HW 5 – Answers

2) $Q(N,V,T) = V^N / N!\,\lambda^{3N}$, $\quad \lambda = \sqrt{\dfrac{h^2}{2\pi m k_B T}}$

$$\Delta = \frac{1}{V_0}\int_0^\infty dV\, e^{-\beta P V}\, Q(N,V,T)$$

$$= \frac{1}{V_0 N!\,\lambda^{3N}} \int_0^\infty dV\, e^{-\beta P V}\, \underbrace{V^N}_{(x/\beta P)^N}$$ ← looks like gamma func ← β & P constant

$x = \beta P V$, $\quad V = \frac{x}{\beta P}$ $\quad dV = \frac{1}{\beta P}dx$

$x(0)=0$, $\quad x(\infty)=\infty$

$$= \frac{1}{V_0 N!\,\lambda^{3N} (\beta P)^{N+1}} \int_0^\infty dx\, e^{-x} x^N$$

$\quad$ " $\Gamma(N+1) = N!$

$$= \frac{1}{V_0}\cdot\frac{1}{\lambda^{3N}}\cdot\frac{1}{(\beta P)^{N+1}}$$

$$\langle V\rangle_{NPT} = -k_B T\,\frac{\partial \log\Delta}{\partial P} = -k_B T\frac{\partial}{\partial P}\left(\log(P^{-(N+1)}) + \text{const}\right)$$

$$= (N+1)k_B T\cdot\frac{1}{P}$$

so $P\langle V\rangle = (N+1)k_B T \approx N k_B T$ for large N

Also, $\langle P V\rangle = \dfrac{1}{\Delta V_0}\displaystyle\int_0^\infty dV\, e^{-\beta P V}\, Q(N,V,T)\cdot P V$ (internal)

$$PV = V\cdot k_B T\frac{\partial \ln Q}{\partial V} = k_B T V \frac{1}{Q}\frac{\partial Q}{\partial V}$$ for a particular V

$$= \frac{1}{\Delta V_0}\int_0^\infty dV\, [\underbrace{V e^{-\beta P V}}_{x}][\underbrace{k_B T \tfrac{\partial Q}{\partial V}}_{dy}]$$

$$\underset{\text{by parts}}{=} \frac{1}{\Delta V_0}\left[\underbrace{V e^{-\beta P V} k_B T Q}_{0}\right]_{V=0}^{V=\infty} - \int_{V=0}^{V=\infty} k_B T Q\cdot d\left[V e^{-\beta P_i V}\right]$$

$$= -\frac{1}{\Delta V_0}\int_{V=0}^{\infty} k_B T\, Q\left[e^{-\beta P V} + (-\beta P)e^{-\beta P V}\cdot V\right]$$

$$= \langle -k_B T + PV\rangle_{NPT} = -k_B T + P\langle V\rangle_{NPT}$$

$$\Rightarrow \langle P^{\text{internal}} V\rangle_{NPT} = P\langle V\rangle - k_B T$$

so $\langle P^{\text{internal}} V\rangle_{NPT} = N k_B T$ exactly ✓

3) $$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{N,T}$$

$$V = -k_BT\left(\frac{\partial \ln \Delta}{\partial P}\right)_{N,T}$$

$$\Delta = \frac{1}{V_0}\int_0^\infty dV\, e^{-\beta P V} Q(N,V,T)$$

$$-k_BT\frac{\partial \ln \Delta}{\partial P} = \cancel{\frac{-k_BT}{\Delta}}\cdot\frac{1}{V_0}\int_0^\infty dV\,(-\cancel{\beta} V)e^{-\beta P V} Q(N,V,T)$$

$$\left(\frac{\partial V}{\partial P}\right)_{N,T} = \left(\frac{\partial}{\partial P}\frac{1}{V_0\Delta}\int_0^\infty dV\, V e^{-\beta P V} Q(N,V,T)\right)$$

Quotient rule
$$= \frac{V_0\Delta\cdot\int_0^\infty dV\cdot(-\beta V)e^{-\beta V}\cdot V\, Q(N,V,T) - \int_0^\infty V e^{-\beta P V} Q(N,V,T)\frac{\partial V_0\Delta}{\partial P}}{(V_0\Delta)^2}$$

$$= \frac{1}{V_0\Delta}\int_0^\infty dV\,(-\beta V^2)e^{-\beta P V}Q(N,V,T) - \langle V\rangle\cdot\underbrace{\frac{1}{\Delta}\frac{\partial\Delta}{\partial P}}_{\frac{\partial \log\Delta}{\partial P} = -\beta\langle V\rangle}$$

$$= -\beta\langle V^2\rangle - \beta\langle V\rangle^2$$

$$= -\beta\,\mathrm{Var}[V]$$

$$\boxed{K = \beta\,\mathrm{Var}[V]/V}$$

4) For an ideal gas, we showed

$$Z(\lambda, V, T) = \sum_{N=0}^{\infty} \frac{\lambda^N}{N!} \left(\frac{V}{\Lambda^3}\right)^N \qquad \lambda = e^{\beta\mu}$$

$$\Lambda = \sqrt{h^2/2\pi m k_B T}$$

$$= \exp(V\lambda/\Lambda^3) \qquad = \sqrt{\frac{h^2}{2\pi m}}\, \beta^{1/2}$$

In Grand canonical

$$S(\lambda, V, T) = k_B \log Z(\lambda, V, T) - k_B \beta \frac{\partial}{\partial \beta} \log(Z(\lambda, V, T))$$

In class $\hookrightarrow$

$$\log Z = V\lambda/\Lambda^3 = V\lambda\left(\frac{h^2}{2\pi m}\right)^{-3/2} \beta^{3/2} = V\left(\frac{h^2}{2\pi m}\right)^{-3/2} \beta^{-3/2} e^{\beta\mu}$$

$$= \langle N \rangle$$

$$S(\mu, V, T) = \langle N \rangle k_B - k_B \beta \frac{\partial}{\partial \beta}\left[V\left(\frac{h^2}{2\pi m}\right)^{-3/2} \beta^{-3/2} e^{\beta\mu}\right]$$

$$= \langle N \rangle k_B - k_B \beta\, V(h^2/2\pi m)^{-3/2}\left[\beta^{-3/2} \mu e^{\beta\mu} - 3/2\, \beta^{-5/2} e^{\beta\mu}\right]$$

$$= \langle N \rangle k_B - k_B V\left[\beta/\Lambda^3\, \mu\lambda - \frac{3}{2}\lambda/\Lambda^3\right]$$

$$= \frac{3}{2}\langle N \rangle k_B + \langle N \rangle k_B - k_B \cdot \beta \cdot \frac{V}{\Lambda^3}\mu\lambda \rightarrow k_B \beta \langle N \rangle \mu$$

$$\text{b/c } \langle N \rangle = V\lambda/\Lambda^3 \Rightarrow e^{\beta\mu} = \lambda = \frac{\Lambda^3 \langle N \rangle}{V}$$

$$\mu = \frac{1}{\beta}\log\left(\Lambda^3 \langle N \rangle / V\right)$$

$$= 5/2 \langle N \rangle k_B - k_B \langle N \rangle \log(\Lambda^3 \langle N \rangle / V)$$

$$= 5/2 \langle N \rangle k_B + k_B \langle N \rangle \log\left(\frac{V}{\Lambda^3 \langle N \rangle}\right)$$

Sackur, Tetrode ✓