

Chapter 2 Conditions for Equilibrium and Stability

Ye Liang

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2.1

Suppose we have v different heterogeneous phases instead of two. Starting from the variation of energy

$$\delta E = \sum_{\alpha=1}^v \left[T^{(\alpha)} \delta S^{(\alpha)} - p^{(\alpha)} \delta V^{(\alpha)} + \sum_{i=1}^r \mu_i^{(\alpha)} \delta n_i^{(\alpha)} \right] \quad (1)$$

and the condition for equilibrium

$$(\delta E)_{S,V,n_i} \geq 0, \quad (2)$$

first we have

$$\sum_{\alpha=1}^v \delta S^{(\alpha)} = 0, \quad \sum_{\alpha=1}^v \delta V^{(\alpha)} = 0, \quad \sum_{\alpha=1}^v \delta n_i^{(\alpha)} = 0 \text{ for } i = 1, 2, \dots, r. \quad (3)$$

Thus

$$\sum_{\alpha=1}^{v-1} \delta S^{(\alpha)} = -\delta S^{(v)}, \quad \sum_{\alpha=1}^{v-1} \delta V^{(\alpha)} = -\delta V^{(v)}, \quad \sum_{\alpha=1}^{v-1} \delta n_i^{(\alpha)} = -\delta n_i^{(v)} \text{ for } i = 1, 2, \dots, r. \quad (4)$$

$$\sum_{\alpha=1}^v T^{(\alpha)} \delta S^{(\alpha)} - \sum_{\alpha=1}^v p^{(\alpha)} \delta V^{(\alpha)} + \sum_{i=1}^r \sum_{\alpha=1}^v \mu_i^{(\alpha)} \delta n_i^{(\alpha)} \geq 0 \quad (5)$$

$$\sum_{\alpha=1}^{v-1} (T^{(\alpha)} - T^{(v)}) \delta S^{(\alpha)} - \sum_{\alpha=1}^{v-1} (p^{(\alpha)} - p^{(v)}) \delta V^{(\alpha)} + \sum_{i=1}^r \sum_{\alpha=1}^{v-1} (\mu_i^{(\alpha)} - \mu_i^{(v)}) \delta n_i^{(\alpha)} \geq 0 \quad (6)$$

Because $\delta S^{(\alpha)}, \delta V^{(\alpha)}, \delta n_i^{(\alpha)}$ ($\alpha = 1, \dots, v-1$) are independent arbitrary reals, their coefficients have to be zero to make the inequality valid. Therefore

$$T^{(1)} = T^{(2)} = \dots = T^{(v)}, \quad (7)$$

$$p^{(1)} = p^{(2)} = \dots = p^{(v)}, \quad (8)$$

$$\mu_i^{(1)} = \mu_i^{(2)} = \dots = \mu_i^{(v)} \text{ for } i = 1, 2, \dots, r. \quad (9)$$

2.2

We can separate the only phase into several regions and regard them as different “heterogeneous phases”. Then we apply the above conclusion and find so.

2.3

From the condition $(\delta E)_{S,V,n_i} \geq 0$ we have got the criteria equations (7) (8) (9). On the other hand, starting from the three criteria, the inequality (6) is satisfied. Thus these criteria are both necessary and sufficient conditions for equilibrium.

2.4

Starting from the condition of a stable equilibrium state,

$$\because \left(\frac{\partial^2 H}{\partial S^2} \right)_{p,n} \geq 0, \quad \left(\frac{\partial H}{\partial S} \right)_{p,n} = T, \quad (10)$$

$$\therefore \left(\frac{\partial T}{\partial S} \right)_{p,n} \geq 0. \quad (11)$$

By definition,

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{p,n}. \quad (12)$$

Therefore

$$\frac{T}{C_p} \geq 0. \quad (13)$$

$$\because T > 0, \quad \therefore C_p \geq 0. \quad (14)$$

2.5

We noticed that

$$dH = TdS + Vdp + \mu dn, \quad \left(\frac{\partial H}{\partial p} \right)_{S,n} = V, \quad \left(\frac{\partial^2 H}{\partial p^2} \right)_{S,n} \leq 0, \quad (15)$$

$$\left(\frac{\partial V}{\partial p} \right)_{S,n} = \left(\frac{\partial^2 H}{\partial p^2} \right)_{S,n} \leq 0. \quad (16)$$

Thus

$$K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{S,n} \geq 0. \quad (17)$$

2.6

Because we know that

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_{T,n} \left(\frac{\partial V}{\partial T} \right)_{p,n}^2 \quad (18)$$

and

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_{T,n} \geq 0, \quad (19)$$

it can be seen

$$C_p - C_V = \frac{T}{VK_T} \left(\frac{\partial V}{\partial T} \right)_{p,n}^2 \geq 0. \quad (20)$$

2.7

The equation $\left(\frac{\partial p}{\partial v} \right)_T = 0$ indicates that when the concentration is uniform, we have $(\delta^3 A)_{T,V,n} \geq 0$. That would mean

$$\left(\frac{\partial^4 A}{\partial V^4} \right)_{T,n} \geq 0. \quad (21)$$

Then we find

$$\left(\frac{\partial^3 p}{\partial v^3} \right)_T = n^3 \left(\frac{\partial^3 p}{\partial V^3} \right)_T = -n^3 \left(\frac{\partial^4 A}{\partial V^4} \right)_{T,n} \leq 0. \quad (22)$$

2.8

Variation of the function Φ at equilibrium gives $\delta^2\Phi \geq 0$. This means Φ is a convex function of the extensive variables

$$\left(\frac{\partial^2\Phi}{\partial X_i^2}\right)_{X_j, j \neq i, I_r} \geq 0. \quad (23)$$

Using the fact

$$\left(\frac{\partial\Phi}{\partial X_i}\right)_{X_j, j \neq i, I_r} = I_i, \quad (24)$$

we get

$$\left(\frac{\partial I_i}{\partial X_i}\right)_{X_j, j \neq i, I_r} \geq 0. \quad (25)$$

2.9

(a)

$$\left(\frac{\partial p}{\partial v}\right)_T = -n \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n} \leq 0 \quad (26)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial S}{\partial V}\right)_{T,n}, \quad \text{not decided by stability conditions.} \quad (27)$$

From Gibbs-Duhem equation,

$$d\mu = -sdT + vdp = -sdT + v \left[\left(\frac{\partial p}{\partial v}\right)_T dv + \left(\frac{\partial p}{\partial T}\right)_v dT \right] \quad (28)$$

Thus

$$\left(\frac{\partial\mu}{\partial v}\right)_T = v \left(\frac{\partial p}{\partial v}\right)_T = -V \left(\frac{\partial^2 A}{\partial V^2}\right)_{T,n} \leq 0. \quad (29)$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v, \quad \text{not decided by the stability conditions.} \quad (30)$$

(b) Considering

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial s}{\partial v}\right)_T = -\left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial p}{\partial v}\right)_T \quad (31)$$

as well as the condition of (ii) and equation (26), it should be

$$\left(\frac{\partial s}{\partial p}\right)_T \geq 0. \quad (32)$$

Because from condition (iv),

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v > 0, \quad (33)$$

condition (ii) contradicts with condition (iv).

2.10

Because we can rewrite the Gibbs-Duhem equation as

$$dp = \frac{1}{v}d\mu + \frac{s}{v}dT, \quad (34)$$

when two phases coexist under equilibrium, $dp^{(\alpha)} = dp^{(\beta)}$,

$$\frac{1}{v^{(\alpha)}}d\mu + \frac{s^{(\alpha)}}{v^{(\alpha)}}dT = \frac{1}{v^{(\beta)}}d\mu + \frac{s^{(\beta)}}{v^{(\beta)}}dT, \quad (35)$$

$$\frac{\partial\mu}{\partial T} = -\frac{\frac{s^{(\alpha)}}{v^{(\alpha)}} - \frac{s^{(\beta)}}{v^{(\beta)}}}{\frac{1}{v^{(\alpha)}} - \frac{1}{v^{(\beta)}}}. \quad (36)$$

2.11

$$\frac{dp}{dT} = \frac{\Delta s(T)}{\Delta v(T)} \quad (37)$$

Intuitively, when water freezes into ice under a common condition, the volume will increase while the entropy will decrease. Thus $\frac{dp}{dT} < 0$, which means under a higher pressure, the ice can melt below its original melting point.

Liquid argon, similar to many other ordinary matters, has its volume and entropy both decrease after freezing into solid. Thus under a higher pressure, the melting point will rise.

2.12

The commonsense tells that after being frozen, the volume of water increases. Thus Fig2.7b is correct for water and Fig2.7b for other common matters. When the pressure is high above 1 atm, the melting point decreases, so that at 0 °C and pressure higher than 1 atm, water should be in the state of liquid.

2.13

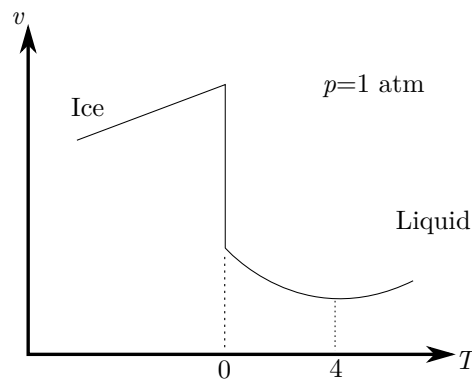


Figure 1: A sketch of water's v-t phase diagram at $\sim 1^\circ\text{C}$ and 1 atm.

2.14

Considering

$$\left(\frac{\partial \frac{A}{V}}{\partial \frac{n}{V}}\right)_T = \left(\frac{\partial A}{\partial n}\right)_{T,V} = \mu, \quad (38)$$

$$\left(\frac{\partial^2 A}{\partial n^2}\right)_{T,V} \geq 0. \quad (39)$$

Suppose $\mu > 0$ then we have the following graph.

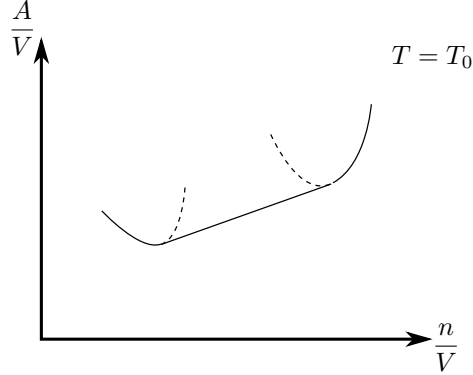


Figure 2: A demonstrative graph of A/V vs. v^{-1} to illustrate the tangent construction.

2.15

$$\begin{aligned} \left(\frac{\partial p}{\partial v}\right)_T &= RT \left[\frac{-\frac{1}{v^2} \left(1 - \frac{b}{v}\right) - \frac{b}{v^3}}{\left(1 - \frac{b}{v}\right)^2} - \frac{a}{RT} \frac{(-2)}{v^3} \right] \\ &= -\frac{RT}{v^2 \left(1 - \frac{b}{v}\right)^2} + \frac{2a}{v^3} \end{aligned} \quad (40)$$

To find the unstable temperature range, let $\left(\frac{\partial p}{\partial v}\right)_T > 0$,

$$\begin{aligned} \frac{RT}{\left(1 - \frac{b}{v}\right)^2} &< \frac{2a}{v}, \\ RT &< \frac{2a}{v} \left(1 - \frac{b}{v}\right)^2. \end{aligned} \quad (41)$$

2.16

Considering a phase diagram under $p = 1$ atm. The main difference of that of water from that of a simple material is the transition to the solid.

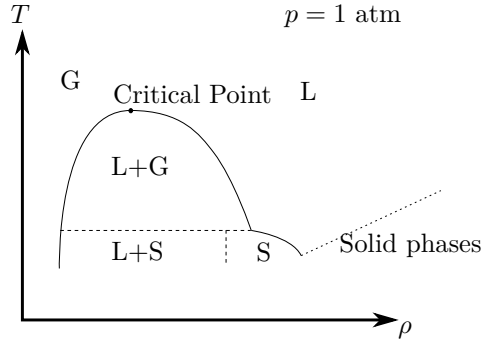


Figure 3: A sketch of the phase diagram of water.

2.17

When we measure the total energy of the system when changing the size of the system, we should always think of the boundary of the system, especially when we investigating properties related to the surface between the phases. Way (i) always gets rid of the outer surface energy, so that the surface energies are comparable after resize the system; while way (ii) is an imaginary setting in most situations. There are no external interaction with the boundary any more in the system.

2.18

Because “surface tension decreases when a solute accumulates on a surface”, when the surface tension decreases as the soap touches the water surface, the pepper powder particles are pushed away from the spot touched by the soap, and get gathered on the boundary where the water surface contacts the container.

After touching enough times, the surface tension becomes uniform again, and then the pepper powder is spreaded evenly on the surface again.

The system spontaneously evolves to the low free energy states. According to the Gibbs adsorption isotherm, the only way here is to increase the surface tension. Thus the “solute“ pepper powder is pushed far away from the low- γ spot.

2.19

(i)

$$\frac{K_S}{K_T} = \left(\frac{\partial V}{\partial p} \right)_{S,n} / \left(\frac{\partial V}{\partial p} \right)_{T,n} \quad (42)$$

$$\frac{C_V}{C_p} = \left(\frac{\partial S}{\partial T} \right)_{V,n} / \left(\frac{\partial S}{\partial T} \right)_{p,n} \quad (43)$$

$$\therefore (dS)_n = \left(\frac{\partial S}{\partial T} \right)_{V,n} dT + \left(\frac{\partial S}{\partial V} \right)_{T,n} dV = \left(\frac{\partial S}{\partial T} \right)_{V,n} dT + \left(\frac{\partial S}{\partial V} \right)_{T,n} \left[\left(\frac{\partial V}{\partial p} \right)_{T,n} dp + \left(\frac{\partial V}{\partial T} \right)_{p,n} dT \right] \quad (44)$$

$$\therefore \left(\frac{\partial S}{\partial T} \right)_{p,n} = \left(\frac{\partial S}{\partial T} \right)_{V,n} + \left(\frac{\partial S}{\partial V} \right)_{T,n} \left(\frac{\partial V}{\partial T} \right)_{p,n} \quad (45)$$

$$\therefore \left(\frac{\partial S}{\partial V} \right)_{T,n} = - \left(\frac{\partial S}{\partial T} \right)_{V,n} \left(\frac{\partial T}{\partial V} \right)_{S,n} \quad (46)$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_{p,n} = \left(\frac{\partial S}{\partial T}\right)_{V,n} - \left(\frac{\partial S}{\partial T}\right)_{V,n} \left(\frac{\partial T}{\partial V}\right)_{S,n} \left(\frac{\partial V}{\partial T}\right)_{p,n} \quad (47)$$

which is

$$\left(\frac{\partial S}{\partial T}\right)_{p,n} / \left(\frac{\partial S}{\partial T}\right)_{V,n} = 1 - \left(\frac{\partial T}{\partial V}\right)_{S,n} \left(\frac{\partial V}{\partial T}\right)_{p,n}. \quad (48)$$

$$\therefore (dT)_n = \left(\frac{\partial T}{\partial V}\right)_{p,n} dV + \left(\frac{\partial T}{\partial p}\right)_{V,n} dp = \left(\frac{\partial T}{\partial V}\right)_{p,n} dV + \left(\frac{\partial T}{\partial p}\right)_{V,n} \left[\left(\frac{\partial p}{\partial S}\right)_{V,n} dS + \left(\frac{\partial p}{\partial V}\right)_{S,n} dV \right] \quad (49)$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_{S,n} = \left(\frac{\partial T}{\partial V}\right)_{p,n} + \left(\frac{\partial T}{\partial p}\right)_{V,n} \left(\frac{\partial p}{\partial V}\right)_{S,n} \quad (50)$$

$$\begin{aligned} \therefore \left(\frac{\partial S}{\partial T}\right)_{p,n} / \left(\frac{\partial S}{\partial T}\right)_{V,n} &= 1 - \left(\frac{\partial T}{\partial V}\right)_{p,n} \left(\frac{\partial V}{\partial T}\right)_{p,n} - \left(\frac{\partial T}{\partial p}\right)_{V,n} \left(\frac{\partial p}{\partial V}\right)_{S,n} \left(\frac{\partial V}{\partial T}\right)_{p,n} \\ &= - \left(\frac{\partial T}{\partial p}\right)_{V,n} \left(\frac{\partial p}{\partial V}\right)_{S,n} \left(\frac{\partial V}{\partial T}\right)_{p,n} \end{aligned} \quad (51)$$

$$\therefore - \left(\frac{\partial T}{\partial p}\right)_{V,n} \left(\frac{\partial V}{\partial T}\right)_{p,n} = \left(\frac{\partial V}{\partial p}\right)_{T,n} \quad (52)$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_{p,n} / \left(\frac{\partial S}{\partial T}\right)_{V,n} = \left(\frac{\partial V}{\partial p}\right)_{T,n} / \left(\frac{\partial V}{\partial p}\right)_{S,n}. \quad (53)$$

Therefore

$$\frac{C_p}{C_V} = \frac{K_T}{K_S}. \quad (54)$$

(ii) We have already proven that $C_p > C_v$ in Exercise 2.6. Because of equation (54), we have $K_T > K_S$.

2.20

(a) According to the given fact,

$$\left(\frac{\partial T}{\partial L}\right)_{S,n} > 0. \quad (55)$$

It is also known that for a rubber band,

$$dE = TdS + fdL + \mu dn \quad (56)$$

Because

$$\left(\frac{\partial T}{\partial L}\right)_{S,n} = - \left(\frac{\partial T}{\partial S}\right)_{L,n} \left(\frac{\partial S}{\partial L}\right)_{T,n} \quad (57)$$

and

$$\left(\frac{\partial T}{\partial S}\right)_{L,n} = \left(\frac{\partial^2 E}{\partial S^2}\right)_{L,n} > 0, \quad (58)$$

$$\therefore \left(\frac{\partial S}{\partial L}\right)_{T,n} < 0. \quad (59)$$

Because

$$\left(\frac{\partial L}{\partial T}\right)_{f,n} = - \left(\frac{\partial L}{\partial f}\right)_{T,n} \left(\frac{\partial f}{\partial T}\right)_{L,n} \quad (60)$$

and

$$\left(\frac{\partial L}{\partial f}\right)_{T,n} = 1 / \left(\frac{\partial^2 E}{\partial L^2}\right)_{S,n} > 0, \quad \left(\frac{\partial f}{\partial T}\right)_{L,n} = \left(\frac{\partial S}{\partial L}\right)_{T,n} < 0 \quad (61)$$

we finally have

$$\left(\frac{\partial L}{\partial T}\right)_{f,n} > 0 \quad (62)$$

That is, a rubber band will contract when it is cooled at constant tension.

(b)

$$\therefore \left(\frac{\partial S}{\partial T}\right)_{f,n} = \left(\frac{\partial S}{\partial T}\right)_{L,n} + \left(\frac{\partial S}{\partial L}\right)_{T,n} \left(\frac{\partial L}{\partial T}\right)_{f,n} \quad (63)$$

$$\left(\frac{\partial S}{\partial T}\right)_{f,n} - \left(\frac{\partial S}{\partial T}\right)_{L,n} = \left(\frac{\partial S}{\partial L}\right)_{T,n} \left(\frac{\partial L}{\partial T}\right)_{f,n}. \quad (64)$$

Because of inequality (59) and (62),

$$\left(\frac{\partial S}{\partial T}\right)_{f,n} < \left(\frac{\partial S}{\partial T}\right)_{L,n}. \quad (65)$$

Therefore

$$\left(\frac{\partial T}{\partial S}\right)_{f,n} > \left(\frac{\partial T}{\partial S}\right)_{L,n}, \quad (66)$$

which means the rubber band held at constant tension has larger increase in temperature.

2.21

(a) (i) $\delta W = HdM$.

(ii) Since

$$dE = TdS - pdV + HdM + \mu dn, \quad (67)$$

$$\left(\frac{\partial H}{\partial M}\right)_{T,V,n} = \left(\frac{\partial^2 E}{\partial M^2}\right)_{T,V,n} \geq 0. \quad (68)$$

Thus

$$\chi_T \geq 0. \quad (69)$$

After the Legendre transform,

$$dA = -SdT - pdV + HdM + \mu dn. \quad (70)$$

$$\left(\frac{\partial H}{\partial M}\right)_{S,V,n} = \left(\frac{\partial^2 A}{\partial M^2}\right)_{S,V,n} \geq 0. \quad (71)$$

Thus

$$\chi_S \geq 0. \quad (72)$$

(iii) Considering $H = H(M, T, V, n) = H(M, S, V, n)$,

$$\begin{aligned} (dH)_{V,n} &= \left(\frac{\partial H}{\partial M}\right)_{T,V,n} (dM)_{V,n} + \left(\frac{\partial H}{\partial T}\right)_{M,V,n} (dT)_{V,n} \\ &= \left(\frac{\partial H}{\partial M}\right)_{T,V,n} (dM)_{V,n} + \left(\frac{\partial H}{\partial T}\right)_{M,V,n} \left[\left(\frac{\partial T}{\partial M}\right)_{S,V,n} (dM)_{V,n} + \left(\frac{\partial T}{\partial S}\right)_{M,V,n} (dS)_{V,n} \right] \end{aligned} \quad (73)$$

$$\left(\frac{\partial H}{\partial M}\right)_{S,V,n} = \left(\frac{\partial H}{\partial M}\right)_{T,V,n} + \left(\frac{\partial H}{\partial T}\right)_{M,V,n} \left(\frac{\partial T}{\partial M}\right)_{S,V,n} \quad (74)$$

$$\begin{aligned}
\therefore \left(\frac{\partial H}{\partial M}\right)_{S,V,n} - \left(\frac{\partial H}{\partial M}\right)_{T,V,n} &= \left(\frac{\partial H}{\partial T}\right)_{M,V,n} \left(\frac{\partial T}{\partial M}\right)_{S,V,n} \\
&= - \left(\frac{\partial S}{\partial M}\right)_{T,V,n} \left(\frac{\partial T}{\partial M}\right)_{S,V,n} \\
&= \left(\frac{\partial S}{\partial T}\right)_{M,V,n} \left(\frac{\partial T}{\partial M}\right)_{S,V,n} \left(\frac{\partial T}{\partial M}\right)_{S,V,n} > 0.
\end{aligned} \tag{75}$$

Thus

$$\frac{1}{\chi_S} - \frac{1}{\chi_T} > 0, \tag{76}$$

which is equivalent to

$$\chi_T - \chi_S > 0. \tag{77}$$

(b) The given condition is

$$\left(\frac{\partial M}{\partial T}\right)_{H,V,n} < 0. \tag{78}$$

$$\left(\frac{\partial T}{\partial H}\right)_{S,V,n} = \left(\frac{\partial T}{\partial H}\right)_{M,V,n} + \left(\frac{\partial T}{\partial M}\right)_{H,V,n} \left(\frac{\partial M}{\partial H}\right)_{S,V,n}. \tag{79}$$

$$\therefore \left(\frac{\partial T}{\partial H}\right)_{M,V,n} = - \left(\frac{\partial T}{\partial M}\right)_{H,V,n} \left(\frac{\partial M}{\partial H}\right)_{T,V,n} \tag{80}$$

$$\begin{aligned}
\therefore \left(\frac{\partial T}{\partial H}\right)_{S,V,n} &= - \left(\frac{\partial T}{\partial M}\right)_{H,V,n} \left[\left(\frac{\partial M}{\partial H}\right)_{T,V,n} - \left(\frac{\partial M}{\partial H}\right)_{S,V,n} \right] \\
&= - \left(\frac{\partial T}{\partial M}\right)_{H,V,n} (\chi_T - \chi_S) > 0.
\end{aligned} \tag{81}$$

2.22

(i)

$$\therefore sdT - vdp + d\mu = 0 \tag{82}$$

$$\therefore dp = \frac{s}{v}dT + \frac{1}{v}d\mu \tag{83}$$

When the two phases are equilibrium,

$$dp^{(\alpha)} = dp^{(\beta)} = dp, \quad dT^{(\alpha)} = dT^{(\beta)} = dT, \quad d\mu^{(\alpha)} = d\mu^{(\beta)} = d\mu. \tag{84}$$

$$\therefore \frac{s^{(\alpha)}}{v^{(\alpha)}}dT + \frac{1}{v^{(\alpha)}}d\mu = \frac{s^{(\beta)}}{v^{(\beta)}}dT + \frac{1}{v^{(\beta)}}d\mu \tag{85}$$

$$\therefore \left(\frac{s^{(\alpha)}}{v^{(\alpha)}} - \frac{s^{(\beta)}}{v^{(\beta)}}\right)dT = \left(\frac{1}{v^{(\beta)}} - \frac{1}{v^{(\alpha)}}\right)d\mu \tag{86}$$

$$\therefore \frac{d\mu}{dT} = \frac{\frac{s^{(\alpha)}}{v^{(\alpha)}} - \frac{s^{(\beta)}}{v^{(\beta)}}}{\frac{1}{v^{(\beta)}} - \frac{1}{v^{(\alpha)}}} = \frac{s^{(\alpha)}v^{(\beta)} - s^{(\beta)}v^{(\alpha)}}{v^{(\alpha)} - v^{(\beta)}}. \tag{87}$$

(ii) From the Gibbs-Duhem equation of a two-species system,

$$SdT - Vdp + n_1d\mu_1 + n_2d\mu_2 = 0 \tag{88}$$

or, defining the total moles of species $n = n_1 + n_2$ and the mole fraction $x_i = n_i/n$,

$$s dT - v dp + x_1 d\mu_1 + (1 - x_1) d\mu_2 = 0. \quad (89)$$

Since $\mu_2 = \mu_2(T, p, x_1)$,

$$\begin{aligned} d\mu_2 &= \left(\frac{\partial \mu_2}{\partial T} \right)_{p, x_1} dT + \left(\frac{\partial \mu_2}{\partial p} \right)_{T, x_1} dp + \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p} dx_1 \\ &= - \left(\frac{\partial S}{\partial n_2} \right)_{T, p, n_1} dT + \left(\frac{\partial V}{\partial n_2} \right)_{T, p, n_1} dp + \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p} dx_1 \\ &= -s_2 dT + v_2 dp + \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p} dx_1. \end{aligned} \quad (90)$$

Then the equation becomes

$$(s - x_2 s_2) dT - (v - x_2 v_2) dp + x_1 d\mu_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p} dx_1 = 0, \quad (91)$$

or, by definition,

$$x_1 s_1 dT - x_1 v_1 dp + x_1 d\mu_1 + x_2 \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p} dx_1 = 0, \quad (92)$$

$$s_1 dT - v_1 dp + d\mu_1 + \frac{x_2}{x_1} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p} dx_1 = 0. \quad (93)$$

The equilibrium of two phases gives

$$\frac{s_1^{(\alpha)}}{v_1^{(\alpha)}} dT + \frac{1}{v_1^{(\alpha)}} d\mu_1 + \frac{1}{v_1^{(\alpha)}} \frac{x_2^{(\alpha)}}{x_1^{(\alpha)}} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p}^{(\alpha)} dx_1 = \frac{s_1^{(\beta)}}{v_1^{(\beta)}} dT + \frac{1}{v_1^{(\beta)}} d\mu_1 + \frac{1}{v_1^{(\beta)}} \frac{x_2^{(\beta)}}{x_1^{(\beta)}} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T, p}^{(\beta)} dx_1 \quad (94)$$

Therefore

$$\left(\frac{\partial \mu_1}{\partial T} \right)_{x_1} = - \frac{\frac{s_1^{(\alpha)}}{v_1^{(\alpha)}} - \frac{s_1^{(\beta)}}{v_1^{(\beta)}}}{\frac{1}{v_1^{(\alpha)}} - \frac{1}{v_1^{(\beta)}}} = \frac{s_1^{(\alpha)} v_1^{(\beta)} - s_1^{(\beta)} v_1^{(\alpha)}}{v_1^{(\alpha)} - v_1^{(\beta)}}. \quad (95)$$

2.23

(a)

$$dE = T dS + f dL + \mu dM, \quad (96)$$

$$dA = -S dT + f dL + \mu dM. \quad (97)$$

Before the spring breaks,

$$A = \frac{k}{2M} L^2 \quad (98)$$

$$f = \left(\frac{\partial A}{\partial L} \right)_{T, M} = \frac{kL}{M} = kx. \quad (99)$$

After it breaks,

$$A = \frac{h}{2M} (L - L_0)^2 + cM = \frac{hL^2}{2M} + \frac{hMx_0}{2} - hLx_0 + cM \quad (100)$$

$$f = \left(\frac{\partial A}{\partial L} \right)_{T,M} = \frac{h(L - L_0)}{M} = h(x - x_0). \quad (101)$$

(b) Before the spring breaks,

$$\mu = \left(\frac{\partial A}{\partial M} \right)_{T,L} = -\frac{kL^2}{2M^2} = -\frac{1}{2}kx^2, \quad (102)$$

and after the spring breaks,

$$\mu = \left(\frac{\partial A}{\partial M} \right)_{T,L} = -\frac{hL^2}{2M^2} + \frac{hx_0^2}{2} + c = -\frac{h}{2}(x^2 - x_0^2) + c \quad (103)$$

(c) Before the spring breaks,

$$\frac{A}{M} - fx = \frac{1}{2}kx^2 - kx^2 = -\frac{1}{2}kx^2 = \mu, \quad (104)$$

and after the spring breaks,

$$\frac{A}{M} - fx = \frac{1}{2}h(x - x_0)^2 + c - h(x - x_0) = -\frac{1}{2}h(x^2 - x_0^2) + c = \mu. \quad (105)$$

(d) We may regard this breaking point as a phase transition. Then the intensive properties should be equal at this point. Let 1 and 2 in the subscripts of the variables denote the of the spring in the states before and after breaking, respectively. Then we have the equations

$$f_1 = f_2, \quad \mu_1 = \mu_2, \quad (106)$$

$$kx_1 = h(x_2 - x_0), \quad -\frac{1}{2}kx_1^2 = -\frac{1}{2}h(x_2^2 - x_0^2) + c \quad (107)$$

Eliminating x_1 gives the second order equation for x_2

$$\left(\frac{h^2}{k} - h \right) x_2^2 - \frac{2h^2}{k} x_0 x_2 + \left(\frac{h^2}{k} + h \right) x_0^2 + 2c = 0. \quad (108)$$

The solution is

$$x_2 = \frac{-x_0 h^2 + \sqrt{x_0^2 h^2 k^2 + 2hkc(k-h)}}{hk - h^2} \quad (109)$$

Thus the force is

$$f = \frac{-x_0 hk + \sqrt{x_0^2 h^2 k^2 + 2hkc(k-h)}}{k-h}. \quad (110)$$

(e)

$$x_2 - x_1 = x_2 - \frac{f}{k} = \frac{\sqrt{x_0^2 h^2 k^2 + 2hkc(k-h)}}{kh}. \quad (111)$$

2.24

(a), (b)

$$A^{(l)} = \frac{\alpha n^{(l)2}}{2TV^{(l)}}, \quad A^{(s)} = \frac{\beta n^{(s)3}}{3TV^{(s)2}} \quad (112)$$

The Helmholtz free energy has the differential form

$$dA = -SdT - pdV + \mu dn \quad (113)$$

from which we have

$$p_s = - \left(\frac{\partial A^{(l)}}{\partial V^{(l)}} \right)_{T,n} = \frac{\alpha n^{(l)2}}{2TV^{(l)2}} = \frac{\alpha}{2T} \rho^{(l)2} \quad (114)$$

$$\therefore \rho^{(l)} = \sqrt{\frac{2Tp_s}{\alpha}}. \quad (115)$$

Also,

$$p_s = - \left(\frac{\partial A^{(s)}}{\partial V^{(s)}} \right)_{T,n} = \frac{\beta n^{(s)3}}{3TV^{(s)3}} = \frac{2\beta}{3T} \rho^{(s)3} \quad (116)$$

$$\therefore \rho^{(s)} = \sqrt[3]{\frac{3Tp_s}{2\beta}} \quad (117)$$

Because of the equilibrium,

$$\mu = \left(\frac{\partial A^{(l)}}{\partial n^{(l)}} \right)_{T,V} = \left(\frac{\partial A^{(s)}}{\partial n^{(s)}} \right)_{T,V} \quad (118)$$

$$\frac{\alpha \rho^{(l)}}{T} = \frac{\beta \rho^{(s)2}}{T} \quad (119)$$

Then we can solve for p_s ,

$$p_s = \frac{2^7}{3^4} \frac{\alpha^3}{\beta^2 T}. \quad (120)$$

Then

$$\rho^{(l)} = \frac{16}{9} \frac{\alpha}{\beta}, \quad \rho^{(s)} = \frac{4}{3} \frac{\alpha}{\beta}. \quad (121)$$

(c)

$$\Delta s = -\frac{1}{n^{(s)}} \left(\frac{\partial A^{(s)}}{\partial T} \right)_{V,n} + \frac{1}{n^{(l)}} \left(\frac{\partial A^{(l)}}{\partial T} \right)_{V,n} = \frac{\beta \rho^{(s)2}}{3T^2} - \frac{\alpha \rho^{(l)}}{2T^2} = -\frac{8}{27} \frac{\alpha^2}{T^2 \beta}. \quad (122)$$

(d)

$$\Delta v = 1/\rho^{(s)} - 1/\rho^{(l)} = \frac{3}{16} \frac{\beta}{\alpha} \quad (123)$$

Thus

$$\frac{dp_s}{dT} = \frac{\Delta s}{\Delta v} = -\frac{128}{81} \frac{\alpha^3}{T^2 \beta^2}. \quad (124)$$

This result can be obtained from taking derivative on equation (120) as well.

2.25

(i) The stability condition is

$$\left(\frac{\partial p}{\partial \rho} \right)_{T,n} = \left(\frac{\partial p}{\partial V} \right)_{T,n} \left(\frac{\partial V}{\partial \rho} \right)_n = -\frac{V^2}{n} \left(\frac{\partial p}{\partial V} \right)_{T,n} > 0. \quad (125)$$

For the EOS of the VdW gas,

$$\left(\frac{\partial p}{\partial \rho} \right)_T = \frac{RT}{(1-b\rho)^2} - 2a\rho \quad (126)$$

Let

$$\left(\frac{\partial p}{\partial \rho} \right)_T < 0, \quad (127)$$

then we get the instability region of ρ

$$\rho(1 - b\rho)^2 > \frac{RT}{2a}. \quad (128)$$

(ii) And the spinodal is

$$RT = 2a\rho(1 - b\rho)^2 \quad (129)$$

(iii) Proof of the Maxwell construction.

2.26

(i) When the two phases coexists under equilibrium,

$$\beta_\alpha = \beta_\gamma, \quad p_\alpha = p_\gamma, \quad \mu_\alpha = \mu_\gamma \quad (130)$$

Thus

$$a + b\beta\mu = c + d\beta^2\mu^2 \quad (131)$$

Therefore

$$\beta\mu = \frac{b + \sqrt{b^2 + 4d(a - c)}}{2d} \quad (132)$$

From the Gibbs-Duhem equation,

$$v = \left(\frac{\partial \mu}{\partial p} \right)_T, \quad \therefore \rho = \frac{1}{v} = \left(\frac{\partial p}{\partial \mu} \right)_T = \left(\frac{\partial(\beta p)}{\partial(\beta \mu)} \right)_\beta \quad (133)$$

$$\therefore \Delta\rho = \rho_\gamma - \rho_\alpha = 2d\beta\mu - b = \sqrt{b^2 + 4a(a - c)} \quad (134)$$

(ii) At the phase transition, the pressure is

$$p = \frac{a}{\beta} + \frac{b^2 + b\sqrt{b^2 + 4d(a - c)}}{2d\beta}. \quad (135)$$