Problems for chapter 1

1. *Surface tension*: thermodynamic properties of the interface between two phases are described by a state function called the surface tension $\mathcal{S}$. It is defined in terms of the work required to increase the surface area by an amount dA through $đW = \mathcal{S} dA$.

   (a) By considering the work done against surface tension in an infinitesimal change in radius, show that the pressure inside a spherical drop of water of radius R is larger than outside pressure by $2\mathcal{S}/R$. What is the air pressure inside a soap bubble of radius R?

   (b) A water droplet condenses on a solid surface. There are three surface tensions involved, $\mathcal{S}_{aw}$, $\mathcal{S}_{sw}$, and $\mathcal{S}_{sa}$, where a, s, and w refer to air, solid, and water, respectively. Calculate the angle of contact, and find the condition for the appearance of a water film (complete wetting).

   (c) In the realm of "large" bodies gravity is the dominant force, while at "small" distances surface tension effects are all important. At room temperature, the surface tension of water is $\mathcal{S}_o \approx 7 \times 10^{-2}\,\mathrm{N\,m^{-1}}$. Estimate the typical length scale that separates "large" and "small" behaviors. Give a couple of examples for where this length scale is important.

a)

Expanding from $r \rightarrow r + dr$ requires outside work $-pdV$

$$dW_1 = -P_{inside}\, dV_{inside} - P_{outside}\, dV_{outside}$$

$$= -(P - P_0)\, dV$$

$$= -(P - P_0)\, 4\pi r^2\, dr$$

and expanding also requires work

$$dW_2 = S\, dA$$

$$= S(8\pi r\, dr)$$

So, in eq. we have:

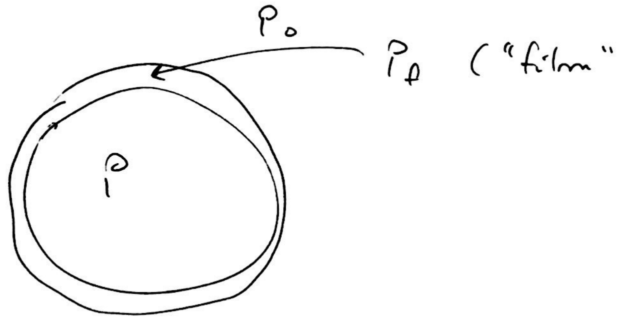
$$dW_1 + dW_2 = 0$$

$$(P - P_0)\, 4\pi r^2\, dr = S(8\pi r\, dr)$$

$$\boxed{(P - P_0) = \frac{2S}{r}}$$

Outside is lower pressure.

Soap?:



$$\boxed{P - P_0 = \frac{4S}{r}}$$

because there is an inner and outer surface!

b)

$$dE = S_{aw}\, dA_w + S_{as}\, dA_{as} + S_{ws}\, dA_{ws} = 0$$

$$dA_{as} + dA_{ws} = 0$$

Reminder Surface element in spherical coords

$$\begin{pmatrix} r\cos\phi\sin\theta \\ r\sin\phi\sin\theta \\ r\cos\theta \end{pmatrix} \times \Big($$

$$\downarrow$$

$$\begin{pmatrix} -r\sin\phi\sin\theta \\ r\cos\phi\sin\theta \\ 0 \end{pmatrix} \times \begin{pmatrix} r\cos\phi\cos\theta \\ r\sin\phi\cos\theta \\ -r\sin\theta \end{pmatrix}$$

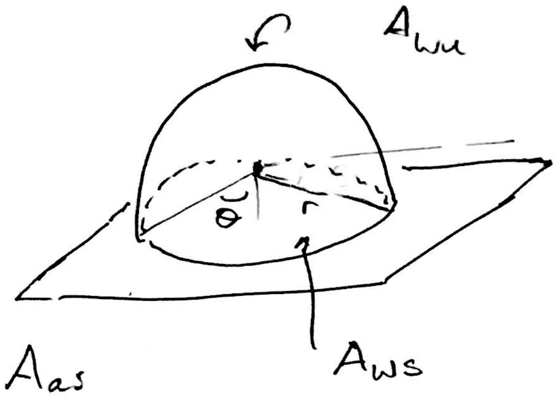
$$= \begin{pmatrix} -r^2\cos\phi\sin^2\theta \\ -r^2\sin\phi\sin^2\theta \\ +\sin\phi^2\cos\theta\sin\theta + r\cos\phi^2\cos\theta\sin\theta \end{pmatrix}$$

$$= r^4\sin^4\theta$$

$$+ \cos^2\theta\sin^2\theta\, r^4$$

$$r^4(\sin^4\theta + (1-\sin^2\theta)\sin^2\theta$$

$$= r^2\sin\theta = \text{surface element.}$$



$$A_{ws} = \pi r^2 \sin^2\theta$$

$$A_{wa} = \int_{\theta'=\theta}^{\pi} r^2 \sin\theta\, d\theta\ (2\pi)$$

$$= 2\pi r^2(-1)(\cos\theta')\Big|_{\theta}^{\pi}$$

$$= 2\pi r^2(1-\cos\theta)$$

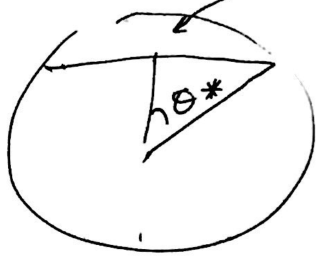
Now, let's makes sure we conserve volume. what is the volume?

$$V = 2\pi \int_{\theta}^{\pi} d\theta' \sin\theta' \int_0^r r^2\, dr$$

$$= 2\pi \int_{\theta}^{\pi} d\theta' \sin\theta' \left(\frac{r^3}{3}\right)$$

$$= \frac{2\pi r^3}{3}(1-\cos\theta)$$

Volume of this ?



limits of r: $(r_{min}, R) \longrightarrow r_{min}\cos\theta = R\cos\theta^*$

$$r_{min} = \frac{R\cos\theta^*}{\cos\theta}$$

So: $$V = 2\pi \int_0^{\theta^*} d\theta \sin\theta \int_{\frac{R\cos\theta^*}{\cos\theta}}^{R} r^2$$

$$= 2\pi \int_0^{\theta^*} d\theta \sin\theta \left(\frac{R^3}{3} - \frac{R^3(\cos\theta^*)^3}{\cos\theta^3} \right)$$

$$= \frac{4\pi R^3}{3} - R^3\cos^3\theta^* \underbrace{\int_0^{\theta^*} \frac{d\theta \sin\theta}{\cos^3\theta}}$$ ← − sign from the integral a one

$$= +\frac{1}{2}\left(\frac{1}{\cos^2\theta}\right)\Big|_0^{\theta^*}$$

$$= \left(\frac{1}{2} - \frac{1}{2\cos^2\theta^*}\right)$$

$$= 2\pi\left(\frac{\cancel{4\pi}2R^3}{3} - R^3\cos^3\theta\left(\frac{1}{2} - \frac{1}{\cos^2\theta^*}\right)\right)$$

$$\cancel{-\frac{4\pi R^3}{3} - R^3}$$

$$= \cancel{\frac{2\pi}{3}} = 2\pi R^3\left(\frac{2}{3} - \frac{\cos^3\theta^*}{2} + \frac{1}{2}\cos\theta^*\right)$$

$$= 2\pi R^3 \left(\frac{2}{3} - \frac{\cos^3\theta^*}{2} + \frac{1}{2}\cos\theta^* \right.$$

$$\boxed{V = \frac{\pi R^3}{3}\left(\cos^3\theta^* - 3\cos\theta + 2\right)}$$

So that :

$$\begin{cases} A_{ws} = \pi R^2 (1-\cos^2\theta) \\ A_{aw} = 2\pi R^2 (1-\cos\theta) \\ V = \dfrac{\pi R^3}{3} (\cos^3\theta - 3\cos\theta + 2) \end{cases}$$

variations are given by

$$dA_{ws} = 2\pi R (1-\cos^2\theta) dR - \pi r^2 (2)\, d\cos\theta$$

$$= 2\pi R \left((1-\cos^2\theta) dR - \pi R\, d(\cos\theta) \right)$$

$$dA_{aw} = 2\pi R \left\{ \left[2(1-\cos\theta)\, dR \right] - R\, d(\cos\theta) \right]$$

$$dV = \pi r^2 \left[dR (x^3 - 3x^2 + 2) + R (x^2 - x) \right] = 0$$

$$\frac{dR}{R} = - \frac{x^2 - x}{(x^3 - 3x^2 + 2)}\, dx \leftarrow \quad x \equiv \cos\theta$$

$$\Rightarrow \quad = - \frac{x(\cancel{x}-1)}{(x} = - \frac{x+1}{(x-1)(x+2)}\, dx$$

$$\Rightarrow dA_{sw} = 2\pi R^2 \left[(1-x^2) \left(\frac{-x+1}{(x-1)(x+2)} \right) - 1 \right]$$

$$= 2\pi R^2 \left[\frac{-(1+x)(1+x)}{x+2} - x \right]$$

$$= 2\pi R^2 \left(\frac{-(x^2+2x+1)}{x+2} - \frac{x+2}{x+2} \right.$$

$\Rightarrow$

$$\boxed{dA_{aw} = dA_{ws} \cos\theta}$$

So that we get

$$dE = (S_{aw} \cos\theta - S_{as} + S_{ws})\, dA_{ws} = 0$$

$$\rightarrow \boxed{\cos\theta = \frac{S_{as} - S_{ws}}{S_{aw}}}$$

in terms of the surface tensions.

Complete wetting?

$\rightarrow$ critical point $\cos\theta = 1 \Rightarrow \theta = 0$

anytime

$$\frac{S_{as} - S_{ws}}{S_{aw}} \geq 1$$ and we have complete wetting

c) $S_0 \approx 7 \times 10^{-2}\ \mathrm{N m^{-1}}$

e.g.

$$S(4\pi R^2) \approx mgR = \rho V g R$$
$$= \frac{4\pi}{3} R^4 g$$

4. *Equations of state*: the equation of state constrains the form of internal energy as in the following examples.

(a) Starting from $dE = TdS - PdV$, show that the equation of state $PV = Nk_BT$ in fact implies that E can only depend on T.

(b) What is the most general equation of state consistent with an internal energy that depends only on temperature?

(c) Show that for a van der Waals gas C_V is a function of temperature alone.

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(4)

a)

$dE = TdS - PdV$

if $S = S(T, V)$, we have:

$$dS = \frac{\partial S}{\partial T}\Big|_V dT + \frac{\partial S}{\partial V}\Big|_T dV$$

$$dE = T\left(\frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV\right) - PdV$$

$$\frac{dE}{dV}\Big|_T = T\frac{\partial S}{\partial V} - P \qquad \left(\frac{dT}{dV} = 0\right)$$

Remember a Maxwell relation:

$$\cancel{dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV}$$

$$dE = TdS - PdV$$

$$\cancel{\frac{dE}{dS} = T} \qquad \cancel{\frac{dE}{\partial V} = -P}$$

$$\cancel{\frac{\partial T}{\partial V}} \qquad \cancel{\frac{\partial^2 E}{\partial V \partial S} = -\frac{\partial P}{\partial S}}$$

$$\Rightarrow \cancel{\frac{\partial T}{\partial V} = -\frac{\partial P}{\partial S}}$$

$$\cancel{dE = TdS - PdV}$$

$$\cancel{\frac{dE}{\partial V} = \frac{TdS}{dV}} +$$

$$\cancel{dE = TdS - PdV}$$

$$\cancel{\frac{dE}{dS} = T} \qquad \cancel{\frac{dE}{\partial V} = -P}$$

$$\cancel{dF = -SdT + \ldots}$$

$$dF = -SdT - PdV$$

$$\frac{dF}{dT} = -S \qquad \frac{dF}{dV} = -P$$

$$\frac{\partial S}{\partial V}\Big|_T = \frac{\partial P}{\partial T}\Big|_V$$

$$\frac{dE}{\partial V}\Big|_T = \underbrace{+\frac{\partial P}{\partial T}\Big|_V T} - P \qquad PV = nT$$

$$T\frac{\partial P}{\partial T} = T\frac{\partial}{\partial T}\left(\frac{NkT}{V}\right)$$

$$= P$$

$$\boxed{\frac{dE}{\partial V}\Big|_T = 0} \rightarrow \text{depends only on temperature.}$$

b)

$E = E(T) \Rightarrow \cancel{\left.\frac{\partial \Psi}{\partial T}\right|_T} = 0$

$\cancel{\Rightarrow E \frac{\partial E}{\partial T}} = 0$

$\frac{\partial E}{\partial V} = 0 \Rightarrow$ but $dE = TdS - PdV$

$$\frac{dE}{dV} = T\frac{dS}{dV} - P$$

$$0 = T\frac{dP}{dT} - P$$

Maxwell again

$$T\frac{dP}{dT} - P = 0$$

$$T\frac{\partial P}{\partial T} = P$$

$$\frac{1}{P}\frac{dP}{dT} = \frac{1}{T}$$

$$\log P = \cancel{k}\log T + f(V)$$

$\boxed{P = f(V)\, T}$ is the most general equation of state.

c) $\left(P - a\left(\frac{N}{V}\right)^2\right)\cdot(V - Nb) = NkT \longrightarrow P = \frac{Nk}{(V-Nb)}T + a\left(\frac{N}{V}\right)^2$

$$\frac{\partial C_V}{\partial T} = \frac{\partial}{\partial T}\frac{\partial E}{\partial V} = \frac{\partial}{\partial T}\left(T\frac{dP}{dT} - P\right)$$

$$= \frac{\partial}{\partial T}\left(T\left(\frac{Nk}{V-Nb}\right) - \left(\frac{Nk}{V-Nb}\right)T + a\left(\frac{N}{V}\right)^2\right)$$

$$= \frac{\partial}{\partial T}\left(a(N/V)^2\right) = 0$$