

Chapter 2 Question 3

Part A

The Helmholtz function for the surface is defined as

$$\begin{aligned} F &= U - TS \\ &= T^{LV} S^{LV} + \gamma^{LV} A^{LV} + \sum_i \mu_i^{LV} N_i^{LV} - T^{LV} S^{LV} \end{aligned}$$

Dividing through by the area

$$f = \gamma^{LV} + \sum_i \mu_i^{LV} N_i^{LV}$$

Since $\gamma^{LV} = \gamma^{LV}(T)$, f is function of T and μ_i^{LV} .

Part B

Constructing the Helmholtz function of the composite system

$$\begin{aligned} F^C &= U^C - T^C S^C \\ &= U^L + U^V + U^{LV} + U^R - T^R(S^L + S^V + S^{LV} + S^R) \end{aligned}$$

From the energy and entropy postulates

$$\begin{aligned} 0 &= \Delta(U^L + U^V + U^{LV} + U^R) \\ 0 &\geq \Delta(S^L + S^V + S^{LV} + S^R) \end{aligned}$$

Any arbitrary change would increase F^C , so at equilibrium, F^C must be at a minimum.

Part C

Taking virtual displacements of F^C

$$dF^C = \sum (\mu^V - \mu^L) dN^V + \sum (\mu^{LV} - \mu^L) dN^{LV} + (-4\pi R^2 P^V + 4\pi R^2 P^L + 8\pi \gamma^{LV} R) dR$$

Thus the constraints for equilibrium are

$$\begin{aligned} \mu^V &= \mu^L = \mu^{LV} \\ P^V &= P^L + \frac{2\gamma^{LV}}{R} \end{aligned}$$

Part D

Following the notes, we take the derivative of the difference between real and virtual states

$$\begin{aligned} \frac{dB(R, R_\epsilon) - B_0}{dR} &= 4\pi \gamma^{LV} (2R - \frac{3R^2}{R_\epsilon}) = 0 \\ R &= \frac{2R_\epsilon}{3} \end{aligned}$$