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

c)

$$G = BT^{1/2} P^2 N$$

$$\frac{\partial^2 G}{\partial T^2} = -\frac{BP^2 N}{4T^{3/2}} < 0$$

$$\frac{\partial^2 G}{\partial P^2} = BT^{1/2} N > 0 \qquad \text{-violates the stability criterion for G, system unstable}$$

d)

$$H = \frac{CS^2 P^{1/2}}{N}$$

$$\frac{\partial^2 H}{\partial S^2} = \frac{2CP^{1/2}}{N} > 0$$

$$\frac{\partial^2 H}{\partial P^2} = -\frac{CS^2}{4NP^{3/2}} < 0$$

Satisfy the stability criteria for H, so the system is stable

e) $U = \dfrac{DS^{3/2}V^2}{N^{5/2}}$

$\dfrac{\partial^2 U}{\partial S^2} = \dfrac{3DV^2}{4S^{1/2}N^{5/2}} > 0$

$\dfrac{\partial^2 U}{\partial V^2} = \dfrac{2DS^{3/2}}{N^{5/2}} > 0$

$\dfrac{\partial^2 U}{\partial V \partial S} = \dfrac{3DS^{1/2}V}{N^{5/2}}$

Checking fluting:

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

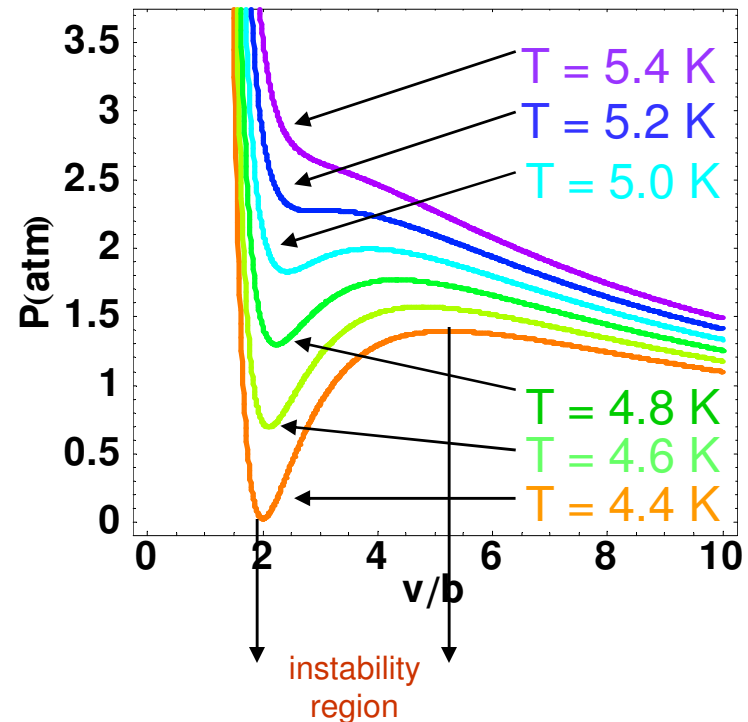The fluting condition is violated, so the system is not stable.

Problem 8.3-3 Instability of vdW Fluid

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

Let us calculate the isothermal compressibility:

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

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

P(atm) vs v/b

T = 5.4 K
T = 5.2 K
T = 5.0 K
T = 4.8 K
T = 4.6 K
T = 4.4 K

instability region

For stability:

$$\kappa_T = \frac{1}{\dfrac{vRT}{(v-b)^2} - \dfrac{2a}{v^2}} > 0 \quad \Longrightarrow \quad \frac{2a}{RT} < \frac{v^3}{(v-b)^2} \quad \Longrightarrow \quad \frac{RTv}{2a} > \left(1 - \frac{b}{v}\right)^2$$

The above condition is not always satisfied at low enough temperature and volume.

Problem 9.3-3 Boiling point versus height

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: $\qquad v_g = \frac{RT}{P}$

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

$$\frac{dP}{P} = \frac{\ell dT}{RT^2} \qquad \Longrightarrow \qquad \ln\left(\frac{P}{P_0}\right) = \frac{\ell}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)$$

Approximately: $\qquad \Delta P = \frac{\ell \Delta T}{RT^2} P$

Problem 9.3-3 Boiling point versus height

The change of pressure is $\quad \Delta P = \rho g \Delta h$

Where ρ is the density of air, g is the acceleration of free fall, and Δh is the height difference. Substituting in the Clapeyron equation:

$$\Delta h = \frac{\ell \Delta T}{g \rho R T^2} P = \frac{4.2[J/cal]*10^3[cal/mole]*10[K]}{10[m/s^2]*1.3[kg/m^3]*8.3[J/K]*(373[K])^2}10^5[Pa] = 281[m]$$

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:

$$\Delta v \approx \frac{RT}{P} \qquad \Longrightarrow \qquad \frac{dP}{dT} = \frac{\ell P}{RT^2} \qquad \Longrightarrow \qquad \ell = \frac{RT^2}{P}\frac{dP}{dT}$$

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 ($P \approx P_{tp}$ 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: $v = xv_S + (1-x)v_L$

(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:

$$\frac{dv}{dT} = \frac{dx}{dT}v_S + x\frac{dv_S}{dT} + \frac{dv_L}{dT} - \frac{dx}{dT}v_L - x\frac{dv_L}{dT} = 0 \qquad (2)$$

Solving equation (2) for dx/dT:

$$\frac{dx}{dT} = \frac{x\dfrac{dv_S}{dT} + (1-x)\dfrac{dv_L}{dT}}{(v_L - v_S)} \qquad (3)$$

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:

$$\frac{dv_{L,S}(P,T)}{dT} = \left(\frac{\partial v_{L,S}}{\partial T}\right)_P + \left(\frac{\partial v_{L,S}}{\partial P}\right)_T \frac{dP}{dT} \qquad (4)$$

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

$$\frac{dv_{L,S}(P,T)}{dT} = \alpha_{(L,S)}v_{L,S} - \kappa_{T(L,S)}v_{L,S}\frac{dP}{dT} \qquad (5)$$

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

$$\frac{dP}{dT} = \frac{\ell}{T(v_L - v_S)} \qquad (6)$$

Problem 9.3-6 Liquid-solid system

Substituting in eq. (5):

$$\frac{dv_{L,S}(P,T)}{dT} = \alpha_{(L,S)}v_{L,S} - \kappa_{T(L,S)}v_{L,S}\frac{\ell}{T(v_L - v_S)} \tag{7}$$

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

$$\frac{dx}{dT} = \frac{x\dfrac{dv_S}{dT} + (1-x)\dfrac{dv_L}{dT}}{(v_L - v_S)} = \frac{x}{(v_L - v_S)}\left(\alpha_S v_S - \kappa_{TL}v_S\frac{\ell}{T(v_L - v_S)}\right) + \frac{1-x}{(v_L - v_S)}\left(\alpha_L v_L - \kappa_{TL}v_L\frac{\ell}{T(v_L - v_S)}\right)$$

Simplifying:

$$\frac{dx}{dT} = \frac{x\alpha_S v_S + (1-x)\alpha_L v_L}{(v_L - v_S)} - \frac{\ell}{T}\frac{x\kappa_{TL}v_S + (1-x)\kappa_{TL}v_L}{(v_L - v_S)^2}$$

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

$$\Longrightarrow \quad 8\tilde{T}\tilde{v}^2 - 9\tilde{v} + 3 = 0 \quad \Longrightarrow \quad \tilde{v} = \frac{9 \pm \sqrt{81-96\tilde{T}}}{16\tilde{T}}$$

Two real solutions exist for:

$$81 - 96\tilde{T} > 0 \quad \Longrightarrow \quad \tilde{T} < \frac{27}{32} \quad \Longrightarrow \quad T < \frac{27}{32}\frac{8a}{27bR} \quad \Longrightarrow \quad T < \frac{a}{4bR}$$

Therefore, vdW model fails even qualitatively for $\quad T < \dfrac{a}{4bR}$

Problem 9.7-1 Phase diagram of a solution

Upper boundary $\quad T = T_0 - (T_0 - T_1)x_A^2$

Lower boundary $\quad T = T_0 - (T_0 - T_1)x_A(2 - x_A)$

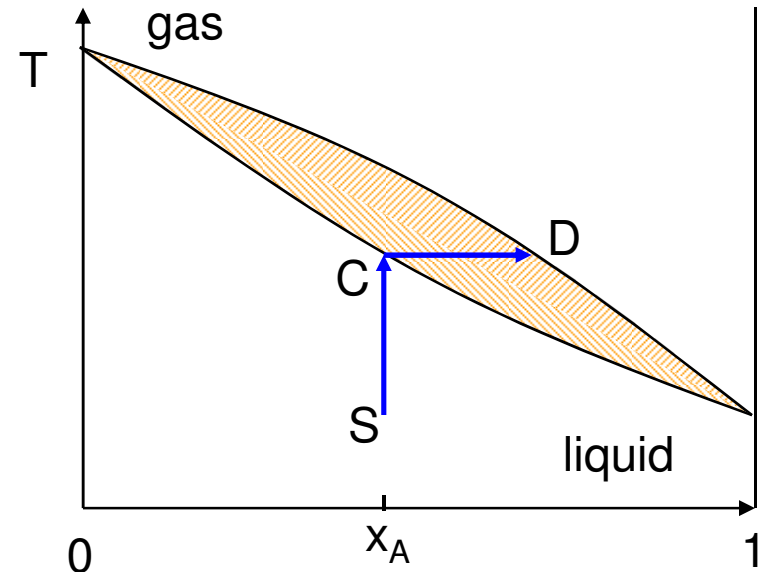Initially: $\qquad x_{A0} = \dfrac{N_A}{N_A + N_B} = \dfrac{1}{2}$
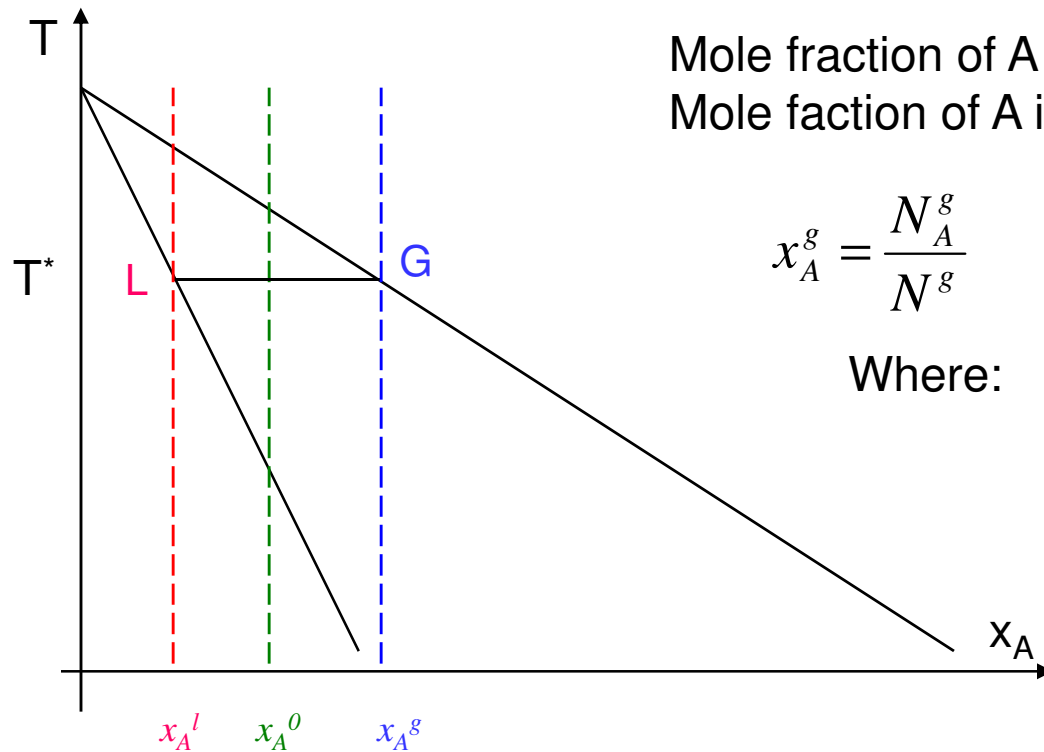
The temperature where boiling first occurs:

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

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

$$T_0 - (T_0 - T_1)x_A^2 = T_B = T_0 - \frac{3}{4}(T_0 - T_1) \implies x_A^2 = \frac{3}{4} \implies x_A = 0.866$$

Problem 9.7-3 Binary liquid composition

T (vertical axis), x_A (horizontal axis)

T* marked on vertical axis; points L and G on the horizontal tie line; dashed vertical lines at x_A^l, x_A^0, x_A^g.

Mole fraction of A in the binary liquid is x_A^l
Mole faction of A in the gas phase is x_A^g

$$x_A^g = \frac{N_A^g}{N^g} \qquad\qquad x_A^l = \frac{N_A^l}{N^l}$$

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:

$$T_0 - Dx_A^l = T_0 - Cx_A^g \qquad\Longrightarrow\qquad x_A^g = \frac{D}{C}x_A^l$$

Therefore: $\qquad \dfrac{N_A^g}{N^g} = x_A^g = \dfrac{D}{C}x_A^l = \dfrac{D}{C}\dfrac{N_A^l}{N^l} \qquad\qquad$ (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:

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

From (1): $\qquad N_A^g = \frac{D}{C} \frac{N_A^l}{N^l} \left(N - N^l \right)$

Substituting in (2):

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

Where we have introduced the liquid fraction of material: $\qquad f = \dfrac{N^l}{N}$

Problem 9.7-3 Binary liquid composition

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

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?