HW 3 solutions

$v = N_\ell v_0$

1) a) $Q_1(V) = \left(\frac{N_\ell v_0}{\lambda^3}\right) e^{\beta \varepsilon}$

$$Q_N = \frac{1}{N_\ell!}\left(\frac{N_\ell v_0}{\lambda^3}\right)^{N_\ell} e^{\beta N_\ell \varepsilon}$$

b) $\mu_\ell = \frac{\partial F}{\partial N_\ell} = \frac{\partial}{\partial N_\ell}\left(-kT \ln\left[\left(\frac{N_\ell v_0}{\lambda^3}\right)^{N_\ell}\frac{1}{N_\ell!}\right] - \varepsilon N_\ell\right)$

liquid phase

$$= -\varepsilon - kT \frac{\partial}{\partial N_\ell}\left[N_\ell \ln\frac{N_\ell v_0}{\lambda^3} - N_\ell \ln N_\ell + N_\ell\right]$$

$$= -\varepsilon - kT\left[\ln\frac{v_0}{\lambda^3} + 1\right]$$

gas $\mu_g = kT\ln(P\beta\lambda^3)$ ← lecture #3

$$\ln(P\beta\lambda^3) = \frac{-\varepsilon}{kT} - \ln\frac{v_0}{\lambda^3} - 1$$

$$\frac{P\lambda^3}{kT} = \frac{\lambda^3}{v_0} e^{-\beta\varepsilon - 1}$$

$$P = \frac{kT}{v_0} e^{-\beta(\varepsilon) - 1}$$

Pathria 4.5) $S = kT\left(\frac{\partial q}{\partial T}\right)_{zV} - Nk\ln z + k_B q$

$q(z, V, T)$ so

$$dq = \left(\frac{\partial q}{\partial z}\right)_{VT} dz + \left(\frac{\partial q}{\partial V}\right)_{zT} dV + \left(\frac{\partial q}{\partial T}\right)_{zV} dT$$

but z is function of μ, T so

$$dz = \left(\frac{\partial z}{\partial \mu}\right)_T d\mu + \left(\frac{\partial z}{\partial T}\right)_\mu dT$$

plug this into expression for dq

$$dq = \left(\frac{\partial q}{\partial z}\right)_{VT}\left(\frac{\partial z}{\partial \mu}\right)_T d\mu + \left(\frac{\partial q}{\partial z}\right)_{VT}\left(\frac{\partial z}{\partial T}\right)_\mu dT + \left(\frac{\partial q}{\partial V}\right)_{zT} dV + \left(\frac{\partial q}{\partial T}\right)_{zV} dT$$

so

$$\left(\frac{\partial q}{\partial T}\right)_{\mu V} = \left(\frac{\partial q}{\partial z}\right)_{VT}\left(\frac{\partial z}{\partial T}\right)_\mu + \left(\frac{\partial q}{\partial T}\right)_{zV}$$

recall $N = z\left(\frac{\partial q}{\partial z}\right)_{VT}$

$$\left(\frac{\partial q}{\partial T}\right)_{\mu V} = \frac{N}{z}\left(\frac{\partial z}{\partial T}\right)_\mu + \left(\frac{\partial q}{\partial T}\right)_{zV} \qquad \left(\frac{\partial z}{\partial T}\right)_\mu = \frac{\partial}{\partial T} e^{\mu/kT} = \frac{-\mu}{kT^2} z$$

$$= -\frac{N\mu}{kT^2} + \left(\frac{\partial q}{\partial T}\right)_{zV}$$

plug into expression for S

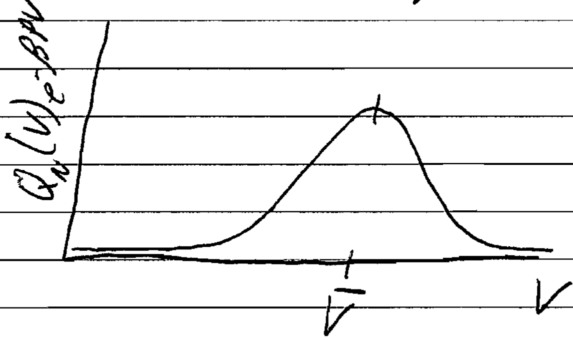
$$S = kT\left(\left(\frac{\partial q}{\partial T}\right)_{\mu V} + \frac{N\mu}{kT^2}\right) - Nk\ln z + kq$$

$$= k\left[T\left(\frac{\partial q}{\partial T}\right)_{\mu V} + \cancel{N\underbrace{\frac{\mu}{kT}}_{\ln z}} - \cancel{N\ln z} + q\right]$$

$$= k\left[T\left(\frac{\partial q}{\partial T}\right)_{\mu V} + q\right] = k\left(\frac{\partial Tq}{\partial T}\right)_{\mu V}$$

Pathria 4.6)

For large systems the probability distribution will be peaked around the most likely volume $\bar{V}$



Therefore we will manipulate the isobaric partition function so that we can Taylor expand around $\bar{V}$

$$Y_N(P,T) = \frac{1}{\lambda^3}\int_0^{\infty} Q_N(V,T)\, e^{-\beta PV}\, dV \qquad \text{(given)}$$

$$= \frac{1}{\lambda^3}\int e^{\ln Q(V,T) - \beta PV}\, dV$$

$$= \frac{1}{\lambda^3}\int e^{-\beta(F+PV)}\, dV \qquad F = -kT\ln Q$$

expand exponent

$$F(V) + PV = F(\bar{V}) + P\bar{V} + \underbrace{(V-\bar{V})\left.\frac{\partial(F+PV)}{\partial V}\right|_{V=\bar{V}}}_{\substack{\text{This equals zero} \\ \text{by definition of } \bar{V}}} + \frac{1}{2}(V-\bar{V})^2 \left.\frac{\partial^2(F+PV)}{\partial V^2}\right|_{V=\bar{V}}$$

$$\left.\frac{\partial^2}{\partial V^2}(F+PV)\right|_{V=\bar{V}} = \left.\frac{\partial^2 F}{\partial V^2}\right|_{\bar{V}} = \left.-\frac{\partial P}{\partial V}\right|_{\bar{V}} = \frac{K}{\bar{V}} \qquad \text{where } K = \text{bulk modulus}$$

so

$$Y_N \simeq \frac{1}{\lambda^3} e^{-\beta(F(\bar{V}) + P\bar{V})} \int e^{-\frac{\beta K}{2\bar{V}}(V-\bar{V})^2}\, dV + \text{higher order terms}$$

$$Y_N \simeq \frac{1}{\lambda^3} e^{-\beta(F(\bar{V}) + P\bar{V})} \sqrt{\frac{\pi\, 2 \bar{V}}{\beta K}}$$

$$\ln Y_N = \underbrace{-\beta\left(F(\bar{V}) + P\bar{V}\right)}_{O(V)} \underbrace{- 3\ln\lambda^3}_{O(1)} + \underbrace{\frac{1}{2}\ln\frac{2\pi\bar{V}}{\beta K}}_{O[\ln(V)]}$$

in thermo limit $(N, V \to \infty)$

only first term contributes

$$-k_B T \ln Y_N = F(\bar{V}) + PV = G \quad \text{Gibbs free energy}$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

Ideal Gas $\quad Q_N = \left(\frac{V}{\lambda^3}\right)^N \frac{1}{N!}$

$$Y_N = \frac{1}{\lambda^3 N!\, \lambda^{3N}} \int V^N e^{-\beta P V} dV \qquad \begin{aligned} x &= \beta P V \\ dx &= \beta P\, dV \end{aligned}$$

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

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

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} = \frac{\partial}{\partial P}\left(+kT \ln\left(\lambda^{3(N+1)} (\beta P)^{N+1}\right)\right) = kT(N+1)\frac{\partial}{\partial P}\ln(\lambda^3 \beta P)$$

$$= \frac{kT(N+1)}{P}$$

$$PV = NkT \qquad N \simeq N+1 \quad \text{in thermo limit}$$

Pathria 4 8

Hamiltonian $\rightarrow H = \frac{p^2}{2m} + j\mu_B H$ ← external field where $j = \pm 1$

$$Q_1 = \frac{1}{h^3} \underbrace{\int d^3r}_{V} \underbrace{\int d^3p}_{(\sqrt{2\pi m k T})^3} \sum_{j=\pm 1} e^{-\beta H j \mu_B}$$

$$= \frac{V}{\lambda^3} 2\cosh(\beta \mu_B H)$$

$$Q_N = \frac{1}{N!} Q_1^N$$

$$\mathcal{Q} = \sum_N e^{\beta \mu N} Q_N = \sum_N \frac{z^N Q_1^N}{N!}$$

$$= e^{z Q_1}$$

$$= \exp\left[\frac{2Vz}{\lambda^3} \cosh(\beta \mu_B H)\right]$$

$$-\frac{dQ_1}{d(\beta H)} = \frac{-dQ_1}{\beta dH}$$

$$\langle M \rangle = \frac{\sum_N e^{\beta \mu N} \frac{1}{N! h^3} \int d^3r \int d^3p \sum_{j=\pm 1} j \mu_B e^{-\beta j \mu_B H}}{\mathcal{Q}}$$

$$= -\frac{1}{\beta} \frac{d \ln \mathcal{Q}}{dH}$$

$$= \frac{-\exp\left[\frac{2Vz}{\lambda^3} \cosh(\beta \mu_B H)\right] \frac{2Vz}{\lambda^3} \mu_B \cancel{\beta} \sinh(\beta \mu_B H)}{\cancel{\beta}\ \mathcal{Q}}$$

$$= \frac{-2Vz}{\lambda^3} \mu_B \sinh(\beta \mu_B H)$$

48 (cont.) $\Delta Q = T\Delta S$

$$S = \frac{\partial}{\partial T}\left(kT \ln Q\right)_{\mu V}$$

$$S = k\frac{\partial}{\partial T}\left[\frac{T\,2Vz}{\lambda^3}\cosh(\beta\mu_B H)\right]$$

$$= k\left[2Vz\cosh(\beta\mu_B H)\underbrace{\frac{\partial\, T/\lambda^3}{\partial T}}_{\frac{5}{2\lambda^3}} + \frac{2TV}{\lambda^3}\underbrace{\frac{\partial z}{\partial T}}_{\frac{-\mu}{kT^2}z}\cosh(\beta\mu_B H) + \frac{2TVz}{\lambda^3}\mu_B H\underbrace{\frac{\partial\beta}{\partial T}}_{\frac{-1}{kT^2}}\sinh(\beta\mu_B H)\right]$$

$$= \frac{2Vzk}{\lambda^3}\left[\frac{5}{2}\cosh(\beta\mu_B H) - \frac{\mu}{kT}\cosh(\beta\mu_B H) - \frac{\mu_B H}{kT}\sinh(\beta\mu_B H)\right]$$

$$\Delta Q = T\Delta S = T\left[S(H=0) - S(H)\right]$$

$$= \frac{2VzkT}{\lambda^3}\left[\frac{5}{2} - \frac{\mu}{kT} - \frac{5}{2}\cosh(\beta\mu_B H) + \frac{\mu}{kT}\cosh(\beta\mu_B H) + \frac{\mu_B H}{kT}\sinh(\beta\mu_B H)\right]$$