HW #2 solutions

(1.) 2.19

Recall that
$$\begin{cases} C_V = T\left(\frac{\partial S}{\partial T}\right)_V, & C_p = T\left(\frac{\partial S}{\partial T}\right)_p \\ K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S, & K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \end{cases}$$

assume that $n = \text{const}$.

Consider $\frac{K_S}{K_T} = \left(\frac{\partial V}{\partial p}\right)_S \Big/ \left(\frac{\partial V}{\partial p}\right)_T$ $\ominus$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

$$\ominus \left(\frac{\partial V}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_V \left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_p = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_p \boxed{=}$$

chain rule

$\boxed{=}$ $\frac{C_V}{C_p}$, as desired.

Moreover, recall that

$$C_p - C_V = \underbrace{-T\left(\frac{\partial p}{\partial V}\right)_T}_{\substack{<0 \\ \text{by stability}}} \underbrace{\left[\left(\frac{\partial V}{\partial T}\right)_p\right]^2}_{>0} > 0$$

$$\boxed{C_p > C_V}$$

But then $\frac{K_T}{K_S} = \frac{C_p}{C_V} > 1 \Rightarrow \boxed{K_T > K_S}$

It is easier to compress gases isothermically than adiabatically.

(2.) 2.21

(a) In general, $dE = TdS + \underset{\text{intensive}}{\vec{f}} \cdot d\underset{\text{extensive}}{\vec{X}}$

For magnetic systems, $\vec{f} \cdot d\vec{X} \Rightarrow \underset{\text{intensive}}{H}\, d\overset{\text{extensive}}{M}$

Thus, $dE = TdS + HdM - pdV + \mu dN$, and

$$dA = -SdT + HdM - pdV + \mu dN.$$

Stability: $\begin{cases} \overbrace{\left(\frac{\partial H}{\partial M}\right)_{S,V,N}}^{= \left(\frac{\partial^2 E}{\partial M^2}\right)_{S,V,N}} > 0, \\ \underbrace{\left(\frac{\partial H}{\partial M}\right)_{T,V,N}}_{= \left(\frac{\partial^2 A}{\partial M^2}\right)_{T,V,N}} > 0 \end{cases} \Rightarrow \begin{cases} \chi_S^{-1} > 0, \\ \chi_T^{-1} > 0 \end{cases}$

Now, consider $\Phi = E - HM$:

$d\Phi = TdS - MdH - pdV + \mu dN$, yielding

$\Phi = \Phi(S, H, V, N)$.

But then $M = -\left(\frac{\partial \Phi}{\partial H}\right)_{S,V,N} = M(S, H, V, N)$ as well

Moreover, [V = const, N = const] $\begin{cases} \left(\frac{\partial M}{\partial S}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_S, \\ \left(\frac{\partial T}{\partial S}\right)_H = \left(\frac{\partial^2 \Phi}{\partial S^2}\right)_H > 0 \text{ by stability} \end{cases}$

as $T\uparrow$, $S\uparrow$ as well

Next, $$\chi_T = \left(\frac{\partial M}{\partial H}\right)_T \underset{\substack{\uparrow \\ M=M(S,H) \\ [N,V=\text{const}]}}{=} \left(\frac{\partial M}{\partial H}\right)_S + \left(\frac{\partial M}{\partial S}\right)_H \left(\frac{\partial S}{\partial H}\right)_T, \text{ or}$$

$\left(\frac{\partial H}{\partial H}\right)_T = 1$

$$\chi_T - \chi_S = \underbrace{\left(\frac{\partial M}{\partial S}\right)_H}_{-\left(\frac{\partial T}{\partial H}\right)_S} \underbrace{\left(\frac{\partial S}{\partial H}\right)_T}_{-\left(\frac{\partial T}{\partial H}\right)_S \left(\frac{\partial S}{\partial T}\right)_H} = \left(\frac{\partial T}{\partial H}\right)_S^2 \Big/ \left(\frac{\partial T}{\partial S}\right)_H > 0.$$

Thus, $\underline{\underline{\chi_T > \chi_S}}$

(b) Assume $V, N = \text{const}$ everywhere.

We need $$\left(\frac{\partial T}{\partial H}\right)_S = -\underbrace{\left(\frac{\partial T}{\partial S}\right)_H}_{>0 \text{ by stability}} \left(\frac{\partial S}{\partial H}\right)_T$$

Consider $\tilde{\Phi} = E - ST - HM$:

$$d\tilde{\Phi} = -S\,dT - M\,dH - p\,dV + \mu\,dN$$

$$\left(\frac{\partial S}{\partial H}\right)_T = \underbrace{\left(\frac{\partial M}{\partial T}\right)_H}_{<0 \text{ by assumption}}$$

Finally, $$\left(\frac{\partial T}{\partial H}\right)_S = -\underbrace{\left(\frac{\partial T}{\partial S}\right)_H}_{>0} \underbrace{\left(\frac{\partial M}{\partial T}\right)_H}_{<0} \underline{\underline{> 0.}}$$

③ 2.25

a & b are constants

vdW equation: $\dfrac{P}{RT} = \dfrac{\rho}{1-b\rho} - a\rho^2\dfrac{1}{RT}$ (*)

$\rho = \dfrac{N}{V}$

Stability implies: $N = const$

$-\left(\dfrac{\partial P}{\partial V}\right)_T > 0$, or

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial P}{\partial V}\right)_T \underbrace{\frac{dV}{d\rho}} = -\frac{V^2}{N}\left(\frac{\partial \overset{\text{pressure}}{P}}{\partial V}\right)_T > 0.$$

$$\frac{d\rho}{dV} = -\frac{N}{V^2}$$

From (*) we obtain:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = RT\left[\frac{1}{1-b\rho} - \frac{\rho(-b)}{(1-b\rho)^2}\right] - 2a\rho =$$

$$= \frac{RT}{(1-b\rho)^2} - 2a\rho.$$

$\left(\dfrac{\partial P}{\partial \rho}\right)_T = 0$ at the boundary of the instability region:

$$RT = 2a\rho(1-b\rho)^2 \quad (**)$$ cubic polynomial

Eq. (**) is the eq'n of the spinodal in the T-ρ plane.

$$\frac{dT}{d\rho} = 0 \Rightarrow (1-b\rho)^2 + 2\rho(1-b\rho)(-b) =$$

$$= (1-b\rho)[1-b\rho-2b\rho] =$$

$$= (1-b\rho)(1-3b\rho) \overset{\text{extrema}}{=} 0$$

$$\rightarrow \rho = \frac{1}{b}, \frac{1}{3b} \text{ @ extrema}$$

Further, $\dfrac{d^2T}{dp^2} \Rightarrow \underbrace{(-b)(1-3bp) + (1-bp)(-3b) = 0}_{\text{inflection point}}$, or

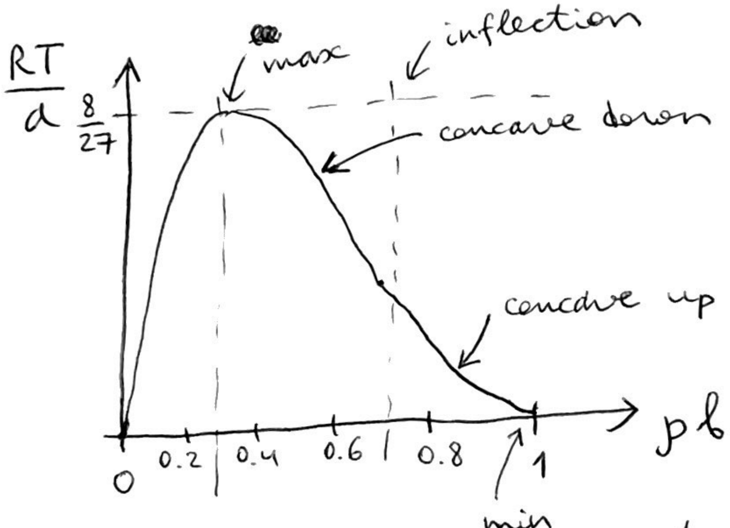
$$1-3bp + 3(1-bp) = 0,$$

$$4 - 6bp = 0 \Rightarrow \underline{p = \frac{2}{3b}} \quad \text{inflection point}$$

Now, $\dfrac{RT}{a} = 0$ @ $p = 0, \dfrac{1}{b}$

We only plot $0 \leq p \leq \dfrac{1}{b}$ since $p > \dfrac{1}{b}$ will give $P < 0$ in Eq. (*)

$$\frac{RT}{a} = 2\,\frac{1}{3b}\left(1-\frac{1}{3}\right)^2 = \frac{8}{27b} \quad @ \quad p = \frac{1}{3b}$$



Finally, $P_{spinodal} = \overbrace{P[T_{spinodal}(p), p]}^{\text{Eq. (*)}} =$

$$= 2ap(1-bp)^{\cancel{2}}\frac{p}{\cancel{1-bp}} - ap^2 = 2ap^2(1-bp) - ap^2 =$$

$$= \underline{\underline{ap^2(1-2bp)}} \quad \text{becomes} < 0 \text{ for } pb > \frac{1}{2}.$$