# Phys 630 S'24 Problem Set 2 Solutions

Kardar, Chapter 1

6. a) $dE = TdS + \underbrace{\mu dN}$

chemical work in converting $dN$ liquid quartz molecules to crystal or glass

$S = S(E,N)$, $dS = \frac{dE}{T} - \frac{\mu}{T}dN = \left.\frac{\partial S}{\partial E}\right|_N dE + \left.\frac{\partial S}{\partial N}\right|_E dN$

$\Rightarrow \left.\frac{\partial S}{\partial E}\right|_N = \frac{1}{T}$, $\left.\frac{\partial S}{\partial N}\right|_E = -\frac{\mu}{T}$

Extensivity: $S(\lambda E, \lambda N) = \lambda S(E,N)$

$\left.\frac{\partial}{\partial \lambda}\right|_{\lambda=1}$ : $\left.\frac{\partial S}{\partial E}\right|_N \cdot E + \left.\frac{\partial S}{\partial N}\right|_E \cdot N = S$

$$\boxed{S = \frac{1}{T}E - \frac{\mu}{T}N}$$

$\Rightarrow \mu = \frac{E - TS}{N}$ (Different for crystal and glass)

b) $C_x = \alpha T^3$, $C_G = \beta T$

crystal glass

$$\boxed{S = \int \frac{dQ}{T} = \int_0^T \frac{C_V\, dT'}{T'} = \begin{cases} \int_0^T \alpha T'^2 dT' = \frac{\alpha}{3}T^3 & \text{crystal} \\ \int_0^T \beta\, dT' = \beta T & \text{glass} \end{cases}}$$

c) $dE = TdS = C_v dT \quad , \quad E(T=0) = E_0$

$$= \begin{cases} \alpha T^3 \, dT & \text{crystal} \\ \beta T & \text{glass} \end{cases}$$

$$\boxed{E = \begin{cases} E_0 + \int_0^T \alpha T'^3 \, dT' = E_0 + \frac{\alpha T^4}{4} & \text{crystal} \\ E_0 + \int_0^T \beta T' \, dT' = E_0 + \frac{\beta T^2}{2} & \text{glass} \end{cases}}$$

d) Chemical Equilibrium between crystal and glass phases:

$\mu_X = \mu_G$ at melting transition

$$\frac{1}{N}(E - TS)\Big|_X = \frac{1}{N}(E - TS)\Big|_G$$

$$\frac{1}{N}\left(E_0 + \frac{\alpha T^4}{4} - T \cdot \frac{\alpha T^3}{3}\right) = \frac{1}{N}\left(E_0 + \frac{\beta T^2}{2} - T \cdot \beta T\right)$$

$$\Rightarrow -\frac{\alpha}{12} T^4 = -\frac{\beta}{2} T^2$$

$$\Rightarrow \boxed{T_{melt} = \sqrt{\frac{6\beta}{\alpha}}}$$

e) Latent heat for liquid (or glass) to crystal transition

$$L = (E_{glass} - E_{crystal})\Big|_{T_{melt}}$$

$$= T_{melt}(S_a - S_x) + N\cancel{(\mu_a - \mu_x)}^{0}\Big|_{T_{melt}}$$

$$= T_{melt}\left(\beta T_{melt} - \frac{\alpha}{3} T_{melt}^{?}\right)$$

$$= \beta \cdot \left(\frac{6\beta}{\alpha}\right) - \frac{\alpha}{3}\left(\frac{6\beta}{\alpha}\right)^2$$

$$\boxed{L = -\frac{6\beta^2}{\alpha}}$$

$(< 0\ ??!!)$

$\downarrow$

glasses don't satisfy $S(T=0) = 0$, so we found a nonphysical result by assuming the 3rd law.

8. a) We want a Maxwell relation for $\frac{\partial S}{\partial V}\Big|_{T,N}$, so we need a relation between differentials $dV$, $dT$, $dN$.

Fix $N \to dN = 0$

Consider $F = E - TS$

$$dF = -S\,dT - P\,dV$$
$$= \frac{\partial F}{\partial T}\Big|_{V,N} dT + \frac{\partial F}{\partial V}\Big|_{T,N} dV$$

$$\Rightarrow \boxed{\frac{\partial S}{\partial V}\Big|_{T,N} = \frac{\partial P}{\partial T}\Big|_{V,N}}$$

b) $dE = T\,dS - P\,dV$

$\rightarrow$ $E$ is naturally a fn. of $S$ and $V$.

We want to consider $E$ as a fn. of $T$ and $V$.

$$dE = T\,dS - P\,dV \qquad (\text{constant } N)$$

$$= T\left(\frac{\partial S}{\partial T}\bigg|_V dT + \frac{\partial S}{\partial V}\bigg|_T dV\right) - P\,dV$$

(part a)

$$= T\left(\frac{\partial S}{\partial T}\bigg|_V dT + \frac{\partial P}{\partial T}\bigg|_V dV\right) - P\,dV$$

$$= T\frac{\partial S}{\partial T}\bigg|_V dT + \left(T\frac{\partial P}{\partial T}\bigg|_V - P\right)dV$$

Equation of state: $P(V-Nb) = Nk_B T$

$$\rightarrow \frac{\partial P}{\partial T}\bigg|_{V,N} = \frac{Nk_B}{V-Nb} = \frac{P}{T}$$

$$\Rightarrow dE = T\frac{\partial S}{\partial T}\bigg|_{V,N} dT \qquad \text{for const. } N$$

$$\Rightarrow \frac{\partial E}{\partial V}\bigg|_{T,N} = 0$$

$$\rightarrow \boxed{E(T,V,N) = E(T,N)}$$

c) To find $C_p$ and $C_V$, use

$$đQ = dE + P\,dV \quad (\text{constant } N)$$

$$= \left( \frac{\partial E}{\partial T}\Big|_V dT + \cancel{\frac{\partial E}{\partial V}}\Big|_T dV \right) + P\,dV$$

$$= \frac{\partial E}{\partial T} dT + P\,dV$$

$$C_V = \frac{đQ}{dT}\Big|_V = \frac{\partial E}{\partial T}\Big|_V$$

In terms of $T$ and $P$,

$$đQ = \left( \frac{\partial E}{\partial T}\Big|_p dT + \frac{\partial E}{\partial p}\Big|_T dp \right) + P\left( \frac{\partial V}{\partial T}\Big|_p dT + \frac{\partial V}{\partial p}\Big|_T dp \right)$$

$$= \left( \frac{\partial E}{\partial T} + P\frac{\partial V}{\partial T}\Big|_p \right) dT + \left( \frac{\partial E}{\partial p}\Big|_T + \frac{\partial V}{\partial P}\Big|_T \right) dP$$

$$C_p = \frac{đQ}{dT}\Big|_p = \frac{\partial E}{\partial T}\Big|_p + P\frac{\partial V}{\partial T}\Big|_p$$

$$C_p = \frac{\partial E}{\partial T}\Big|_V + P\frac{\partial}{\partial T}\left(\frac{Nk_BT}{P}\right)\Big|_P$$

(because $E=E(T)$, $\frac{\partial E}{\partial T}\Big|_P = \frac{\partial E}{\partial T}\Big|_V$)

$$= C_V + Nk_B$$

$$\boxed{\gamma \equiv \frac{C_P}{C_V} = \frac{C_V + Nk_B}{C_V} = 1 + \frac{Nk_B}{C_V}}$$

d) $$dE = C_V\, dT = C_V\, d\left(\frac{P(V-Nb)}{Nk_B}\right)$$

$$= \frac{C_V}{Nk_B}\left(P\,dV + (V-Nb)\,dP\right)$$

$$dQ = dE + P\,dV = 0 \qquad \text{Adiabatic}$$

$$\rightarrow \frac{C_V}{Nk_B}\left(P\,dV + (V-Nb)\,dP\right) + P\,dV = 0$$

$$\frac{dP}{P} = -\left(1 + \frac{Nk_B}{C_V}\right)\frac{dV}{V-Nb}$$

$$\frac{dP}{P} = -\gamma \frac{d(V-Nb)}{V-Nb}$$

$$\ln\left(\frac{P}{P_0}\right) = -\gamma \ln\left(\frac{V-Nb}{V_0}\right)$$

for constants $P_0, V_0$.

$$\rightarrow \boxed{P(V-Nb)^{\gamma} = \text{constant}}$$

9. a) $đQ = TdS = C\,dT$

$$\rightarrow S_s(T) = \int_0^T \frac{C_s(T')}{T'}\,dT' = \int_0^T \frac{(V\alpha T'^3)}{T'}\,dT'$$

$$\boxed{S_s = \frac{V\alpha T^3}{3}}$$

$$S_n(T) = \int_0^T \frac{C_n(T')}{T'}\,dT' = \int_0^T \frac{V(\beta T'^3 + \gamma T')}{T'}\,dT'$$

$$\boxed{S_n = V\left(\frac{\beta T^3}{3} + \gamma T\right)}$$

b) Latent Heat $L = T_c\left(S_n(T_c) - S_s(T_c)\right) = 0$

$$\rightarrow V\left(\frac{\beta T_c^3}{3} + \gamma T_c\right) - \frac{V\alpha T_c^3}{3} = 0$$

$$\boxed{T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}}$$

($T_c = 0$ solution is due to $S(0) = 0$ by the 3rd Law, and does not represent the phase transition.)

c) $E_n(T=0) = E_0$, $\quad E_s(T=0) = E_0 - V\Delta$

Fix the magnetization $M$, # electrons $N$.

$$dE = TdS = C\,dT$$

$$E_s(T) = E_s(T=0) + \int_0^T C_s(T')\,dT'$$

$$= E_0 - V\Delta + \int_0^T V\alpha T'^3\,dT'$$

$$= \boxed{E_0 - V\Delta + \frac{V\alpha T^4}{4}}$$

$$E_n(T) = E_n(T=0) + \int_0^T C_n(T')\,dT'$$

$$= E_0 + \int_0^T V(\beta T'^3 + \gamma T')\,dT'$$

$$= \boxed{E_0 + V\left(\frac{\beta T^4}{4} + \frac{\gamma T^2}{2}\right)}$$

d) Gibbs Free Energy $G = E - TS - BM = \mu N$, $B = 0$

At the transition temperature $T_c$, the two phases are in chemical equilibrium $\rightarrow \mu_s = \mu_n$

$\rightarrow G_s = G_n$

$$G_s(T_c) = \left(E_0 - V\Delta + \frac{V\alpha T_c^4}{4}\right) - TV\frac{\alpha T_c^3}{3}$$

$$= E_0 - V\left(\Delta + \frac{\alpha T_c^4}{12}\right)$$

$$G_n(T_c) = E_0 + V\left(\frac{\beta T_c^4}{4} + \frac{\gamma T_c^2}{2}\right) - TV\left(\frac{\beta T_c^3}{3} + \gamma T_c\right)$$

$$= E_0 - V\left(\frac{\beta T_c^4}{12} + \frac{\gamma T_c^2}{2}\right)$$

Solve for the gap $\Delta$ using $G_s(T_c) = G_n(T_c)$

$$\Rightarrow \Delta + \frac{\alpha T_c^4}{12} = \frac{\beta T_c^4}{12} + \frac{\gamma T_c^2}{2}$$

$$\Delta = \frac{(\beta - \alpha) T_c^4}{12} + \frac{\gamma T_c^2}{2}$$

with $T_c$ from part (a),

$$\Delta = \frac{(\beta - \alpha)}{12}\left(\frac{3\gamma}{\alpha - \beta}\right)^2 + \frac{\gamma}{2}\left(\frac{3\gamma}{\alpha - \beta}\right)$$

$$\boxed{\Delta = \frac{3}{4}\frac{\gamma^2}{\alpha - \beta}} = \frac{1}{4}\gamma T_c^2$$

e) In magnetic field $B$, $\begin{cases} M_s = -\frac{VB}{4\pi} \\ M_n = 0 \end{cases}$

$dE = TdS + B\,dM + \mu dN$ , $N$ fixed ($dN=0$)

In the presence of $B$,

$dG = -SdT - M\,dB + \mu dN$

$$G_s(T,B) = E - TS - BM$$

$$= G_s(T, B=0) - \int_0^B M(B')\,dB'$$

$$= G_s(T, B=0) + \int_0^B \frac{VB'}{4\pi}\,dB'$$

$$= G_s(T, B=0) + \frac{VB^2}{8\pi}$$

$$= E_0 - V\left(\Delta + \frac{\alpha T^4}{12}\right) + \frac{B^2}{8\pi}$$

$$G_n(T,B) = G_n(T, B=0)$$

$$= E_0 - V\left(\frac{\beta T^4}{12} + \frac{\gamma}{2}T^2\right)$$

Chemical Equilibrium: $G_s(T, B_c) = G_n(T)$

$$\rightarrow \frac{B_c^2}{8\pi} = \Delta - \frac{\gamma}{2}T^2 + \frac{\alpha - \beta}{12}T^4$$

$$\frac{B_c^2}{8\pi} = \underbrace{\frac{3}{4}\frac{\gamma^2}{\alpha-\beta}}_{\Delta \text{ from part d}} - \frac{\gamma}{2}T^2 + \frac{\alpha-\beta}{12}T^4$$

$$= \frac{\alpha-\beta}{12}\left(\frac{3\gamma}{\alpha-\beta} - T^2\right)^2$$

$$= \frac{\alpha-\beta}{12}\left(T_c^2 - T^2\right)^2$$

$$= \frac{\alpha-\beta}{12}T_c^4\left(1 - \frac{T^2}{T_c^2}\right)^2$$

$$= \frac{\alpha-\beta}{12}\cdot\left(\frac{3\gamma}{\alpha-\beta}\right)^2\left(1 - \frac{T^2}{T_c^2}\right)^2$$

$$= \frac{3}{4}\frac{\gamma^2}{\alpha-\beta}\left(1 - \frac{T^2}{T_c^2}\right)^2$$

$$= \Delta\left(1 - \frac{T^2}{T_c^2}\right)^2$$

$$\Rightarrow \boxed{B_c(T) = \sqrt{8\pi\Delta}\left(1 - \frac{T^2}{T_c^2}\right)}$$

$$= \sqrt{8\pi\cdot\frac{1}{4}\gamma T_c^2}\left(1 - \frac{T^2}{T_c^2}\right)$$

$$\boxed{= T_c\sqrt{2\pi\gamma}\left(1 - T^2/T_c^2\right)}$$

$$= B_0\left(1 - \frac{T^2}{T_c^2}\right) \quad \text{with} \quad \boxed{B_0 = \sqrt{8\pi\Delta} = \sqrt{2\pi\gamma}\,T_c}$$

Kardar, Chapter 2

1. a) $p(x) = \begin{cases} \frac{1}{2a} & , -a < x < a \\ 0 & , \text{otherwise} \end{cases}$

Characteristic function

$$\tilde{p}(k) = \int_{-\infty}^{\infty} p(x)\, e^{-ikx}\, dx$$

$$= \int_{-a}^{a} \frac{1}{2a} e^{-ikx}\, dx$$

$$= -\frac{1}{2aik} e^{-ikx} \Big|_{-a}^{a}$$

$$\boxed{\tilde{p}(k) = \frac{1}{ka} \sin(ka)}$$

We can find the moments of $p(x)$ by expanding $\tilde{p}(k)$ in a Taylor series:

$$\tilde{p}(k) = \frac{1}{ka} \sum_{n=0}^{\infty} (-1)^n \frac{(ka)^{2n+1}}{(2n+1)!}$$

$$= \sum_{n=0}^{\infty} \frac{(-ika)^{2n}}{(2n+1)!}$$

$\boxed{\langle x \rangle_c = \langle x \rangle = 0}$ from coeff. of $(-ik)^1$

$\boxed{\langle x^2 \rangle_c = \langle x^2 \rangle - \langle x \rangle^2 = \langle x^2 \rangle = \frac{1}{3} a^2}$ from coeff. of $\frac{(-ik)^2}{2!}$