S}{\partial U_0}\right)_{N_0}\right]$$

combine terms: $\Delta S = -(N_1-N_2)\underbrace{\left(\frac{\partial S}{\partial N_0}\right)_{U_0}}_{-\mu/T} - (\varepsilon_1-\varepsilon_2)\underbrace{\left(\frac{\partial S}{\partial U_0}\right)_{N_0}}_{1/T} = \frac{(N_1-N_2)\mu}{T} - \frac{(\varepsilon_1-\varepsilon_2)}{T}$

thus $\boxed{\frac{P(N_1,\varepsilon_1)}{P(N_2,\varepsilon_2)} = e^{\frac{N_1\mu-\varepsilon_1}{k_BT}} \Big/ e^{\frac{N_2\mu-\varepsilon_2}{k_BT}}}$ chemical potential is key!

don't forget k_B

We should normalize as before, this time with $\mathcal{Z} = \sum_{ASN} e^{\frac{(N\mu-\varepsilon)}{k_BT}}$
Grand or Gibbs sum → "All States + # (of particles)"

Now we can get the "observables" for open systems: $\langle N \rangle = \frac{\sum_{ASN} N e^{\frac{(N\mu-\varepsilon)}{k_BT}}}{\mathcal{Z}}$
since $\frac{d\mathcal{Z}}{d\mu} = \frac{1}{k_BT}\sum_{ASN} N e^{(N\mu-\varepsilon)/k_BT}$, $\langle N \rangle = \frac{k_BT}{\mathcal{Z}}\frac{d\mathcal{Z}}{d\mu} = k_BT\frac{d\ln\mathcal{Z}}{d\mu}$
do this also for $\langle \varepsilon \rangle = U = \left(k_BT\frac{d}{d\mu} - \frac{d}{d(1/T)}\right)\ln\mathcal{Z}$

Finally, what is μ in stat. mech? Recall: $F = -k_BTN[\ln Z_{1\,part} - \ln N!]$

but $\frac{\partial \ln N!}{\partial N} = \frac{\partial(N\ln N - N)}{dN} = \left(1\cdot\ln N + N\underbrace{\frac{d\ln N}{dN}}_{\frac{N}{N}\frac{dN}{dN}}\right) - 1 = \ln N$ so $\frac{dF}{dN} = \boxed{\mu} \Rightarrow$

$\Rightarrow -k_BT\ln Z_{1\,part} + k_BT\ln N = k_BT\ln\frac{N}{Z_{1\,part}} = k_BT\ln\frac{N}{n_Q V} = \boxed{k_BT\ln\frac{n}{n_Q}}$

What more did we accomplish? We used $S = k_B \ln \Omega$ and the macro-thermo relations: $\left(\frac{\partial S}{\partial N}\right)_u = \mu/T$ and $\left(\frac{\partial S}{\partial u}\right)_N = 1/T$ to get a probability ratio for open systems, and an absolute probability by normalizing with $\mathcal{Z}$ → like the partition function but called the "Gibbs" sum. We used the abs. prob. to get the average value of 2 "observables", $\langle N \rangle$ and $\langle \varepsilon \rangle$. We also showed $\boxed{\mu = k_B T \ln \frac{n}{n_Q}}$, where $n = N/V$ = conc. and n_Q = quantum conc.

Now we're ready to do some real-life examples!

Consider myoglobin and hemoglobin (Mb + Hb). Mb either has 0 or 1 O_2 molecules bound. Hb has, 0, 1, 2, 3, or 4 O_2's. Carbon monoxide is known to compete with O_2, even at low [CO]. Can we find the fraction of O_2 bound to Mb + Hb, and the energy of CO binding by using stat. mech? Yes!

<u>O_2 fraction in Mb</u>: $\mathcal{Z} = \sum_{ASN} \Big(\underbrace{e^{\mu/k_BT}}_{a\ (\text{activity})}\Big)^{N \leftarrow =1 \text{ for } 1\,O_2} e^{-\varepsilon/k_BT}$ for Mb, $\varepsilon = 0$ or ε_{O_2}, so

$\mathcal{Z}_{1O_2} = 1 + a_{O_2} e^{-\varepsilon_{O_2}/k_BT}$, we know $\mu = k_B T \ln \frac{n}{n_Q}$ so $a = e^{\frac{k_BT \ln n/n_Q}{k_BT}} = \frac{n}{n_Q} = \frac{\overset{\text{ideal gas}}{P}}{(k_BT)\, n_Q}$

$\frac{\Omega_{O_2}}{\mathcal{Z}_{1O_2}} = \text{Fraction } O_2 \text{ bound} = \overset{\text{probability}}{P}(N_{O_2}, \varepsilon_{O_2}) = \frac{a_{O_2} e^{-\varepsilon_{O_2}/k_BT}}{1 + a_{O_2} \underbrace{e^{-\varepsilon_{O_2}/k_BT}}_{X}} = \frac{a_{O_2} X}{1 + a_{O_2} X} = \frac{1}{(a_{O_2} X)^{-1} + 1} = \frac{1}{\frac{k_BT n_Q}{P} X^{-1} + 1}$

$= \frac{P}{k_BT n_Q X^{-1} + P} = \frac{P}{P_0 + P}$ where $P_0 = k_BT n_Q e^{+\varepsilon/k_BT}$ = Pressure when $\frac{[Mb\text{-}O_2]}{[Mb]} = 1$

macroscopically $P_0 = K_{eq}^{-1}$ for $O_2 + Mb \rightleftarrows Mb\text{-}O_2$, ↑this result gives us more insight

<u>O_2 fraction in Hb</u>: $\mathcal{Z}_{4O_2} = \frac{1}{4!} \mathcal{Z}_{1O_2}^4 = \frac{1}{24}\left[1 + a_{O_2} X\right]^4 = \frac{1}{24}\left[1 + 4 a_{O_2} X + \cdots + a_{O_2}^4 X^4\right]$

since $\mathcal{Z}_{4O_2} = \Omega_{\text{zero } O_2} + \Omega_{1O_2} + \cdots + \Omega_{4O_2}$, $P(1\,O_2) = \frac{\Omega_{1O_2}}{\mathcal{Z}} = \frac{\frac{1}{24}[4 a_{O_2} X]}{1/24\,[1 + a_{O_2} X]^4}$ and $P(4\,O_2) = \frac{a_{O_2}^4 X^4}{[1 + a_{O_2} X]^4}$

graphing these probabilities as a function of a_{O_2} gives  and 

SM 6

<u>CO poisoning</u>: at low conc. of CO relative to O_2 – such that the a_{CO} + a_{O_2} are 10^{-7} and 10^{-5} — we observe only 10% of Hb bound to O_2. What is the relative binding strengths of CO + O_2?

<u>First</u> given that 90% of Hb binds O_2 when $a_{O_2} = 10^{-5}$, solve for ε_{O_2}.

→ as for Mb $F_{O_2} = \frac{a_{O_2}X}{1+a_{O_2}X}$ (F_{O_2}: Fraction $\overset{O_2}{\wedge}$ bound) so $a_{O_2}X = \frac{F}{1-F} = \frac{0.9}{1-0.9} = 9$

→ $X = e^{-\varepsilon_{O_2}/k_BT}$, $\varepsilon_{O_2} = -k_BT \ln\left(\frac{9}{a_{O_2}}\right) = -1.38\times10^{-23}\,\text{J/K}\cdot(273+37)\,\text{K}\,\ln\left(\frac{9}{10^{-5}}\right) = -5.9\times10^{-20}\,\text{J}$

$E^{O_2}_{bind} = 35\,\text{kJ/mol}$

Now solve for ε_{CO}. $F_{O_2} = \frac{a_{O_2}X}{\mathcal{Z}} = \frac{a_{O_2}X}{1+a_{O_2}X+a_{CO}y}$ $\quad y = e^{-\varepsilon_{CO}/k_BT}$

For $a_{O_2}X = 9$ and $F_{O_2} = 0.1$ we get $a_{CO}y = \frac{a_{O_2}X}{F_{O_2}} - (1-a_{O_2}X) = 90-(10) = 80$

→ $y = e^{-\varepsilon_{CO}/k_BT}$, $\varepsilon_{CO} = -k_BT\ln\left(\frac{80}{a_{CO}}\right) = -1.38\times10^{-23}\,\text{J/K}\cdot(310\,\text{K})\cdot\ln\left(\frac{80}{10^{-7}}\right) = -8.77\times10^{-20}\,\text{J}$

$E^{CO}_{Bind} = 53\,\text{kJ/mol}$, $E^{CO}_{bind} - E^{O_2}_{bind} = 18\,\text{kJ/mol}$ → big difference! $RT \approx 2.6\,\text{kJ/mol}$

So, we get a variety of things with the tools of stat. mech.

→ The overall strategy is to find $\mathcal{Z}$ (or Z for a closed system) either at the detail of knowing ε, like for a P-in-a B, or more generically, like for ε_{O_2} and ε_{CO}, in which we don't know the details of ε.

→ Once we have $\mathcal{Z}$ we can find fraction bound, populations, etc., just like we get from $K_{eq} = e^{-\Delta G/RT}$, with added insight into the connection between the molecular energies and the distributions.

→ We also use $\mathcal{Z}$ to get "observables", some of which allow us to show the molecular bass for empirical laws, like $PV = NRT$ or $U = \frac{3}{2}RT$.

→ Chemical potential, μ, is the theme of our Thermo class. Knowing μ and T tells us how particles and heat will flow. Typically $\mu = RT\ln \frac{P}{P_0}\}$ or $\frac{C}{C_0}$ or $\frac{\text{moles}}{\text{moles}_{Total}} = x$, but via stat. mech we learned $\mu = k_BT\ln\frac{n}{n_Q}$ where the denominator (normalizer) is n_Q: quantum conc. This means we have an "absolute zero" for μ just like for T, some systems break this zero (fermions), just as "neg. temp" do w/ T, but others (bosons) obey it.