Phys. 301 Fall 2019

## Lec #9+ more on chemical potential

refer to p. 3.37.

$U_K \equiv$ molecular kinetic energy

Sackur-Tetrode eq

$$S = Nk\left[\ln\left(V\left(\frac{4\pi m U_K}{3h^2}\right)^{3/2}\right) + \frac{5}{2}(\ln N - 1)\right]$$

chemical potential

$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V} = k\ln\left(\frac{V}{N}\left(\frac{4\pi m U_K}{3h^2}\right)\right)$$

now that derivative is done we may substitute $U_K = \frac{3}{2}NkT$,

$$-\frac{\mu}{T} = k\ln\left(\frac{V}{N}\frac{1}{\ell_Q^3}\right)$$

We also have $\mu = \left(\frac{\partial U_K}{\partial N}\right)_{S,V} \neq \frac{\partial}{\partial N}(NkT) = kT$

& must keep S constant.

if we consider molecules varying in height in constant temp. atmosphere,

$$U(z) = U_K + Nmgz$$

$$\mu(z) = \left(\frac{\partial U}{\partial N}\right)_{S,V} = \left(\frac{\partial U_K}{\partial N}\right)_{S,V} + mgz$$

$$= -kT\ln\left(\frac{V}{N}\frac{1}{\ell_Q^3}\right) + mgz$$

Now $F = U - TS = -kT \ln Z$

$$\frac{\partial \ln Z}{\partial N} = \frac{\ln Z(N) - \ln Z(N-1)}{\Delta N = 1} = \ln\left[\frac{Z(N)}{Z(N-1)}\right]$$

for monatomic ideal gas

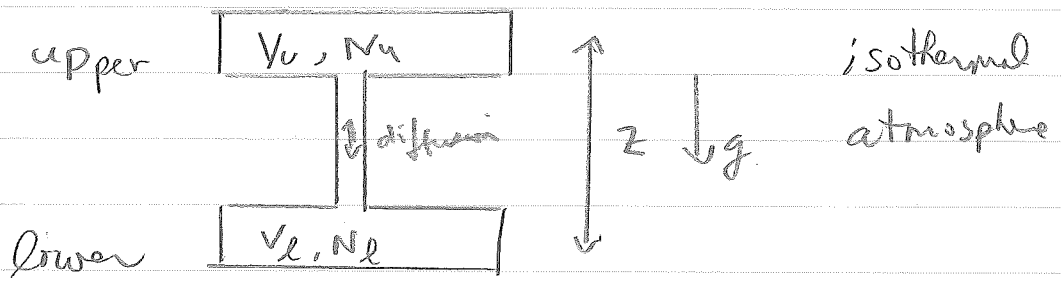
$$Z(N) = \frac{1}{N!}\left(\frac{V}{\ell_Q^3}\right)^N \quad \text{so} \quad \frac{Z(N)}{Z(N-1)} = \frac{1}{N}\frac{V}{\ell_Q^3}$$

giving $\frac{\partial \ln Z}{\partial N} = \ln\left(\frac{V}{N}\frac{1}{\ell_Q^3}\right)$ which we will use later

From $U + kT \ln Z = TS$ we get

$$\boxed{\begin{aligned} \left(\frac{\partial U}{\partial N}\right)_{S,V} &= \mu = -kT\frac{\partial \ln Z}{\partial N} \\ T\left(\frac{\partial S}{\partial N}\right)_{U,V} &= -\mu = +kT\frac{\partial \ln Z}{\partial N} \\ \left(\frac{\partial F}{\partial N}\right)_{T,V} &= \mu = -kT\frac{\partial \ln Z}{\partial N} \end{aligned}}$$

From Baierlein (Ch7), "discovering the chemical potential"




$$P(N_\ell, N_u) = \frac{1}{Z} Z(N_\ell, N_u)$$

$$Z(N_\ell, N_u) = \left(\frac{V_\ell}{N_\ell!}\frac{1}{\ell_Q^3}\right)^{N_\ell}\left(\frac{V_u}{N_u!}\frac{1}{\ell_Q^3}\right)^{N_u}\left(e^{-mgz/kT}\right)^{N_u}$$

$$\ell_Q = \left(\frac{h^2}{2\pi mkT}\right)^{1/2}$$ constant for isothermal

so $Z(N_\ell, N_u) = Z(N_\ell)\,Z(N_u)$ factors

since $N = N_u + N_\ell$ = constant, Max probability is

$$\frac{\partial}{\partial N_\ell}\log\left[Z(N_\ell)Z(N_u)\right] = 0 = \frac{\partial \log Z(N_\ell)}{\partial N_\ell} - \frac{\partial \log Z(N_u)}{\partial N_u}$$

We found $\dfrac{\partial \ln Z(N_\ell)}{\partial N_\ell} = \ln\left(\dfrac{V}{N_\ell}\dfrac{1}{\ell_Q^3}\right)$

similarly $\dfrac{\partial \ln Z(N_u)}{\partial N_u} = \ln\left[\dfrac{V}{N_u}\dfrac{1}{\ell_Q^3}e^{-mgz/kT}\right]$

then

$$\boxed{\frac{N_u}{V_u} = \frac{N_\ell}{V_\ell}e^{-mgz/kT}}$$ exponential density

since $\frac{\partial \ln Z}{\partial N} = \frac{-\mu}{kT}$ we also have

equal chemical potentials in diffusive equilibrium.

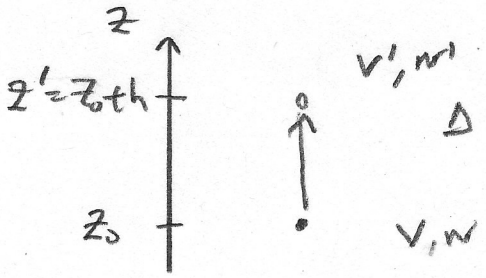
$$\frac{\mu_\ell}{kT} = -\ln\left(\frac{V_\ell}{N_\ell}\frac{1}{\ell_Q^3}\right) =$$

$$\boxed{\begin{aligned}\frac{\mu_u}{kT} &= -\ln\left(\frac{V_u}{N_u}\frac{1}{\ell_Q^3}e^{-mgz/kT}\right)\\ &= \frac{mgz}{kT} - \ln\left(\frac{V_u}{N_u}\frac{1}{\ell_Q^3}\right)\end{aligned}}$$

So the # density that comes in to the formula is at the upper height $\left(\frac{N_u}{V_u}\right)$

## Chemical Potential (refer to Bairlein)

① law of atmosphere




$\Delta PE = mgh$ energy required to move molecule $z_0 \to z' = z_0 + h$

$$\frac{\tilde{p}'}{\tilde{p}} = e^{-mgh/kT}$$ Boltzmann factor

$$Z = \left(\frac{V}{\ell_Q^3}\right)^N \frac{1}{N!} \qquad Z' = \left(\frac{V'}{\ell_Q^3}\right)^{N'} \frac{1}{N'!} \left(e^{-\frac{mgh}{kT}}\right)^{N'}$$

$$F = -kT \ln Z = -kTN \ln\left(\frac{V}{\ell_Q^3}\right) + kT \ln N!$$

$$\mu = \frac{\partial F}{\partial N} = -kT \ln\left(\frac{V}{\ell_Q^3}\right) + \underbrace{\frac{d}{dN} \ln N!}_{\frac{d}{dN}(N \ln N - N) = \ln N}$$

$$= -kT \ln\left(\frac{V}{N\ell_Q^3}\right)$$

similarly,

$$F' = -kTN' \ln\left(\frac{V}{\ell_Q^3}\right) + kT \ln N'! + kTN'\left(\frac{mgh}{kT}\right)$$

$$\mu' = \frac{\partial F'}{\partial N'} = -kT \ln\left(\frac{V'}{N'} \frac{1}{\ell_Q^3}\right) + kT\left(\frac{mgh}{kT}\right)$$

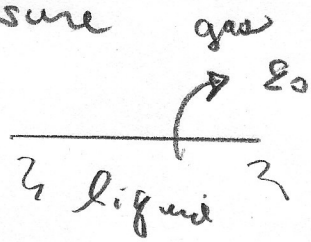
$\mu' = \mu$ in equilibrium,

$$\ln\left(\frac{V'/N'}{V/N}\right) = +\frac{mgh}{kT}$$

ideal gas law $\frac{V}{N} = \frac{kT}{p}$, $\frac{V'}{N'} = \frac{kT}{p'}$

$$\frac{p'}{p} = e^{-mgh/kT}$$

② Vapor pressure



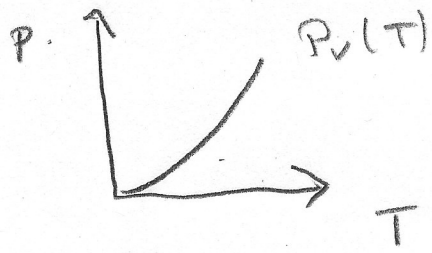

energy needed to move molecule out of liquid

in liquid, $\frac{V}{N} = v_0$ volume of molecule

in gas, $\frac{V'}{N'} = \frac{kT}{p'}$ $p'$ pressure of gas

identical argument gives $\mu_{liquid} = \mu_{gas}$ along vapor pressure curve

$$\frac{\ln\left(\frac{V'}{N'}\right)}{\ln\left(V/N\right)} = \frac{\varepsilon_0}{kT}$$




along vapor pressure curve, chemical potentials are equal

$$\left(\frac{P_v}{kT/V_0}\right) = e^{-\varepsilon_0/kT}$$

$$P_v(T) = \left(\frac{kT}{V_0}\right) e^{-\varepsilon_0/kT}$$

Compare to

$$P_v(T) = \left(\frac{P_0}{e^{L/kT}}\right) e^{-L/NkT}$$

We can interpret specific heat of fusion per molecule $\frac{L}{N} = \varepsilon_0$