Problem 8.2-1 Stability of Fundamental Relations

a) The sign of the second derivative of a function determines if it is convex or concave

\[
\frac{d^2Y}{dX^2} = n(n-1)X^{n-2}
\]

Since \(X>0\), this derivative is negative only for \(0<n<1\), this is the concavity condition

b) \[F = A \left( \frac{N^5T}{V^3} \right)^{1/2} \]

\[
\frac{\partial^2 F}{\partial T^2} = - \frac{4AN^{5/2}V^{3/2}}{T^{3/2}} < 0
\]

\[
\frac{\partial^2 F}{\partial V^2} = \frac{15AN^{5/2}T^{1/2}}{4V^{7/2}} > 0
\]

Satisfy the stability criteria for \(F\), so the system is stable
Problem 8.2-1 Stability of Fundamental Relations

\[ G = B T^{1/2} P^2 N \]

\[ \frac{\partial^2 G}{\partial T^2} = -\frac{B P^2 N}{4T^{3/2}} < 0 \]

\[ \frac{\partial^2 G}{\partial P^2} = B T^{1/2} N > 0 \] - violates the stability criterion for G, system unstable

d) \[ H = \frac{C S^2 P^{1/2}}{N} \]

\[ \frac{\partial^2 H}{\partial S^2} = \frac{2C P^{1/2}}{N} > 0 \]

\[ \frac{\partial^2 H}{\partial P^2} = -\frac{C S^2}{4NP^{3/2}} < 0 \]

\{ \]

Satisfy the stability criteria for H, so the system is stable
Problem 8.2-1 Stability of Fundamental Relations

e) \[ U = \frac{DS^{3/2}V^2}{N^{5/2}} \]

\[ \frac{\partial^2 U}{\partial S^2} = \frac{3DV^2}{4S^{1/2}N^{5/2}} > 0 \]

\[ \frac{\partial^2 U}{\partial V^2} = \frac{2DS^{3/2}}{N^{5/2}} > 0 \]

\[ \frac{\partial^2 U}{\partial V \partial S} = \frac{3DS^{1/2}V}{N^{5/2}} \]

Checking fluting:

\[ \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left( \frac{\partial^2 U}{\partial V \partial S} \right)^2 = -\frac{15D^2SV^2}{2N^5} < 0 \]

The fluting condition is violated, so the system is not stable.
Problem 8.3-3 Instability of vdW Fluid

\[ P = \frac{RT}{v-b} - \frac{a}{v^2} \]

Let us calculate the isothermal compressibility:

\[ \kappa_T = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T = -\frac{1}{v} \left( \frac{\partial P}{\partial v} \right)_T \]

\[ \kappa_T = -\frac{1}{v} \left( \frac{RT}{(v-b)^2} + \frac{2a}{v^3} \right) \]

For stability: \[ \kappa_T = \frac{1}{vRT} \left( \frac{2a}{(v-b)^2} - \frac{2a}{v^2} \right) > 0 \]

\[ \frac{2a}{RT} < \frac{v^3}{(v-b)^2} \]
\[ \frac{RTv}{2a} > \left( 1 - \frac{b}{v} \right)^2 \]

The above condition is not always satisfied at low enough temperature and volume.
Let us use the Clapeyron equation to calculate the change of temperature

\[ \frac{dP}{dT} = \frac{\ell}{T \Delta v} \approx \frac{\ell}{Tv_g} \]

Where \( v_g \) is the molar volume of gas.

Approximating vapor by ideal gas:

\[ v_g = \frac{RT}{P} \]

\[ \frac{dP}{dT} = \frac{\ell P}{RT^2} \]

\[ \frac{dP}{P} = \frac{\ell dT}{RT^2} \quad \Rightarrow \quad \ln \left( \frac{P}{P_0} \right) = \frac{\ell}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right) \]

Approximately:

\[ \Delta P = \frac{\ell \Delta T}{RT^2} P \]
The change of pressure is

$$
\Delta P = \rho g \Delta h
$$

Where $\rho$ is the density of air, $g$ is the acceleration of free fall, and $\Delta h$ is the height difference. Substituting in the Clapeyron equation:

$$
\Delta h = \frac{\ell \Delta T}{g \rho RT^2}
$$

$$
P = \frac{4.2 \text{[J/cal]} \times 10^3 \text{[cal/mole]} \times 10 \text{[K]}}{10 \text{[m/s]}^2 \times 1.3 \text{[kg/m}^3] \times 8.3 \text{[J/K]} \times (373 \text{[K]})^2} \times 10^5 \text{[Pa]} = 281 \text{[m]}
$$
Problem 9.3-5 Triple Point

At the triple point, the coexistence curves intersect:

\[ 24.38 - \frac{3063}{T_c} = 27.92 - \frac{3754}{T_c} \]

\[ T_c = 195.2[K] \]

\[ P_c = \exp\left(24.38 - \frac{3063}{195.2}\right) = 5932.6[Pa] \]

Using the Clapeyron equation and approximating the gas phase by ideal gas:

\[ \Delta v \approx \frac{RT}{P} \quad \Rightarrow \quad \frac{dP}{dT} = \frac{\ell P}{RT^2} \quad \Rightarrow \quad \ell = \frac{RT^2}{P} \frac{dP}{dT} \]
Latent heat of vaporization:

\[ \ell_v = \frac{RT_c^2}{P_c} \frac{dP}{dT} = \frac{RT_c^2}{P_c} \exp\left(24.38 - \frac{3063}{T_c}\right) \frac{3063}{T_c^2} = 3063R = 25453[J/mole] \]

Latent heat of sublimation:

\[ \ell_s = \frac{RT_c^2}{P_c} \frac{dP}{dT} = \frac{RT_c^2}{P_c} \exp\left(27.92 - \frac{3754}{T_c}\right) \frac{3754}{T_c^2} = 3754R = 31196[J/mole] \]

Latent heat of fusion:

\[ \ell_f = \ell_s - \ell_v = 691R = 5742[J/mole] \]

The latter is due to the fact that a process described by a small circle around the triple point should return the system to the initial state with zero net work done in the cycle \((P \approx P_{tp} \text{ and } \Delta V_{cycle}=0)\) and zero total latent heat absorbed/emitted in the cycle.
Problem 9.3-6 Liquid-solid system

We can write the molar volume, $v$, of the solid/liquid system as:

$$v = x v_s + (1 - x)v_L$$  \hspace{1cm} (1)

where $x$ is the mole fraction of solid, and $v_s$ and $v_L$ are the molar volumes of solid and liquid respectively.

Taking total derivative to the above expression with respect to $T$ and noting that the molar volume of the system is restricted, we obtain:

$$\frac{dv}{dT} = \frac{dx}{dT} v_s + x \frac{dv_s}{dT} + \frac{dv_L}{dT} - \frac{dx}{dT} v_L - x \frac{dv_L}{dT} = 0$$  \hspace{1cm} (2)

Solving equation (2) for $dx/dT$:

$$\frac{dx}{dT} = \frac{x \frac{dv_s}{dT} + (1 - x) \frac{dv_L}{dT}}{v_L - v_s}$$  \hspace{1cm} (3)
Problem 9.3-6 Liquid-solid system

Now we need to calculate the total derivatives of molar volume in equation (3). Molar volumes of liquid in solid in equilibrium are functions of pressure and temperature, therefore:

\[
\frac{d\nu_{L,S}(P,T)}{dT} = \left( \frac{\partial \nu_{L,S}}{\partial T} \right)_P + \left( \frac{\partial \nu_{L,S}}{\partial P} \right)_T \frac{dP}{dT} \tag{4}
\]

Recalling the definitions of the coefficient of thermal expansion and isothermal compressibility, we can rewrite (4) as:

\[
\frac{d\nu_{L,S}(P,T)}{dT} = \alpha_{(L,S)} \nu_{L,S} - \kappa_{T(L,S)} \nu_{L,S} \frac{dP}{dT} \tag{5}
\]

Now we can use the Clapeyron equation to express dP/dT in terms of second derivatives of thermodynamic potentials:

\[
\frac{dP}{dT} = \frac{\ell}{T(v_L - v_S)} \tag{6}
\]
Substituting in eq. (5):

\[
\frac{dv_{L,s}(P, T)}{dT} = \alpha_{(L,s)}v_{L,s} - \kappa_{T_{(L,s)}}v_{L,s} \frac{\ell}{T(v_L - v_S)}
\]  \hspace{0.5cm} (7)

Now use eq. (7) in eq. (3):

\[
\frac{dx}{dT} = \frac{x}{dT} \frac{dv_s}{dT} + (1-x)\frac{dv_L}{dT}
= \frac{x}{(v_L - v_S)} \left( \alpha_s v_S - \kappa_{TL}v_s \frac{\ell}{T(v_L - v_S)} \right) + \frac{1-x}{(v_L - v_S)} \left( \alpha_L v_L - \kappa_{TL}v_L \frac{\ell}{T(v_L - v_S)} \right)
\]

Simplifying:

\[
\frac{dx}{dT} = \frac{x\alpha_s v_S + (1-x)\alpha_L v_L}{(v_L - v_S)} - \frac{\ell}{T} \frac{x\kappa_{TL}v_S + (1-x)\kappa_{TL}v_L}{(v_L - v_S)^2}
\]
Problem 9.4-4 vdW isotherm

vdW equation in reduced variables:
\[ \tilde{P} = \frac{8\tilde{T}}{3\tilde{v} - 1} - \frac{3}{\tilde{v}^2} = 0 \]

\[ \Rightarrow 8\tilde{T}\tilde{v}^2 - 9\tilde{v} + 3 = 0 \]
\[ \Rightarrow \tilde{v} = \frac{9 \pm \sqrt{81 - 96\tilde{T}}}{16\tilde{T}} \]

Two real solutions exist for:
\[ 81 - 96\tilde{T} > 0 \]
\[ \Rightarrow \tilde{T} < \frac{27}{32} \]
\[ \Rightarrow T < \frac{27}{32} \cdot \frac{8a}{27bR} \]
\[ \Rightarrow T < \frac{a}{4bR} \]

Therefore, vdW model fails even qualitatively for \( T < \frac{a}{4bR} \)
Problem 9.7-1 Phase diagram of a solution

Upper boundary

\[ T = T_0 - (T_0 - T_1)x_A^2 \]

Lower boundary

\[ T = T_0 - (T_0 - T_1)x_A(2 - x_A) \]

Initially:

\[ x_{A0} = \frac{N_A}{N_A + N_B} = \frac{1}{2} \]

The temperature where boiling first occurs:

\[ T_B = T_0 - (T_0 - T_1) \frac{1}{2} \left( 2 - \frac{1}{2} \right) = T_0 - \frac{3}{4}(T_0 - T_1) \]

The molar fraction of A in the vapor is given by:

\[ T_0 - (T_0 - T_1)x_A^2 = T_B = T_0 - \frac{3}{4}(T_0 - T_1) \quad \Longrightarrow \quad x_A^2 = \frac{3}{4} \quad \Longrightarrow \quad x_A = 0.866 \]
Mole fraction of A in the binary liquid is \( x_A^l \)
Mole fraction of A in the gas phase is \( x_A^g \)

\[
x_A^g = \frac{N_A^g}{N^g} \\
x_A^l = \frac{N_A^l}{N^l}
\]

Where:
- \( N^l \) - mole number of liquid A+B
- \( N^g \) - mole number of gas A+B
- \( N_A^l \) - mole number of liquid A
- \( N_B^l \) - mole number of liquid B
- \( N^l + N^g = N \) - total mole number

Mole fractions of liquid and gas A are related via the phase diagram on the left:

\[
T_0 - Dx_A^l = T_0 - Cx_A^g 
\Rightarrow \quad x_A^g = \frac{D}{C} x_A^l
\]

Therefore:

\[
\frac{N_A^g}{N^g} = x_A^g = \frac{D}{C} x_A^l = \frac{D}{C} \frac{N_A^l}{N^l} \quad (1)
\]
Problem 9.7-3 Binary liquid composition

From the initial condition of all material being liquid with mole fraction of A: $x_A^0$ and taking into account that the total mole fraction of A does not change during boiling:

$$x_A^0 = \frac{N_A^l + N_A^g}{N} \quad (2)$$

From (1):

$$N_A^g = \frac{D}{C} \frac{N_A^l}{N^l} (N - N^l)$$

Substituting in (2):

$$x_A^0 = \frac{N_A^l + \frac{D}{C} \frac{N_A^l}{N^l} (N - N^l)}{N} = \frac{N_A^l}{N^l} \frac{N^l}{N} \left(1 + \frac{D}{C} \frac{N - N^l}{N^l}\right) = x_A^l f \left(1 + \frac{D}{C} \frac{1}{f} - 1\right)$$

Where we have introduced the liquid fraction of material:

$$f = \frac{N^l}{N}$$
Problem 9.7-3 Binary liquid composition

\[ x_A^0 = x_A^l f \left( 1 + \frac{D}{C} \left( \frac{1}{f} - 1 \right) \right) \quad \Rightarrow \quad x_A^l = \frac{x_A^0}{f + \frac{D}{C} (1 - f)} \]

Since the fraction of material remaining in liquid is \( f = 1/2 \) and \( D = 3C \),

\[ x_A^l = \frac{x_A^0}{\left( \frac{1}{2} + \frac{3C}{C} \left( 1 - \frac{1}{2} \right) \right)} = \frac{x_A^0}{2} \]

There is also a one-line geometric solution to this problem. What is it?