Problem 2. Van der Waals equation of state

The main idea of this problem is to express all properties of gaseous and liquid states of matter in terms of just two constants $a$ and $b$. 
Question A1

\[ p(V - b) = RT \]

A1 Estimate \( b \) and express it in terms of the atomic diameter \( d \).

\[ b = \frac{N_A \pi d^3}{6} \]

Alternative!

\[ b = \frac{4}{3} N_A \pi d^3 \]
Question A2

Express the van der Waals constants $\alpha$ and $b$ in terms of $T_c$ and $P_c$.

Alternative!

$$
\left( P + \frac{\alpha}{V^2} \right) (V - b) = RT
$$

$$
P_cV^3 - (RT_c + bP_c)V^2 + aV - ab = 0
$$

$$
P_c(V - V_c)^3 = 0
$$

$$
\alpha = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c}
$$
Questions A2-A3

A3  For water $T_c = 647K$ and $P_c = 2.18 \cdot 10^7$ Pa. Calculate $a_w$ and $b_w$ for water.

$$a = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c}.$$  

$$a_w = 0.560 \frac{m^6 \cdot Pa}{\text{mole}^2}.$$  

$$b_w = 3.08 \cdot 10^{-5} \frac{m^3}{\text{mole}}.$$  

A4  Assuming that the water molecule is spherical in shape, estimate its diameter $d_w$.

$$d_w = \frac{3 \sqrt{6b}}{\sqrt{\pi N_A}} = 4.61 \cdot 10^{-10} \text{ m}.$$  

or  

$$d_w = \frac{3 \sqrt{3b}}{\sqrt{4\pi N_A}} = 2.30 \cdot 10^{-10} \text{ m}.$$
Part B. Properties of gas and liquid
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$t = 100^\circ C$

$T = 373K$

$T_c = 647K$

$\frac{T}{T_c} = 0.58$

$p_0 = 1.00 \cdot 10^5 Pa$

$p_c = 2.18 \cdot 10^7 Pa$

$\frac{p_0}{p_c} = 4.6 \cdot 10^{-3} \ll 1$
Part B. Properties of gas...

\[ (P + \frac{a}{V^2})(V - b) = RT \]

\[ PV = RT \]

\[ V_G \gg b \]

\[ (P + \frac{a}{V^2})(V - b) = RT \]

\[ (p_0 + \frac{a}{V_G^2})V_G = RT \]
Question B1

\[ V_G \gg b \]

B1 Derive the formula for the volume \( V_G \) and express it in terms of \( R, T, p_0 \), and \( a \).

\[
\left( p_0 + \frac{a}{V_G^2} \right) V_G = RT
\]

\[
V_G = \frac{RT}{2p_0} \left( 1 \pm \sqrt{1 - \frac{4ap_0}{R^2T^2}} \right)
\]

\[
a \to 0, \quad V_G \to \frac{RT}{p_0}
\]

\[
V_G = \frac{RT}{2p_0} \left( 1 + \sqrt{1 - \frac{4ap_0}{R^2T^2}} \right)
\]

\[
\frac{ap_0}{(RT)^2} = 5.82 \cdot 10^{-3}
\]

\[
V_G \approx \frac{RT}{p_0} \left( 1 - \frac{ap_0}{R^2T^2} \right) = \frac{RT}{p_0} - \frac{a}{RT}
\]
Question B2

B2 Evaluate in percentage the relative decrease in the gas volume due to intermolecular forces,

\[ \frac{\Delta V_G}{V_{G0}} = \frac{V_{G0} - V_G}{V_{G0}}. \]

\[ PV = RT \]

\[ V_{G0} = \frac{RT}{p_0} \]

\[ V_G \approx \frac{RT}{p_0} \left( 1 - \frac{ap_0}{R^2T^2} \right) = \frac{RT}{p_0} - \frac{a}{RT}. \]

\[ \left( \frac{\Delta V_G}{V_{G0}} \right) = \frac{V_{G0} - V_G}{V_{G0}} = \frac{ap_0}{R^2T^2} = 0.582\% \]
Question B3

B3 Find and evaluate how many times the purified gas can be reduced in volume, $V_G/V_{G_{\text{min}}}$, to assure that it remains in a metastable state.

\[ \frac{dP}{dV}_T < 0 \]

\[ V_{G_{\text{min}}} \rightarrow \left( \frac{dP}{dV} \right)_T = 0 \]

\[ \left( \frac{dP}{dV} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \]

$V_{G_{\text{min}}} \gg b$  

\[ V_{G_{\text{min}}} = \frac{2a}{RT} \]

$V_G \approx V_{G_0} = \frac{RT}{p_0}$

\[ \frac{V_G}{V_{G_{\text{min}}}} = \frac{R^2T^2}{2ap_0} = 85.8 \]
Part B. Properties of... liquid

\[ \left( P + \frac{a}{V^2} \right) (V - b) = RT \]

\[ P \ll \frac{a}{V^2} \Rightarrow \frac{a}{V_L^2} (V_L - b) = RT \]
Express the volume $V_L$ in terms of $a$, $b$, $R$, and $T$. 

$V_L = \frac{a}{2RT} \left( 1 \pm \sqrt{1 - \frac{4bRT}{a}} \right)$

$T \to 0$

$V_L \to b$

$bRT \ll a$

$V_L = \frac{a}{2RT} \left( 1 - \sqrt{1 - \frac{4bRT}{a}} \right) \approx b \left( 1 + \frac{bRT}{a} \right)$
Questions B5-B7

B5 Express the liquid water density $\rho_L$ in terms of $\mu, a, b, R$ and evaluate it.

$$\rho_L = \frac{\mu}{V_L} = \frac{\mu}{b(1 + \frac{bRT}{a})} \approx \frac{\mu}{b} = 583 \frac{\text{kg}}{\text{m}^3}.$$  

B6 Express the volume thermal expansion coefficient $\alpha = \frac{1}{V_L} \frac{\Delta V_L}{\Delta T}$ in terms of $a, b, R$ and evaluate it.

$$\alpha = \frac{1}{V_L} \frac{\Delta V_L}{\Delta T} = \frac{bR}{a + bRT} \approx \frac{bR}{a} = 4.58 \cdot 10^{-4} \text{K}^{-1}$$

B7 Express the specific heat of water vaporization $L$ in terms of $\mu, a, b, R$ and evaluate it.

$$E = L\mu \approx \int_{V_L}^{V_G} \frac{a}{V^2} dV = a \left( \frac{1}{V_L} - \frac{1}{V_G} \right)$$

$V_G \gg V_L$

$$L = \frac{a}{\mu V_L} = \frac{a}{\mu b(1 + \frac{bRT}{a})} \approx \frac{a}{\mu b} = 1.01 \cdot 10^6 \frac{\text{J}}{\text{kg}}$$
Question B8

Considering the monomolecular layer of water, estimate the surface tension \( \sigma \) of water.

\[
A = 2\sigma S \\
Q = Lm \\
m = \rho Sd
\]

\[
\sigma = \frac{a}{2b^2} \sqrt[3]{\frac{3b}{4\pi N_A}} = 6.78 \times 10^{-2} \text{ N/m}
\]

or

\[
\sigma = \frac{a}{2b^2} \sqrt[3]{\frac{6b}{\pi N_A}} = 1.36 \times 10^{-1} \text{ N/m}
\]
Part C. Liquid-gas system

Question C1

\[ S_I = S_{II} \]
\[ \ln p_0 = A + \frac{B}{T} \]

Find \( A, B \) and express them in terms of \( \mu, a, b, R \).

\[ \int_{V_L}^{V_G} P(V) \, dV = p_0 (V_G - V_L) \]
Question C1,C2

\[ \int_{V_L}^{V_G} P(V) dV = RT \ln \frac{V_G - b}{V_L - b} + a \left( \frac{1}{V_G} - \frac{1}{V_L} \right) \]

\[ V_G = \frac{RT}{P_0} \]

\[ V_L = b \]

\[ V_L - b = \frac{b^2 RT}{a} \]

\[ A = \ln \frac{a}{b^2} - 1 \quad B = -\frac{a}{bR} \]

\[ p_0 = \frac{a}{b^2 \exp\left(\frac{a}{bRT} + 1\right)} = 6.21 \cdot 10^5 \text{ Pa} \]
**Question C3**

Find a small change in pressure \( \Delta p_T \) of the saturated vapor over the curved surface of liquid and express it in terms of the vapor density \( \rho_s \), the liquid density \( \rho_L \), the surface tension \( \sigma \) and the radius of surface curvature \( r \).

\[
p_h = p_0 + \rho_s g h
\]

\[
p_0
\]

\[
p = p_0 + \rho_L g h
\]

\[
h = \frac{2 \sigma}{(\rho_L - \rho_S) g r}
\]

\[
\Delta p_T = p_h - p_0 = \rho_s g h = \frac{2 \sigma \rho_s}{r \rho_L - \rho_S} \approx \frac{2 \sigma \rho_s}{r \rho_L}
\]
Question C4

C4 Suppose that at the evening temperature of $t_e = 20^\circ C$ the water vapor in the air was saturated, but in the morning the ambient temperature has fallen by a small amount of $\Delta t = 5.0^\circ C$. Assuming that the vapor pressure has remained unchanged, estimate the minimum radius of droplets that can grow.

### evening

$P_{\text{vapor}} = \text{const} = P_e$

$t = t_e$

$P_{\text{sat}} = P_e$

$P'_{\text{sat}} = P_{\text{sat}} + \Delta P_T$

$P_{\text{vapor}} < P_{\text{sat}} + \Delta P_T$

### morning

$P_{\text{vapor}} = \text{const} = P_e$

$t = t_e - \Delta T$

$P_{\text{sat}} = P_e - \Delta P_{\text{sat}}$

$P'_{\text{sat}} = P_e - \Delta P_{\text{sat}} + \Delta P_T$

$P_{\text{vapor}} > P_{\text{sat}} - \Delta P_{\text{sat}} + \Delta P_T$

$|\Delta P_{\text{sat}}| \geq \Delta P_T$
**Question C4**

**evening**

\[ P_{\text{vapor}} = \text{const} = P_e \]
\[ t = t_e \]

\[ P_{\text{sat}} = P_e \]

\[ P'_{\text{sat}} = P_{\text{sat}} + \Delta P_T \]
\[ P_{\text{vapor}} < P_{\text{sat}} + \Delta P_T \]

**morning**

\[ P_{\text{vapor}} = \text{const} = P_e \]
\[ t = t_e - \Delta T \]

\[ P_{\text{sat}} = P_e - \Delta P_{\text{sat}} \]

\[ P'_{\text{sat}} = P_e - \Delta P_{\text{sat}} + \Delta P_T \]
\[ P_{\text{vapor}} > P_{\text{sat}} - \Delta P_{\text{sat}} + \Delta P_T \]
Question C4

\[ |\Delta P_{sat}| \geq \Delta P_T \]

\[
\ln p_0 = \ln \frac{a}{b^2} - \frac{a}{bRT} - 1
\]

\[
\Delta P_{sat} = P_e \frac{a}{bRT_e^2} \Delta T
\]

\[
\Delta p_T = \frac{2\sigma}{r} \frac{\rho_S}{\rho_L}
\]

\[
\rho_S = \frac{\mu P_e}{RT_e} \ll \rho_L
\]

\[
P_e \frac{a\Delta T_e}{bRT_e^2} = \frac{2\sigma}{r} \frac{\mu P_e}{RT_e}
\]

\[
r = \frac{2\sigma b^2T_e}{a\Delta T_e} = 1.45 \cdot 10^{-8} \text{m}
\]