Chapter 2 Question 2

Part A

From the energy and entropy postulates

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

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

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

Defining

$$D = \Delta(G^S + F^L + F^{LS} + P^S S^L)$$

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

$$\begin{aligned} G^S &= N_1^S \mu_1^S + N_2^S \mu_2^S \\ F^L &= -P^L S^L + N_2^L \mu_S^L \\ F^L &= A^{LS} \gamma^{LS} + N_2^{LS} \mu_2^{LS} + N_1^{LS} \mu_1^{LS} \end{aligned}$$

Part B

Taking virtual displacements of B

$$\begin{aligned} dB &= dG^S + dF^L + dF^{LS} + P^R dS^L \\ &= \sum_i^2 \mu_i^S dN_i^S + (-P^L dS^L + \mu_2^L dN_2^L) + (\gamma^{LS} dA^{LS} + \sum_i^2 \mu_i^{LS} dN_i^{LS}) + P^S dS^L \end{aligned}$$

such that the constraints require

$$\begin{aligned} dN_2^L &= -N_2^S - N_2^{LS} \\ N_1^S &= -N_1^{LS} \\ dS^L &= 4\pi R^2 dR \\ dA^{LS} &= 8\pi R dR \end{aligned}$$

which yields

$$dB = (\mu_2^L - \mu_2^S) dN^S + \sum_i^2 (\mu_i^{LS} - \mu_i^S) dN^{LS} + (-4\pi R^2 P^L + 4\pi R^2 P^S + 8\pi \gamma^{LS} R) dR$$

Thus the constraints for equilibrium are

$$\begin{aligned} \mu_2^S &= \mu_2^L = \mu_2^{LS} \\ P^L &= P^S + \frac{2\gamma^{LS}}{R_\delta} \end{aligned}$$

Part C

Using the Gibbs-Duhem relation

$$v^L = \frac{\partial \mu_2^L(T, P^L)}{\partial P^L}_T = v(T, P^R)\exp[\kappa_T(P^R - P^L)]$$

if $\kappa = \kappa(T)$, then we can write chemical potential of component 2 in the liquid phase

$$\mu_2^L(T, P^L) = \frac{v(T, P^R)}{\kappa_T}\exp[\kappa_T(P^R - P^L)] + f(T)$$

The chemical potential of component 2 in the weak solution

$$\mu_2^L(T, P^S, N_1^S, N_2^S) = \mu_2^0(T, P^R) + RT\ln\frac{N_2^S}{N_{2sat}^2(T, P^S)}$$

Part D

Setting the component 2 chemical potentials equal

$$\mu_2^L(T, P^L) = \mu_2^L(T, P^S, N_1^S, N_2^S)$$

For $\kappa_T(P^R - P^L) << 1$, we have

$$v_{f2}(P^L - P^R) = RT\ln\frac{N_2^S}{N_{2sat}^2(T, P^S)}$$
$$v_{f2}\frac{2\gamma^{LS}}{R_\delta} = RT\ln\frac{N_2^S Kh(T)}{N_1 P^R}$$

Rearranging

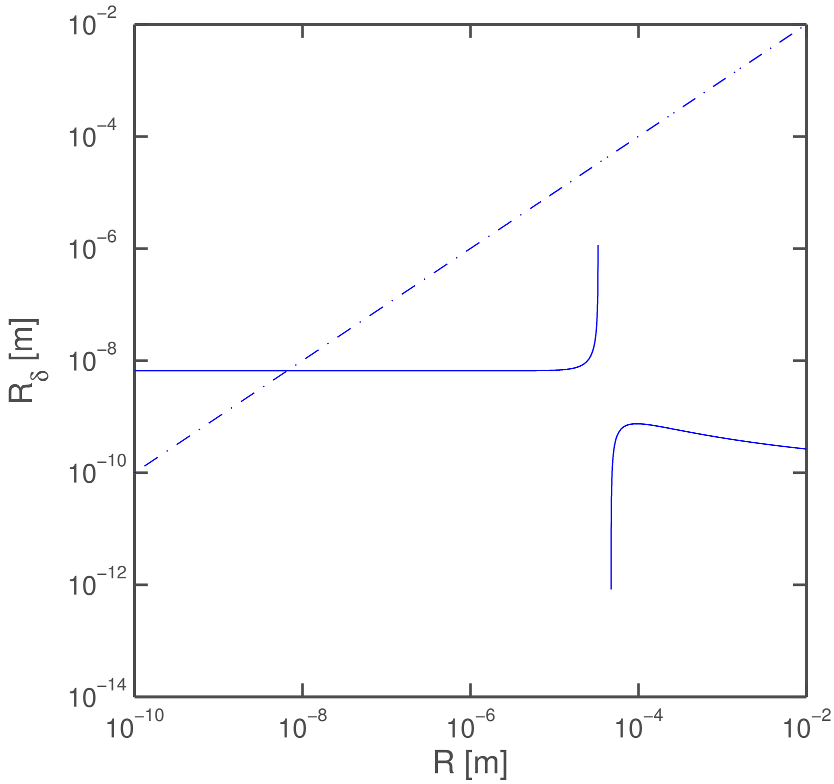
$$R_\delta = \frac{2\gamma^{LS}}{\frac{RT}{v_{f2}}\ln\frac{N_2^S Kh(T)}{N_1 P^R}}$$

Noting that $V^L = v_{f2}N_2^L = \frac{4\pi R^3}{3}$

$$R_\delta = \frac{2\gamma^{LS}}{\frac{RT}{v_{f2}}\ln\frac{(N_2 - \frac{4\pi R^3}{3v_{f2}})Kh(T)}{N_1 P^R}}$$

Part E

The points of intersection with the direct linear plot of R are 6.61e-9 and 3.31e-5 [m].



Part F

For a single phase weak solution

$$D_0 = \mu_1^S N_1^S + \mu_2^S - N_2^S$$

$$D - D_0 = (-P^L + P^R)V^L + \sum_i^2 N^L(\mu_i^L - \mu_i^S) + \sum_i^2 N^{LS}(\mu_i^{LS} - \mu_i^S) + \gamma^{LV} A^{LV}$$

Since the chemical potentials are equal

$$D - D_0 = 4\pi\gamma^{LV}(R^2 - \frac{2R^3}{3R_\delta})$$

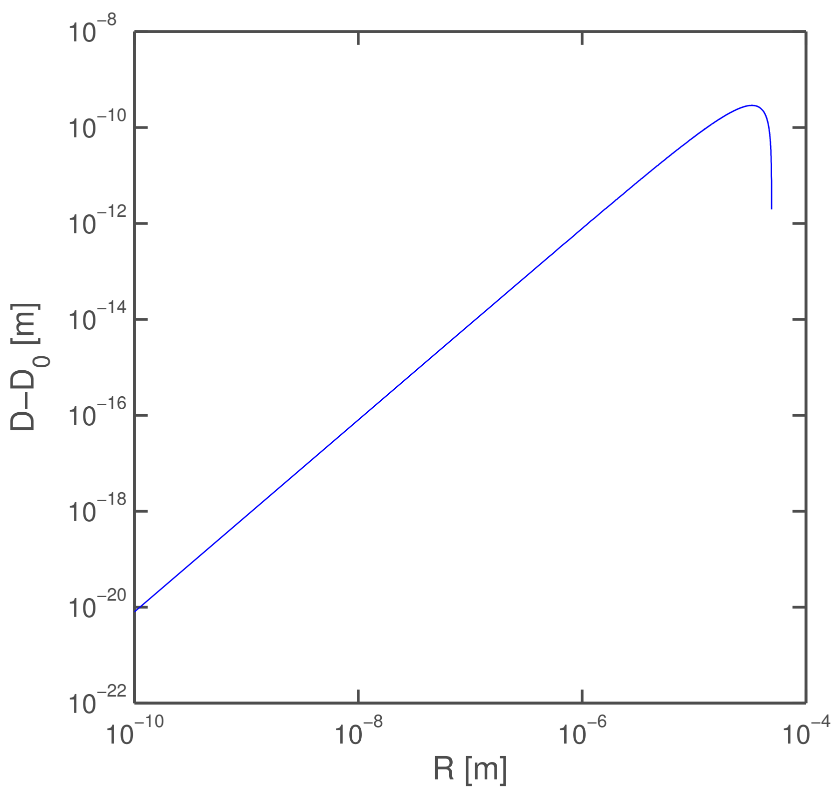


Figure 2: For R_δ=3.31e-5

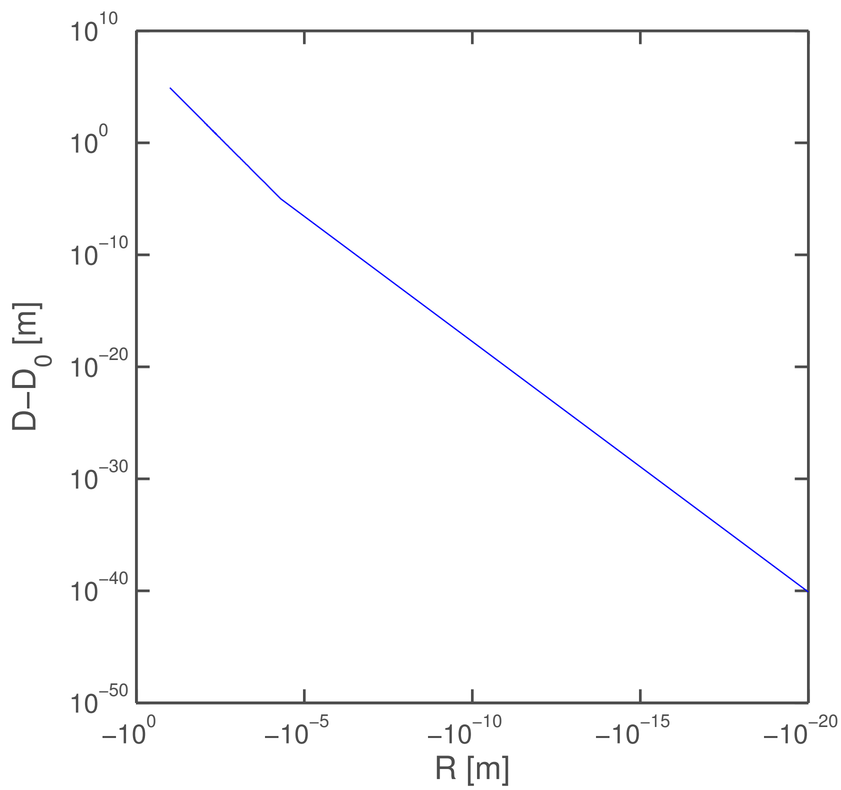


Figure 3: For R_δ=6.6e-9 (Not physical!)