Chapter 2 Question 4

Part A

From the Van der Waals picture, if the system lies inside the vapour dome, a $P > P_s$ pushes the state from equilibrium (stable) to some other state (not stable, could be metastable) since the conditions

$$\frac{\partial P}{\partial v} = 0$$
$$\frac{\partial^2 P}{\partial v^2} = 0$$

are not necessarily true.

Part B

From the energy and entropy postulates

$$0 \geq \Delta U^C - T^R \Delta S^C + P^R \Delta V^C - \mu^R \Delta N^C$$

Expanding and noting conservation of molecules and $P^R = P^V$

$$\begin{aligned} 0 &\geq \Delta(U^L + U^V + U^{LV} + U^R) - T^R \Delta(S^L + S^V + S^{LV} + S^R) + P^R \Delta(V^L + V^V) \\ &\geq \Delta(U^V + T^R S^V + P^R V^V) + \Delta(U^L + T^R S^L) + \Delta(U^{LV} + T^R S^{LV}) + P^R \Delta V^L \\ &\geq \Delta(G^V + F^L + F^{LV} + P^V V^L) \end{aligned}$$

Defining

$$B = \Delta(G^V + F^L + F^{LV} + P^V V^L)$$

Any arbitrary change would increase B, so at equilibrium, B must be at a minimum.

Part C

Taking virtual displacements of B

$$\begin{aligned} dB &= dG^V + dF^L + dF^{LV} + P^R dV^L \\ &= \mu^V dN^V + (-P^L dV^L + \mu^L dN^L) + (\gamma^{LV} dA^{LV} + \mu^{LV} dN^{LV}) + P^V dV^L \end{aligned}$$

such that the constraints require

$$\begin{aligned} dN^L &= -N^V - N^{LV} \\ dV^L &= 4\pi R^2 dR \\ dA^{LV} &= 8\pi R dR \end{aligned}$$

which yields

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

Thus the constraints for equilibrium are

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

Using the chemical potentials of the liquid and vapour phases

$$\mu^V = \mu^L$$
$$\mu^V(T, P_s) + RT \ln \frac{P^V}{P_s} = \mu^L(T, P_s) + v_f(P^L - P_s)$$

Thus

$$P^L = \frac{RT}{v_f} \ln \frac{P^V}{P_s} + P_s$$
$$R_e = \frac{2\gamma^{LV}}{\frac{RT}{v_f} \ln \frac{P^V}{P_s} + P_s - P^V}$$

Substituting in properties at 373 K

$$R_e = \frac{2(0.05891)}{\frac{(101.42E3)(1.6720}{0.001043} \ln(1.4) + (101.42E3) - 1.4 * (101.42E3)}$$
$$= 2.155E - 9[m]$$

Part D

See the attached plots