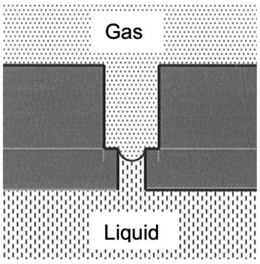
Exercise 3

1

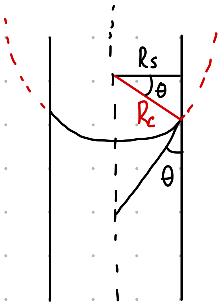
A bottle shaped pore consisting of two cylinders is surrounded by liquid and gas (see Figure). The radii of the pore are 1μm and 2 μm, respectively. The surface tension of the liquid is 70 mN/m and the contact angle with the solid surface is 30 degrees. The pressure in the liquid is 1 bar = 10^5 Pa.
The gas is not soluble in the liquid.



a. What is the minimum gas pressure required to prevent the liquid to pass through the pore and into the gas phase?
b. At which gas pressure will the gas leak into the liquid phase?

a) Young laplace:

$$\Delta P = P_l - P_g = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$



$\cos\theta = \frac{R_s}{R_c}$

$R_c = \frac{R_s}{\cos\theta}$

- Circular pore: $R_1 = R_2 = R_c$
- As the curvature is from gas towards the liquid, the $R_c < 0$

$$\Rightarrow \quad P_l - P_g = -\frac{2\gamma\cos\theta}{R_s}$$

If the liquid leaks into the gas, then we will come upon the wide part of the pore $R_s = 2\,\mu m$

Then $\Delta P < -\frac{2\gamma\cos\theta}{R_s}$

$$P_l - P_g < -\frac{2\gamma\cos\theta}{R_s}$$

$$P_g > P_l + \frac{2\gamma\cos\theta}{R_s} = 10^5\,Pa + \frac{2\cdot 70\cdot 10^{-3}\,N/m\cdot\cos 30}{2\cdot 10^{-6}\,m} = 1\,bar + 0{,}61\,bar = \underline{\underline{1{,}61\,bar}}$$

b) The gas will leak into the liquid if $\Delta P > -\frac{2\gamma\cos\theta}{R_s}$ in the small pore

$$P_l - P_g > -\frac{2\gamma\cos\theta}{R_s}$$

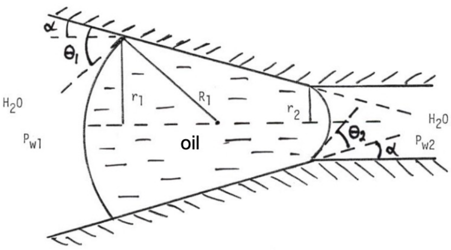
$\boxed{\frac{N}{m^2} = Pa}$

$$P_g < P_l + \frac{2\gamma\cos\theta}{R_s} = 10^5\,Pa + \frac{2\cdot 70\cdot 10^{-3}\,N/m\cdot\cos 30^\circ}{1\cdot 10^{-6}\,m} = 10^5\,Pa + 1{,}212\cdot 10^5\,Pa = \underline{\underline{2{,}21\,bar}}$$

2

The main reason that only 20-30% of the oil in a reservoir is produced during the primary phase (when the reservoir pressure is the driving force) is that oil drops are trapped in "bottlenecks" in the capillaries (pores) of the reservoir.

The figure below shows a (ideal) cross section through an oil drop trapped in the junction between a cone shaped and cylindrical pore. The wall of the cone forms an angle α to the wall of the cylinder. θ_1 and θ_2 is the retarding and advancing contact angle, respectively. It can be assumed that the pressure is similar throughout the oil drop.



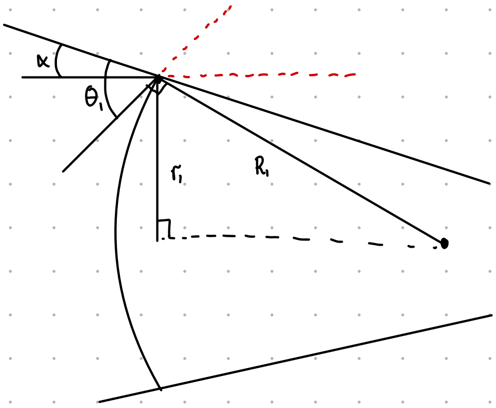
a. Show that the general expression for the pressure difference required in order to have the drop move towards right is given as follows:

$$\Delta P = P_{w1} - P_{w2} = 2\gamma_{ow}\left[\frac{\cos(\theta_2+\alpha)}{r_2} - \frac{\cos(\theta_1-\alpha)}{r_1}\right]$$

b. What is the change in the total free energy (ΔG_t) of the system when the oil drop has moved a distance $\Delta L = 5\mu m$ into the cylindrical pore?

Assume that the changes in r_1 and r_2 are so small that they can be considered constant during the change ΔL.
$\theta_1 = \theta_2 = 60°$
$r_1 = 20\mu m$
$r_2 = 8\mu m$
$\gamma_{ow} = 34mN/m$

c. Assume that the chemical composition of the reservoir is so that $\theta_1 = \theta_2 > 90°$.
What is the consequence for ΔG_t?
What is the consequence for the water pressure (P_{w1}) required to make the oil drop move into the cylindrical pore?



The pressure difference between the bubble, and P_{w_1}:

Circular meniscous => $R_1 = R_2$

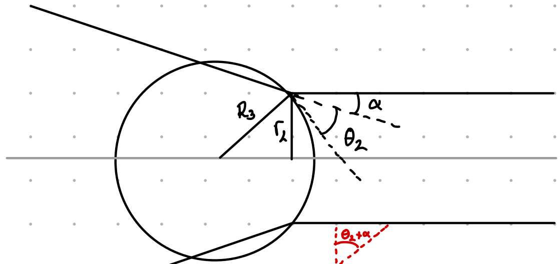
Young's eq: $\Delta P_1 = P_{oil} - P_{w_1} = \frac{2\gamma}{R_1}$

Need eq for R_1: r_1 is 90° on the α "angle leg"
R_1 is 90° on the θ_1 "angle leg"

=> Angle between R_1 and r_1 is equal to the difference between θ_1 and α

$$\Rightarrow \cos(\theta_1 - \alpha) = \frac{r_1}{R_1} \Rightarrow R_1 = \frac{r_1}{\cos(\theta_1-\alpha)}$$

$$\boxed{P_{oil} - P_{w_1} = \frac{2\gamma\cos(\theta_1-\alpha)}{r_1}}$$

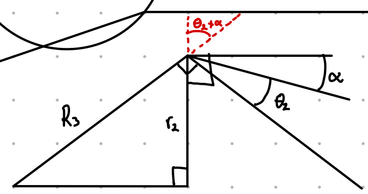


Similarily, for the other side:

$$\Delta P_2 = P_{oil} - P_{w_2} = \frac{2\gamma}{R_3}$$

$$\cos(\theta_2+\alpha) = \frac{r_2}{R_3}$$

$$\Rightarrow R_3 = \frac{r_2}{\cos(\theta_2+\alpha)}$$



$$\Rightarrow \boxed{P_{oil} - P_{w_2} = \frac{2\gamma\cos(\theta_2+\alpha)}{r_2}}$$

We can then find an expression for $P_{w_1} - P_{w_2}$:

$$P_{w_1} - P_{w_2} = \Delta P_2 - \Delta P_1 = \cancel{P_{oil}} - P_{w_2} - \cancel{P_{oil}} + P_{w_1} = \boxed{2\gamma\left[\frac{\cos(\theta_2+\alpha)}{r_2} - \frac{\cos(\theta_1+\alpha)}{r_1}\right]}$$

b) Dividing the total free energy into two parts:

ΔG_1 : Change in free energy on the left side

ΔG_2 : Change in free energy on the right side.

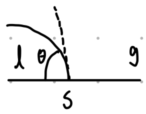
The expression for ΔG_2: $$\Delta G_2 = \underbrace{2\pi r_2}_{\text{Surface area per length}} \underbrace{\Delta L}_{\text{Change in length}} \underbrace{(\gamma_{so} - \gamma_{sw})}_{\text{Change in surface tension (lose surface-water, gain surface-oil)}}$$

to find $\gamma_{so} - \gamma_{sw}$: Young eq

$$\cos\theta = \frac{\gamma_{sw} - \gamma_{so}}{\gamma_{ow}} \Rightarrow \gamma_{sw} - \gamma_{so} = \gamma_{ow}\cos\theta$$
$$\gamma_{so} - \gamma_{sw} = -\gamma_{ow}\cos\theta$$

Then $$\boxed{\Delta G_2 = -2\pi r_2 \Delta L \gamma_{ow} \cos(180-\theta_2)}$$

Definition of θ:



=> As θ_1 and θ_2 is defined opposite (according to sketch, $\theta = 180 - \theta_i$

$$\Delta G_1 = \underbrace{2\pi r_1}_{\text{surface area per length}} \underbrace{\Delta X}_{\text{movement of the drop along the surface}} \underbrace{(\gamma_{sw} - \gamma_{so})}_{\text{Change in surface tension (lose surface-oil, gain surface-water)}}$$

Finding ΔX.

$$V = \text{const}$$
$$\cancel{\pi} r_2^2 \Delta L = \cancel{\pi} r_1^2 \Delta X$$
$$\Delta X = \left(\frac{r_2}{r_1}\right)^2 \Delta L$$

$$\boxed{\Delta G_1 = 2\pi \frac{r_2^2}{r_1} \Delta L \gamma_{ow} \cos(180-\theta_1)}$$

$$\Delta G_t = \Delta G_1 + \Delta G_2 = 2\pi \Delta L \gamma_{ow} \left(\frac{r_2^2}{r_1}\cos\theta_1 - r_2\cos\theta_2\right)$$

$$= 2\pi \cdot 5 \cdot 10^{-6} \cancel{m} \cdot 34 \cdot 10^{-3} \frac{N}{\cancel{m}} \left(\frac{8^2}{20}\cos 120^\circ - 8\cos 120^\circ\right) \cdot 10^{-6} m$$

$$\underline{\underline{= 2{,}56 \cdot 10^{-12}\, J}}$$

c)

As dGt is a function of the cosinus of theta angle, and cosinus of an angle larger than 90 degress is negative, dGt will change sign compared to question 2. As a result, dGt will be negative, and the drop will move to the right spontaneously. This means that the necessary water pressure Pwl is lower than if theta is less than 90 degrees.

3

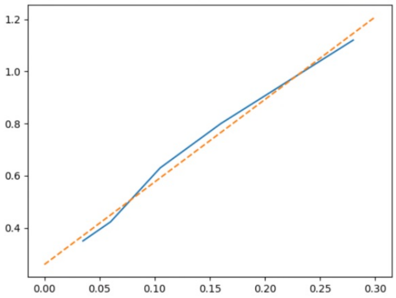
The techniques used to study spread monolayers of insoluble substances can also be applied to study protein films. Proteins adsorb and denaturate at high-energy air-water and oil-water interfaces because unfolding allows the polypeptide chains to be oriented with most of their hydrophilic groups in the water phase and most of the hydrophobic groups pointing away from the water phase. Protein films tend to be gaseous at low concentrations, thus permitting relative molecular weight determination. Based on this assumption, estimate the molecular weight of the protein haemoglobin from the following measurements of the surface pressure for various areas at 25°C. Haemoglobin is regarded as amphiphilic:

Surface pressure (mN/m)	0.28	0.16	0.105	0.06	0.035
Area (m^2/mg)	4.0	5.0	6.0	7.05	10.0

The molecular weight of haemoglobin determined by sedimentation measurements is 68 000 g/mol. Compare your answer with this value and comment on it.

Using linear regression $\pi A = 0{,}259522 \ \frac{\cancel{m}N}{\cancel{m}} \cdot \frac{m^2}{\cancel{m}g} = \frac{Nm}{g} = \frac{J}{g}$ at $\pi = 0$

```python
import numpy as np
import matplotlib.pyplot as plt

SurfacePressure = np.array([0.28, 0.16, 0.105, 0.06, 0.035])        # [mg/N]
Area = np.array([4.0, 5.0, 6.0, 7.05, 10.0])                        # [m2/mg]

y = SurfacePressure*Area
x = SurfacePressure

params1 = np.polyfit(x, y, 1)
function = np.poly1d(params1)
x_list = np.linspace(0,0.3, 100)

plt.plot(x, y)
plt.plot(x_list, function(x_list), linestyle = '--')
plt.show()

print(function(0))
```



For gaseos monolayers $(\pi \to 0)$:

$$\pi A_t = nRT$$

we har $A = \frac{A_t}{m} \Rightarrow \pi A = \frac{nRT}{m}$

$$\pi A = \frac{RT}{M}$$

$$\Rightarrow M = \frac{RT}{\pi A} = \frac{8{,}314 \ \cancel{J}/\cancel{K}\cdot mol \cdot 298\cancel{K}}{0{,}259522 \ \cancel{J}/g} = \underline{\underline{9547 \ g/mol}}$$

We get that the molar mass is less than from sedimentation measurements, this means that the proteins dissolved, and we have more particles than assumed (approximately 7. more on average)