

Homework 6 - Solution

Problem 1: Clausius-Clapeyron relation

A) Consider the phase change occurring at constant temperature and constant pressure

$$h_{lv} = \int_L^V dh = \int_L^V T ds + v dP = \int_L^V T ds = T \Delta s \quad (1)$$

B) Take the difference between the expression of the differential Gibbs equation calculated from the liquid phase and from the vapor phase

$$(v_l - v_v) dP - \Delta s dT = 0 \quad (2)$$

Combining Equation (1) and Equation (2) we obtain the Clausius-Clapeyron relation:

$$\frac{dP}{dT} = \frac{\Delta s}{v_l - v_v} = \frac{h_{lv}}{T(v_v - v_l)}$$

Problem 2: Hsu's model

A) As the boundary layer thins, the maximum bubble size decreases. The top of a large bubble will be surrounded by cooler water, further lowering the upper limit. Consequently, the range of cavity sizes decreases (Figure 1a).

B) Heating the substrate increases the upper limit and decreases the lower limit of the active cavity size, as evident from the graph (shifting toward the right).

C) Lowering the surface tension will reduce the lower limit as the Laplace pressure is smaller at the same bubble size. The range of cavity sizes increases (Figure 1b).

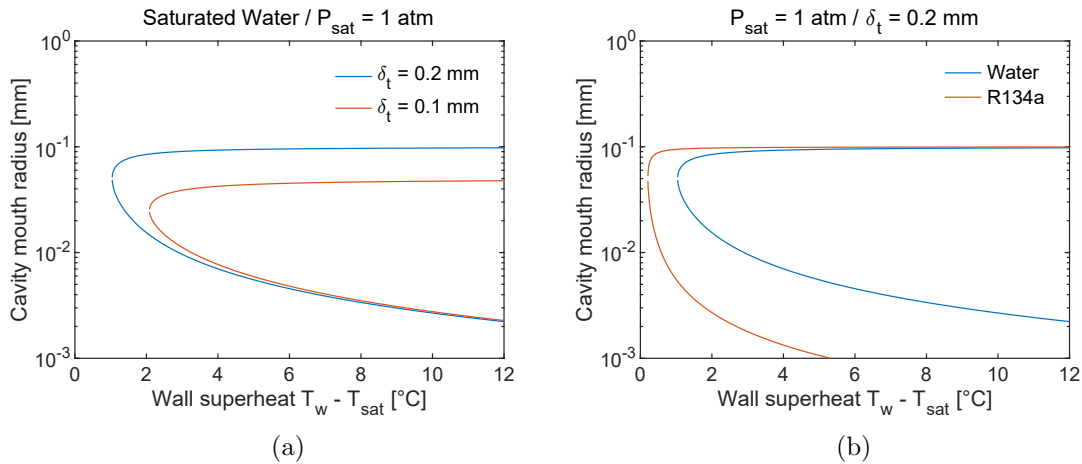


Figure 1: Prediction of the range of cavity sizes using Hsu's model for different boundary layers thicknesses (a) and fluids with different surface tension (b).

Problem 3: Equilibrium vapor pressure for meniscus in a cylindrical pore

A) At the saturation point, we have

$$\hat{g}_{sat,l}(T_l, P_{sat}) = \hat{g}_{sat,v}(T_l, P_{sat}) = \hat{g}_{sat}$$

The deviation of vapor Gibbs free energy:

$$\hat{g}_v - \hat{g}_{sat} = \int_{P_{sat}}^{P_v} v_v dP = \int_{P_{sat}}^{P_v} \frac{RT_l}{P} dP = RT_l \ln \left(\frac{P_v}{P_{sat}} \right)$$

The deviation of liquid Gibbs free energy:

$$\hat{g}_l - \hat{g}_{sat} = \int_{P_{sat}}^{P_l} v_l dP = v_l (P_l - P_{sat})$$

In equilibrium $\hat{g}_v = \hat{g}_l$, and therefore

$$v_l (P_l - P_{sat}) = RT_l \ln \left(\frac{P_v}{P_{sat}} \right)$$

With Young-Laplace equation:

$$P_v - P_l = \frac{2\sigma}{r}$$

Using the two equations above allows you to solve for P_v and P_l .

B) The code has been uploaded separately.

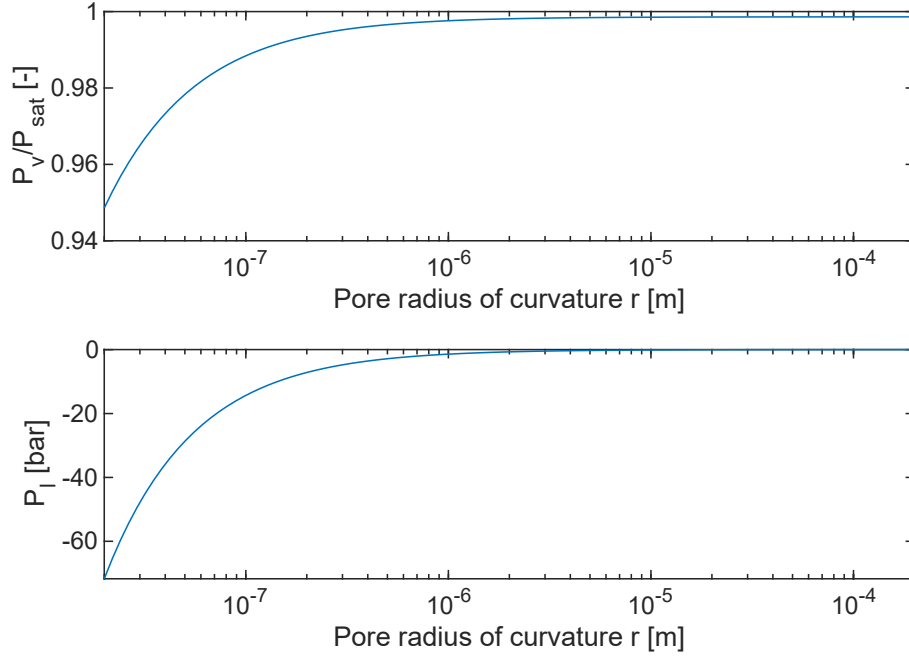


Figure 2: P_v/P_{sat} and P_l as a function of the pore radius of curvature r .