HW #4 Solutions

2) Canonical Partition Function:

$$Q_{N_A N_B} = \frac{N_0!}{(N_0 - N_A - N_B) N_A! N_B!} e^{-(\beta N_A \varepsilon_A + \beta N_B \varepsilon_B)}$$

Grand Canonical Partition function

$$\mathcal{Q} = \sum_{N_A}^{N_0} \sum_{N_B}^{N_0 - N_A} e^{\beta \mu_A N_A} e^{\beta \mu_B N_B} Q_{N_A N_B}$$

$$= \sum_{N_A}^{N_0} \frac{N_0!}{N_A!} e^{-\beta N_A(\varepsilon_A - \mu_A)} \sum_{N_B}^{N_0 - N_A} e^{-\beta N_B(\varepsilon_B - \mu_B)} \frac{1}{N_B! (N_0 - N_A - N_B)!} \underbrace{\frac{(N_0 - N_A)!}{(N_0 - N_A)!}}_{=1}$$

$$= \sum_{N_A}^{N_0} \frac{N_0! \, e^{-\beta N_A(\varepsilon_A - \mu_A)}}{N_A! (N_0 - N_A)!} \left(1 + e^{-\beta(\varepsilon_B - \mu_B)}\right)^{N_0 - N_A}$$

$$= \left(1 + e^{-\beta(\varepsilon_B - \mu_B)}\right)^{N_0} \sum_{N_A} \left(\frac{e^{-\beta(\varepsilon_A - \mu_A)}}{1 + e^{-\beta(\varepsilon_B - \mu_B)}}\right)^{N_A} \frac{N_0!}{N_A! (N_0 - N_A)!}$$

$$= \left(1 + e^{-\beta(\varepsilon_B - \mu_B)}\right)^{N_0} \left(1 + \frac{e^{-\beta(\varepsilon_A - \mu_A)}}{1 + e^{-\beta(\varepsilon_B - \mu_B)}}\right)^{N_0}$$

$$= \underbrace{\left(1 + e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)}\right)^{N_0}}_{\text{Each site has 3 states + the sites are independent}}$$

$$\langle N_A \rangle = N_0 \frac{e^{-\beta(\varepsilon_A - \mu_A)}}{1 + e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)}}$$

$$\langle N_B \rangle = N_0 \frac{e^{-\beta(\varepsilon_B - \mu_B)}}{1 + e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)}}$$

for an ideal gas

$$\mu = kT \ln P + f(T)$$

which we can generalize:

$$\mu_A = kT \ln P_A + f_A(T)$$
$$\mu_B = kT \ln P_B + f_B(T)$$

so the fractional coverages are

$$\theta_A = \frac{\langle N_A \rangle}{N_0} = \frac{P_A e^{-\beta(\varepsilon_A - f_A(T))}}{1 + P_A e^{-\beta(\varepsilon_A - f_A(T))} + P_B e^{-\beta(\varepsilon_B - f_B(T))}}$$

$$\theta_B = \frac{\langle N_B \rangle}{N_0} = \frac{P_B e^{-\beta(\varepsilon_B - f_B(T))}}{1 + P_A e^{-\beta(\varepsilon_A - f_A(T))} + P_B e^{-\beta(\varepsilon_B - f_B(T))}}$$

4 Pathria 5.1)

we can bring σ_x into diagonal form using

$$U = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \quad U^+ = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$$

$$U \sigma_x U^+ = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} 2 & 0 \\ 0 & -2 \end{pmatrix}$$

Alternative: rename axes according to $z \to x$, $y \to y$, $x \to -z$
then we have

$$\sigma_x = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

The density operator is given by

$$\hat{\rho} = \frac{e^{-\beta H}}{Q} \quad \text{where} \quad H = -\mu_B \sigma_z B = \begin{pmatrix} -\mu_B B & 0 \\ 0 & \mu_B B \end{pmatrix}$$

$$e^{-\beta H} = 1 - \beta\begin{pmatrix} -\mu_B B & 0 \\ 0 & \mu_B B \end{pmatrix} + \frac{\beta^2}{2}\begin{pmatrix} \mu_B^2 B^2 & 0 \\ 0 & \mu_B^2 B^2 \end{pmatrix} + \ldots$$

$$= \begin{pmatrix} e^{\beta \mu_B B} & 0 \\ 0 & e^{-\beta \mu_B B} \end{pmatrix}$$

$$Q = T_r\left(e^{-\beta H}\right) = 2\cosh(\beta \mu_B B)$$

in z representation $\rho = \frac{1}{2\cosh(\beta\mu_B B)}\begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}$

Now switch to basis where σ_x is diagonal

$$U\rho U^\dagger = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \frac{1}{2\cosh(\beta\mu_B B)} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix} \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$$

$$= \frac{1}{4\cosh(\beta\mu_B B)} \begin{pmatrix} e^{\beta\mu_B B} & e^{-\beta\mu_B B} \\ -e^{\beta\mu_B B} & e^{-\beta\mu_B B} \end{pmatrix} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}$$

$$= \frac{1}{4\cosh(\beta\mu_B B)} \begin{pmatrix} 2\cosh(\beta\mu_B B) & -2\sinh \beta\mu_B B \\ -2\sinh(\beta\mu_B B) & 2\cosh(\beta\mu_B B) \end{pmatrix}$$

$$= \frac{1}{2}\begin{pmatrix} 1 & -\tanh(\beta\mu_B B) \\ -\tanh(\beta\mu_B B) & 1 \end{pmatrix} = \rho' \checkmark$$

$$\langle \sigma_z \rangle = Tr(\rho' \sigma_z')$$

$$= Tr(U\rho U^\dagger U \sigma_z U^\dagger)$$

$$= Tr(U\rho\, \sigma_z U^\dagger) \qquad U^\dagger U = 1$$

$$= Tr(\rho\sigma_z) \qquad \text{cyclic property of trace}$$

Same as original representation

5.3 free particles $\hat{H} = \frac{\hat{p}^2}{2m}$

$$\hat{\rho} = \frac{e^{-\beta \hat{H}}}{\mathrm{Tr}\, e^{-\beta \hat{H}}}$$

introduce complete set of momentum states $I = \sum_p |p\rangle\langle p|$ ← Identity

$$e^{-\beta \hat{H}} = e^{-\beta \frac{\hat{p}^2}{2m}} = \sum_p |p\rangle e^{-p^2/2m} \langle p|$$

$$\mathrm{Tr}\, e^{-\beta \hat{H}} = \sum_{p'} \langle p'| e^{-\beta \hat{H}} |p'\rangle$$

$$= \sum_{pp'} \langle p'|p\rangle e^{-p^2/2mkT} \underbrace{\langle p|p'\rangle}_{\delta_{pp'}} = \sum_p e^{-p^2/2mkT}$$

to approximate this sum as integral we need density of p states

$$p_x = \hbar k_x = \hbar \frac{2\pi n_x}{L} = \frac{h n_x}{L} \quad (n_x \text{ integer}) \qquad dn_x = \frac{L}{h} dp_x \quad \text{same for } p_y + p_z$$

$$\sum_p e^{-p^2/2mkT} = \frac{V}{h^3} \int e^{-p^2/2mkT} d^3p$$

$$= \frac{V}{h^3} (2m\pi kT)^{3/2}$$

$$\hat{\rho} = \frac{\sum_p e^{-p^2/2m} |p\rangle\langle p|}{\frac{V}{h^3}(2m\pi kT)^{3/2}} = \frac{\sum_p e^{-p^2/2m} |p\rangle\langle p|}{V/\lambda^3}$$

$$\langle H\rangle = \mathrm{Tr}\langle \hat{H}\hat{\rho}\rangle = \frac{\lambda^3}{V} \sum_{pp'p''} \underbrace{\langle p|p'\rangle \frac{p^2}{2m} \langle p|p''\rangle}_{H} \underbrace{e^{-p^2/2mkT} \langle p''|p\rangle}_{\rho}$$

$$= \frac{\lambda^3}{V} \int d^3p \left(\frac{V}{h^3}\right) \frac{p^2}{2m} e^{-p^2/2mkT} = \frac{\lambda^3}{V} \frac{V}{h^3} \frac{4\pi}{2m} \int_0^\infty p^4 e^{-p^2/2mkT} dp$$

$$= \frac{\lambda^3}{h^3} \frac{4\pi}{2m} \frac{1}{2}\sqrt{\pi}\, \frac{3}{4}(2mkT)^{5/2} = \frac{\pi^{3/2}}{(2\pi mkT)^{3/2}} \frac{3}{4m} (2mkT)^{5/2} = \frac{3}{2} kT$$

5.3 cont.) Harmonic Oscillator

$$\langle p|e^{-\beta\hat{H}}|p'\rangle = \sum_{xx'} \langle p\underbrace{|x\rangle}_{=1}\langle x|e^{-\beta\hat{H}}\underbrace{|x'\rangle\langle x'|}_{=1\ \left(\substack{\text{with}\\ \text{sum}}\right)}p'\rangle$$

$$= \sum_{xx'} \underbrace{e^{-ipx/\hbar}}_{\langle p|x\rangle} \underbrace{\left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2} \exp\left[\frac{-m\omega}{4\hbar}\left\{(x+x')^2\tanh\left(\frac{\beta\hbar\omega}{2}\right)+(x-x')^2\coth\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right]}_{\langle x|e^{-\beta H}|x'\rangle \text{ path.u } 5.3.23} \underbrace{e^{ip'x'/\hbar}}_{\langle x'|p'\rangle}$$

define $A = \frac{m\omega}{2\hbar}\tanh\left[\frac{\beta\hbar\omega}{2}\right]$ $\quad A' = \frac{m\omega}{2\hbar}\coth\left[\frac{\beta\hbar\omega}{2}\right]$

$$= \int dx\,dx' \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2} \exp\left[\frac{i(p'x'-px)}{\hbar} - (x+x')^2\frac{A}{2} - (x-x')^2\frac{A'}{2}\right]$$

define $y = \frac{x+x'}{\sqrt{2}}$ $\quad y' = \frac{x-x'}{\sqrt{2}}$

$$= \left[\frac{m\omega}{2\pi\hbar\sinh\beta\hbar\omega}\right]^{1/2} \int dy\,dy' \exp\left[\frac{i}{\hbar}\frac{p'}{\sqrt{2}}(y-y') - \frac{ip}{\sqrt{2}\hbar}(y+y') - Ay^2 - A'y'^2\right]$$

$$= \left[\frac{m\omega}{2\pi\hbar\sinh(\beta\hbar\omega)}\right]^{1/2} \int dy \exp\left[-Ay^2 + y\underbrace{\frac{i}{\sqrt{2}\hbar}(p'-p)}_{\equiv B}\right] \int dy' \exp\left[-A'y'^2 + y'\underbrace{\frac{-i}{\sqrt{2}\hbar}(p+p')}_{B'}\right]$$

complete the square

$$\int dy\, e^{-A\left(y-\frac{B}{2A}\right)^2} e^{A\frac{B^2}{4A^2}} = \sqrt{\frac{\pi}{A}}\, e^{B^2/4A}$$

5.3 (cont)

$$\langle p | e^{-\beta H} | p' \rangle = \frac{\pi}{\sqrt{AA'}} \, e^{B^2/4A} \, e^{B'^2/4A'} \sqrt{\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}}$$

$$= \frac{2\pi\hbar}{m\omega} \Big(\underbrace{\tanh(\,) \coth(\,)}_{=1} \Big)^{-1/2} \sqrt{\frac{m\omega}{2\pi\hbar \sinh(\beta\hbar\omega)}} \, e^{B^2/4A + B'^2/4A'}$$

$$= \sqrt{\frac{2\pi\hbar}{m\omega \sinh(\beta\hbar\omega)}} \, \mathrm{Exp}\left[\frac{-(p'-p)^2}{\hbar^2 2} \frac{\hbar}{(2m\omega)} \coth\left(\frac{\beta\hbar\omega}{2}\right) - \frac{(p'+p)^2}{4\hbar m\omega} \tanh\left(\frac{\beta\hbar\omega}{2}\right) \right]$$

Pathria 6.32 (p 1/3)

$$K(T) = \frac{N_{NO}^2}{N_{O_2} N_{N_2}} = \frac{q_{NO}^2}{q_{O_2} q_{N_2}}$$

where q_i = single particle partition function

$$q_i = q_{pos}\, q_{mom}\, q_{elec}\, q_{vib}\, \underbrace{q_{rot}\, q_{nuc}}_{\text{or } q_{nuc\text{-}rot}}$$

$$q_{pos} = V$$

$$q_{mom} = \frac{1}{\lambda_i^3} \qquad \lambda_i = \frac{h}{\sqrt{2\pi m_i kT}}$$

$$q_{elec} = \sum_s e^{-\beta \varepsilon_s}$$

$$= \underbrace{e^{-\beta\varepsilon_i}}_{\text{ground state}} + \cancel{\text{excited states}} \rightarrow \text{drop}$$

$$q_{vib} = e^{-\beta\hbar\omega_i/2} \sum e^{-\beta\hbar\omega_i n}$$

$$= \frac{e^{-\beta\hbar\omega_i/2}}{1 - e^{-\beta\hbar\omega_i}} = \frac{1}{2\sinh[\beta\hbar\omega_i/2]}$$

Hetero-Nuclear molecules

$$q_{rot} = \sum_{l=0}^{\infty} \underbrace{(2l+1)}_{\text{'m' states}} e^{-\beta l(l+1)\hbar^2/2I} \qquad I = \text{moment of Inertia}$$

Classical limit $\quad kT >> \hbar^2/2I_i$

$$q_{rot} \cong \int (2l+1)\, e^{-l(l+1)\theta_i/T}\, dl \qquad \theta_i = \frac{\hbar^2}{2I_i k}$$

$$= \int_0^\infty \frac{T}{\theta_i} e^{-x} dx = \frac{T}{\theta_i} \qquad x = l(l+1)\frac{\theta}{T}$$

$$dx = (2l+1)\frac{\theta}{T}\, dl$$

For Homonuclear molecules we need to distinguish between even + odd states. But in classical limit

$$q_{even} = q_{odd} = \frac{T}{2\theta_i} \leftarrow \tfrac{1}{2} \text{ classical result}$$

6.32 (p 2/3)

Now consider nuclear states. The atomic spins are

$^{16}O \quad s = 0 \qquad ^{14}N \quad s = 1$

so for NO:

$$q_{rot-nuc} = q_{nuc}\, q_{rot} = 3\frac{T}{\theta_{NO}}$$

^{14}N spin states

$$O_2: \quad q_{rot-nuc} = \frac{T}{2\theta_{O_2}}$$

no spin degeneracy

only even states

$$N_2: \quad q_{rot-nuc} = 6\frac{T}{2\theta_{N_2}} + 3\frac{T}{2\theta_{N_2}}$$

symmetric spin state $(s_n+1)(2s_n+1) = 2\times 3$

even rotation

anti-symmetric spins $\rightarrow (s_n)(2s_n+1) = 1\times 3$

odd rotation states

put it all together

$$q_{NO} = \frac{V}{\lambda_{NO}^3} e^{-\beta\varepsilon_{NO}} \frac{1}{2\sinh[\beta\hbar\omega_{NO}/2]} \frac{3T}{\theta_{NO}}$$

$$q_{O_2} = \frac{V}{\lambda_{O_2}^3} e^{-\beta\varepsilon_{O_2}} \frac{1}{2\sinh[\beta\hbar\omega_{O_2}/2]} \frac{T}{2\theta_{O_2}}$$

$$q_{N_2} = \frac{V}{\lambda_{N_2}^3} e^{-\beta\varepsilon_{N_2}} \frac{1}{2\sinh[\beta\hbar\omega_{N_2}/2]} \frac{T}{\theta_{N_2}}\left[3+\frac{3}{2}\right]$$

$$K = \frac{q_{NO}^2}{q_{O_2}\, q_{N_2}} = \frac{\frac{\cancel{V^2}}{\lambda_{NO}^6}\left(\frac{3T}{\theta_{NO}}\right)^2 \cancel{2}\sinh[\beta\hbar\omega_{O_2}/2]\,\cancel{2}\sinh[\beta\hbar\omega_{N_2}/2]}{\cancel{4}\sinh^2[\beta\hbar\omega_{NO}/2]\,\frac{\cancel{V}}{\lambda_{O_2}^3}\left(\frac{T}{2\theta_{O_2}}\right)\frac{\cancel{V}}{\lambda_{N_2}^3}\left(\frac{T}{\theta_{N_2}}\frac{9}{2}\right)} e^{-\beta\Delta\varepsilon_0}$$

$$\Delta\varepsilon_0 = 2\varepsilon_{NO} - \varepsilon_{N_2} - \varepsilon_{O_2}$$

6.32 (p 3/3)

$$K = \underbrace{\frac{\lambda_{O_2}^3 \lambda^3}{\lambda_{NO}^6}}_{\frac{m_{NO}^3}{(m_{O_2} m_{N_2})^{3/2}}} 4 \underbrace{\frac{\theta_{O_2}\theta_{N_2}}{\theta_{NO}^2}}_{\frac{I_{NO}^2}{I_{O_2} I_{N_2}}} \frac{\sinh\left(\frac{\beta\hbar\omega_{O_2}}{2}\right)\sinh\left[\frac{\beta\hbar\omega_{N_2}}{2}\right]}{\sinh^2\left[\frac{\beta\hbar\omega_{NO}}{2}\right]} e^{-\beta\Delta\varepsilon_0}$$

$$\boxed{K = 4\frac{m_{NO}^3}{(m_{O_2} m_{N_2})^{3/2}} \frac{I_{NO}^2}{I_{O_2} I_{N_2}} \frac{\sinh\left(\frac{\beta\hbar\omega_{O_2}}{2}\right)\sinh\left[\frac{\beta\hbar\omega_{N_2}}{2}\right]}{\sinh^2\left[\frac{\beta\hbar\omega_{NO}}{2}\right]} e^{-\beta\Delta\varepsilon_0}}$$

low temps $\beta\hbar\omega_i \to \infty$ (but rotation still excited)

$$\boxed{K = 4\frac{m_{NO}^3}{(m_{O_2} m_{N_2})^{3/2}} \frac{I_{NO}^2}{I_{O_2} I_{N_2}} e^{\beta\hbar(\omega_{O_2}+\omega_{N_2}-2\omega_{NO})} e^{-\beta\Delta\varepsilon_0}}$$

high temps $\beta\hbar\omega \to 0$ (but still electronic ground state)

$$\boxed{K = 4\frac{m_{NO}^3}{(m_{O_2} m_{N_2})^{3/2}} \frac{I_{NO}^2}{I_{O_2} I_{N_2}} \frac{\omega_{O_2}\omega_{N_2}}{\omega_{NO}^2} e^{-\beta\Delta\varepsilon_0}}$$