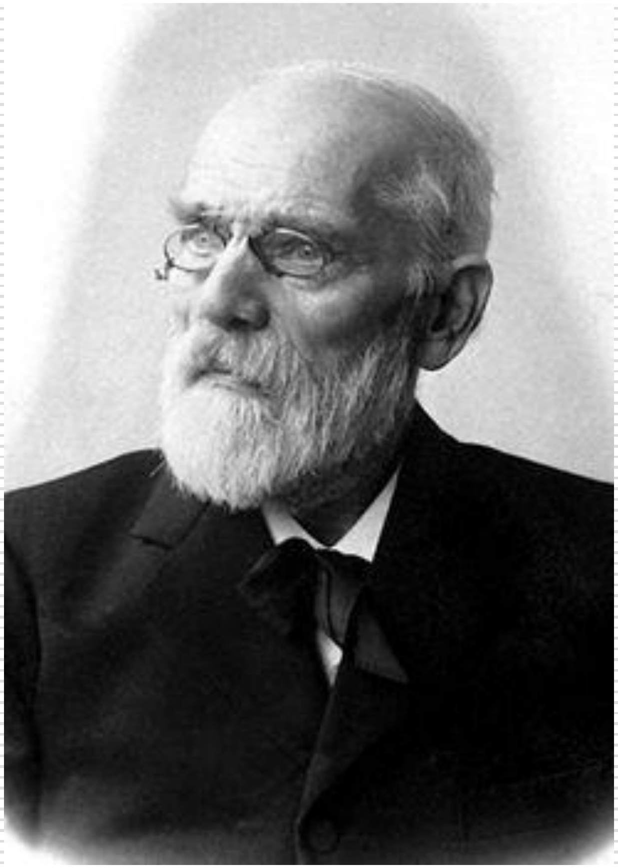
# Problem 2.
# Van der Waals equation of state

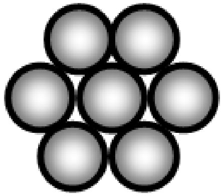


- The main idea of this problem is to express all properties of gaseous and liquid states of matter in terms of just two constants *a* and *b*.

# Question A1

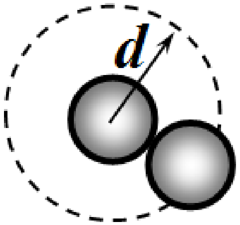
$$P(V-b)=RT$$

**A1** Estimate $b$ and express it in terms of the atomic diameter $d$.



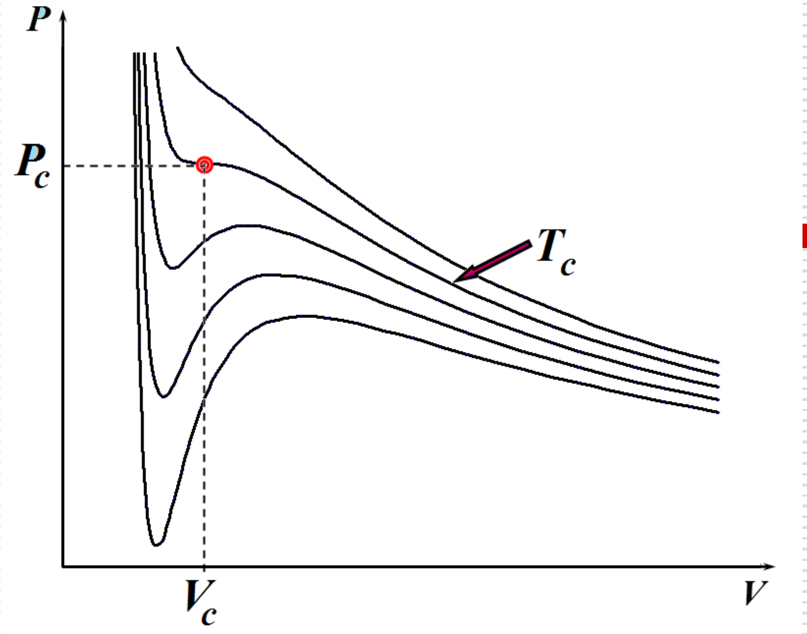
$$b=N_A\pi d^3/6$$

*Alternative!*



$$b=\frac{4}{3}N_A\pi d^3$$

# Question A2



**A2** Express the van der Waals constants $a$ and $b$ in terms of $T_c$ and $P_c$.

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

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

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

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

*Alternative!*

$$\left(\frac{dP}{dV}\right)_T=0\qquad\left(\frac{d^2P}{dV^2}\right)_T=0$$

# Questions A2-A3

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

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

⇓

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

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

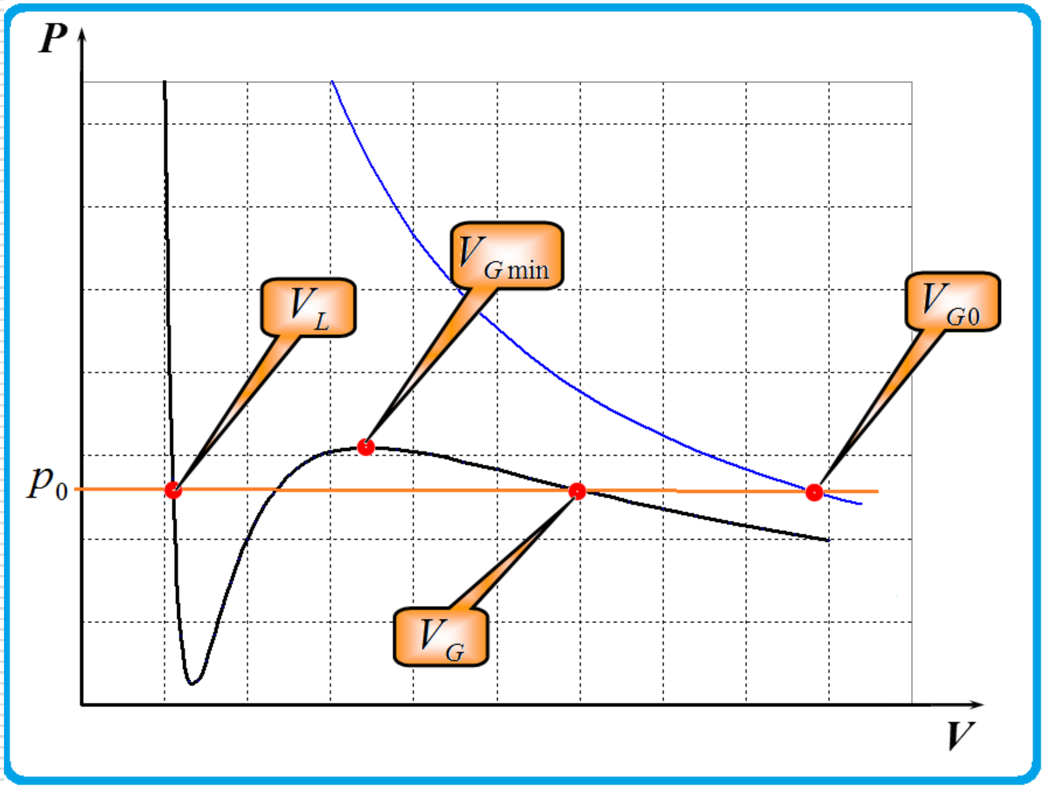
**A4** Assuming that the water molecule
is spherical in shape, estimate its diameter $d_w$.

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

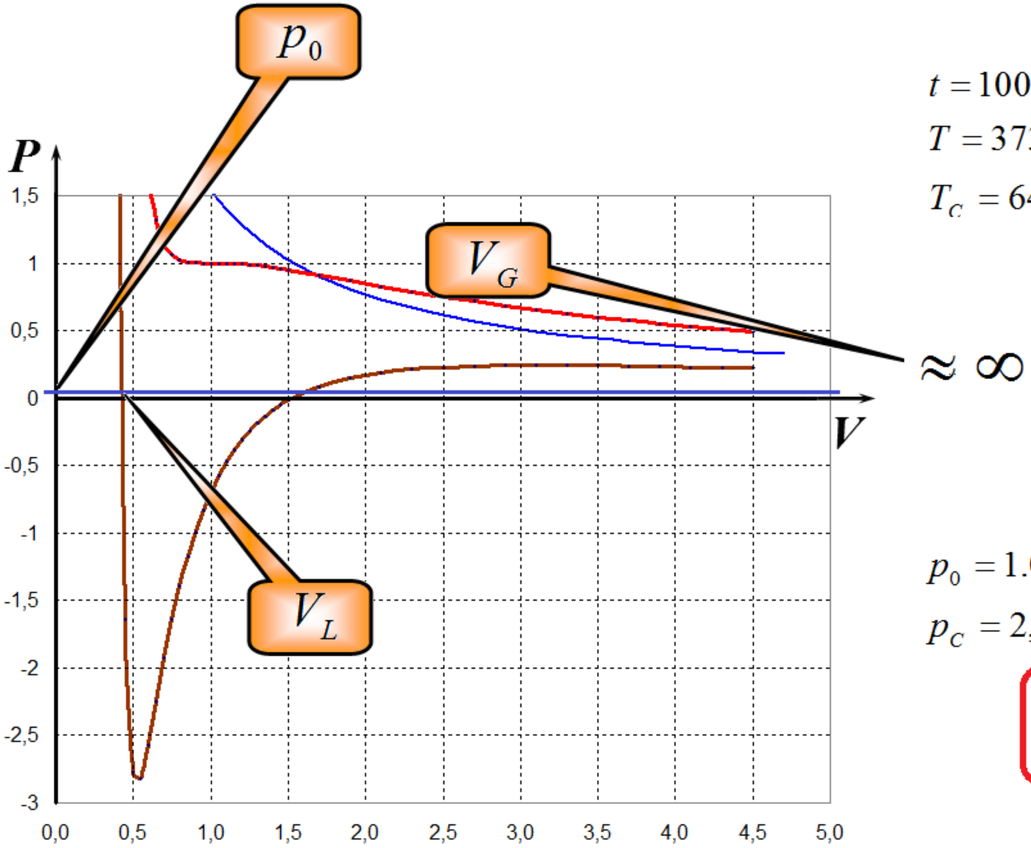
*or*

$$d_w = \sqrt[3]{\frac{3b}{4\pi N_A}} = 2.30 \cdot 10^{-10}\text{m}.$$

# Part B. Properties of gas and liquid



# Part B. Properties of gas and liquid. But…



$t = 100°C$

$T = 373 K$

$T_C = 647 K$

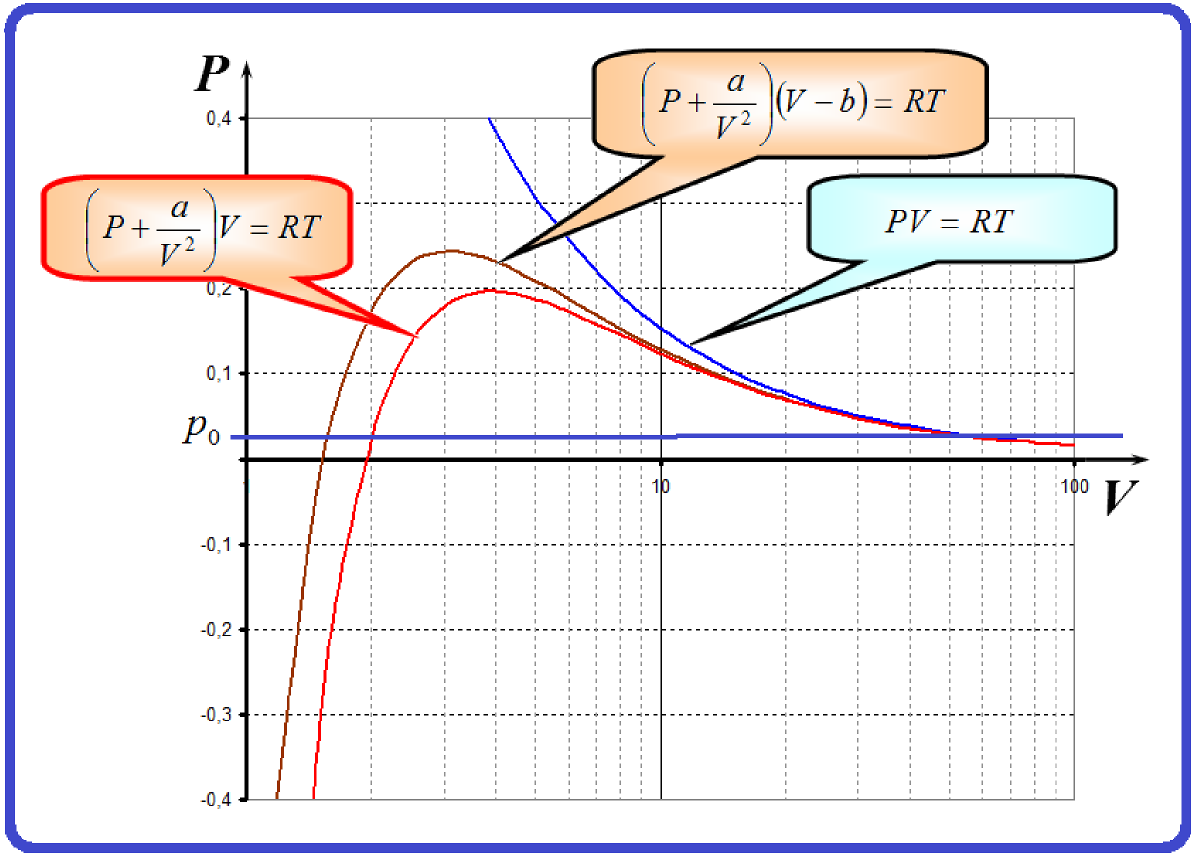
$$\frac{T}{T_C} = 0{,}58$$

$p_0 = 1.00 \cdot 10^5\, Pa$

$p_C = 2{,}18 \cdot 10^7\, Pa$

$$\frac{p_0}{p_C} = 4.6 \cdot 10^{-3} << 1$$

# Part B. Properties of gas…



$$\boxed{V_G \gg b}$$

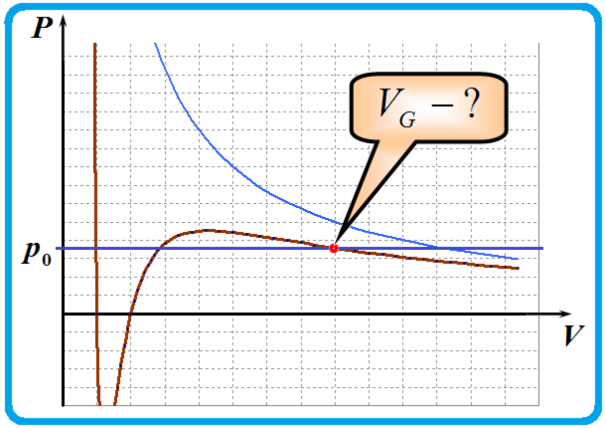
$$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

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

# 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 $a$.



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

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

$$a\to 0,\ V_G\to\frac{RT}{p_0}$$

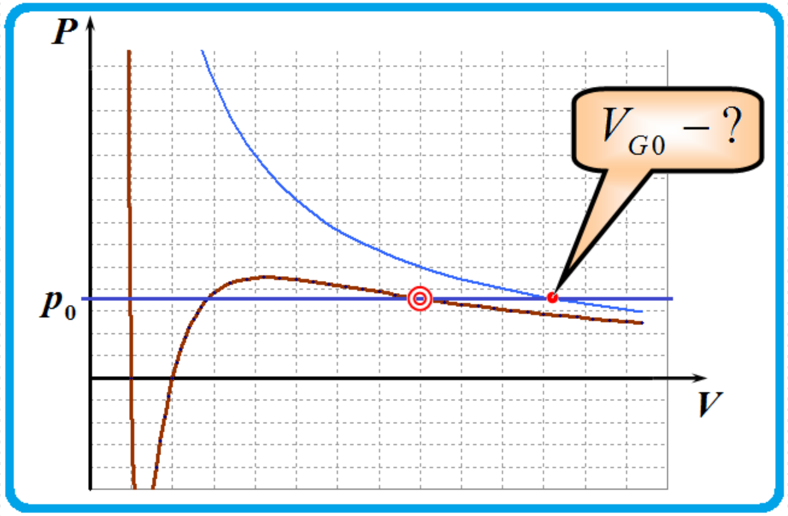
$$V_G=\frac{RT}{2p_0}\left(1+\sqrt{1-\frac{4ap_0}{R^2T^2}}\right)$$

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

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

# Question B2

**B2** Evaluate in percentage the relative decrease in the gas volume due to intermolecular forces, $\frac{\Delta V_G}{V_{G0}} = \frac{V_{G0}-V_G}{V_{G0}}$ .



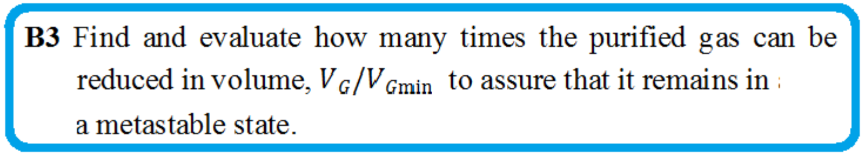
$$PV = RT$$

$$V_{G0} = \frac{RT}{p_0}$$

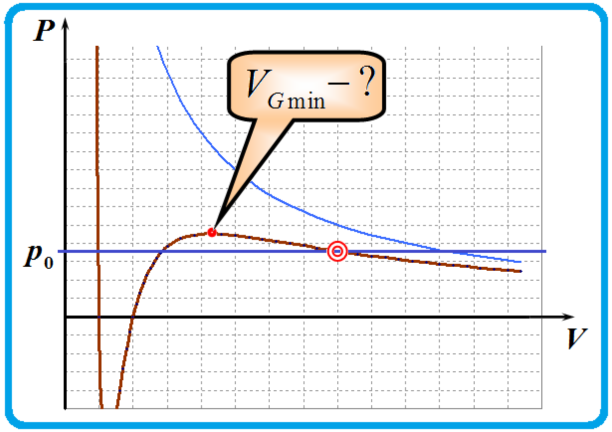
$$V_G \approx \frac{RT}{p_0}\left(1 - \frac{ap_0}{R^2T^2}\right) = \frac{RT}{p_0} - \frac{a}{RT}$$

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

# Question B3



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



$$\left(\frac{dP}{dV}\right)_T < 0$$

$$V_{Gmin} \to \left(\frac{dP}{dV}\right)_T = 0$$

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

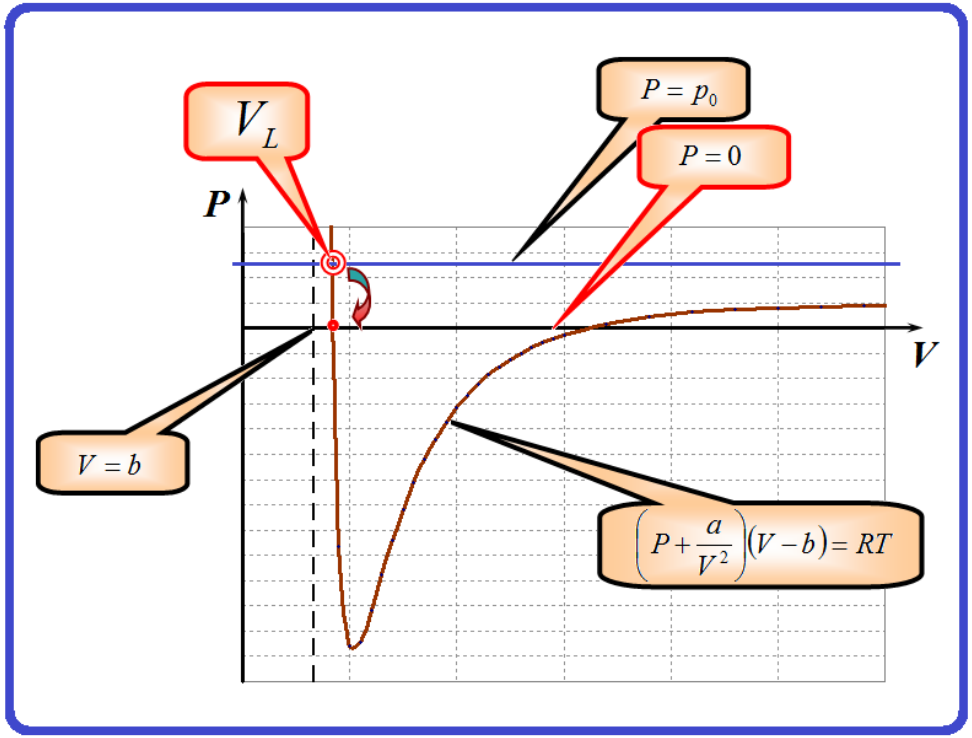
$$V_{Gmin} \gg b$$

$$V_{Gmin} = \frac{2a}{RT}$$

$$V_G \approx V_{G0} = \frac{RT}{p_0}$$

$$\boxed{\frac{V_G}{V_{Gmin}} = \frac{R^2T^2}{2ap_0} = 85.8}$$

# Part B. Properties of... liquid



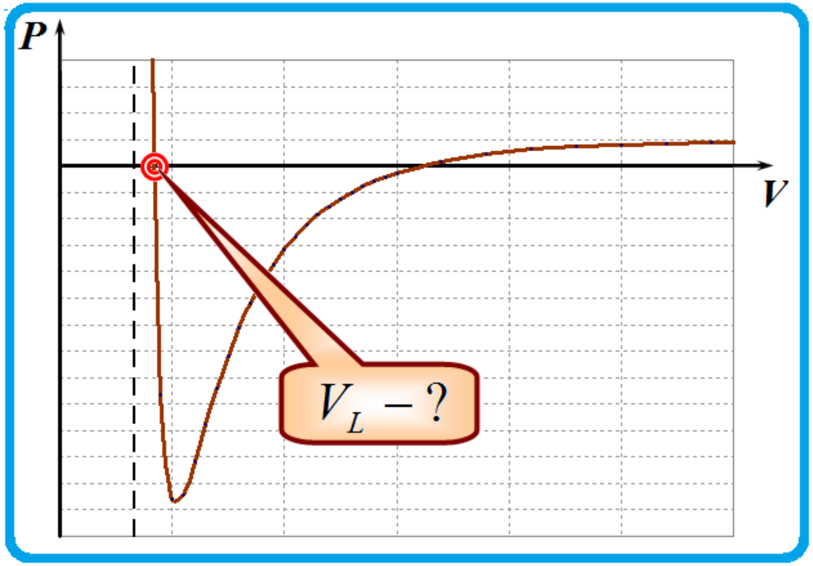
$$\left(P+\frac{a}{V^2}\right)(V-b)=RT$$

$$P \ll a/V^2$$

$$\frac{a}{V_L^2}(V_L-b)=RT$$

# Question B4

**B4** Express the volume $V_L$ in terms of $a, b, R$ and $T$.



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

$T \to 0$

$V_L \to b$

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

$bRT \ll a$

Second order!

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

# Questions B5-B7

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

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

**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.

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

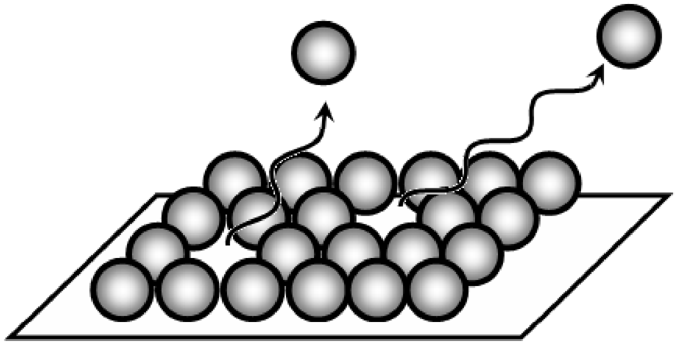
$$V_G \gg V_L \;\longrightarrow\; \Downarrow$$

$$L = \frac{a}{\mu V_L} = \frac{a}{\mu b\left(1+\frac{bRT}{a}\right)} \approx \frac{a}{\mu b} =$$

$$= 1.01 \cdot 10^{6}\,\frac{\text{J}}{\text{kg}}$$

# Question B8

**B8** Considering the monomolecular layer of water, estimate the surface tension $\sigma$ of water.



$$A = 2\sigma S$$

$$Q = Lm$$

$$m = \rho S d$$

$$A = Q$$

$$\sigma = \frac{a}{2b^2}\sqrt[3]{\frac{3b}{4\pi N_A}} = 6.78 \cdot 10^{-2}\,\frac{\mathrm{N}}{\mathrm{m}}$$

*or*

$$\sigma = \frac{a}{2b^2}\sqrt[3]{\frac{6b}{\pi N_A}} = 1.36 \cdot 10^{-1}\,\frac{\mathrm{N}}{\mathrm{m}}$$

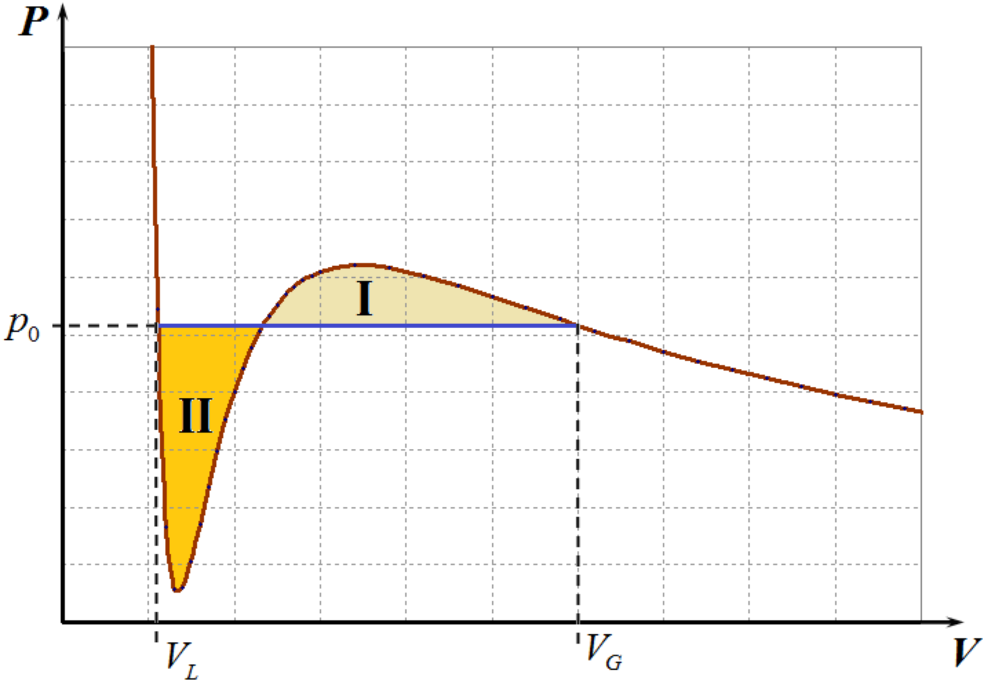
# Part C. Liquid-gas system Question C1

$$S_{\mathrm{I}} = S_{\mathrm{II}}$$

$$\ln p_0 = A + \frac{B}{T}$$

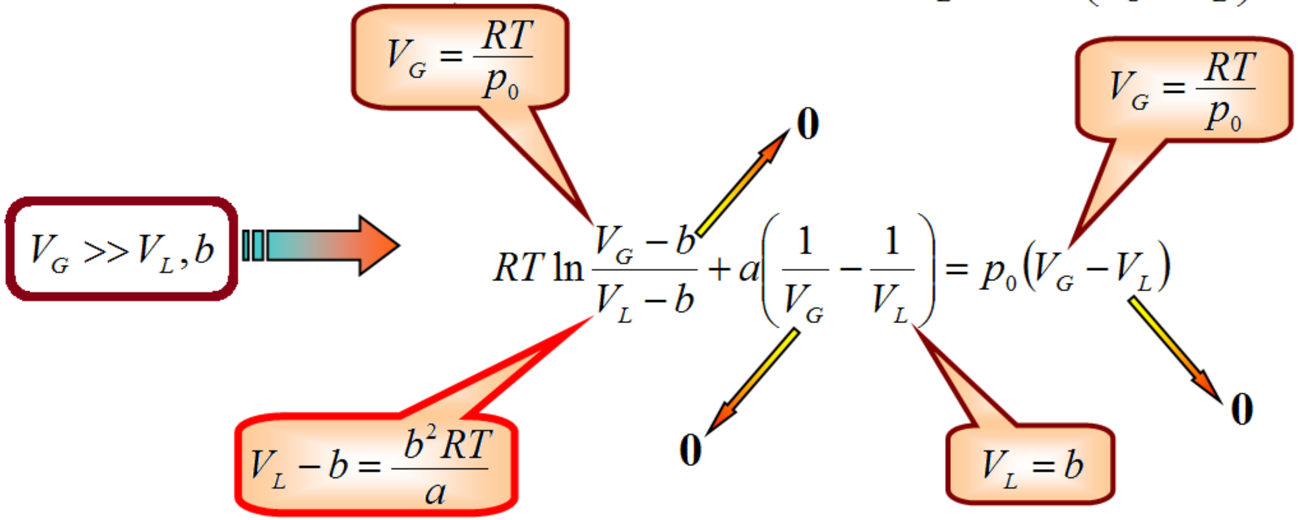
**C1** Find $A, B$ and express them in terms of $\mu, a, b, R$.

$$\int_{V_L}^{V_G} P(V)dV = p_0(V_G - V_L)$$



# Question C1,C2

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



$V_G = \frac{RT}{p_0}$

$V_G = \frac{RT}{p_0}$

$V_G \gg V_L, b$

$$RT\ln\frac{V_G-b}{V_L-b}+a\left(\frac{1}{V_G}-\frac{1}{V_L}\right)=p_0\left(V_G-V_L\right)$$

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

$V_L = b$

$$RT\ln\left(\frac{RT}{p_0}\frac{a}{b^2RT}\right)-\frac{a}{b}=RT$$

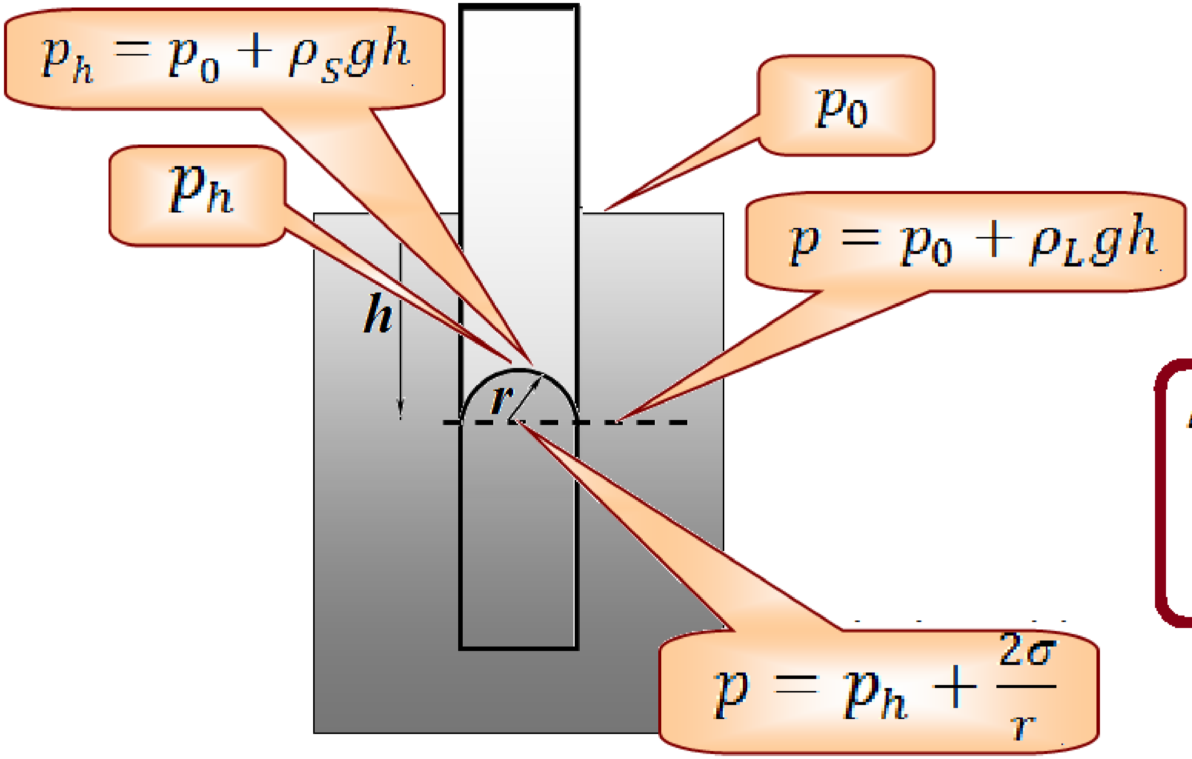
$$\ln p_0 = \ln\frac{a}{b^2}-1-\frac{a}{bRT}$$

$$A=\ln\frac{a}{b^2}-1 \qquad B=-\frac{a}{bR}$$

$$p_0=\frac{a}{b^2\exp\left(\frac{a}{bRT}+1\right)}=6.21\cdot10^5\,\mathrm{Pa}$$

# Question C3

**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 $r$.



$$p_h = p_0 + \rho_S g h$$

$$p_h$$

$$p_0$$

$$p = p_0 + \rho_L g h$$

$$p = p_h + \frac{2\sigma}{r}$$

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

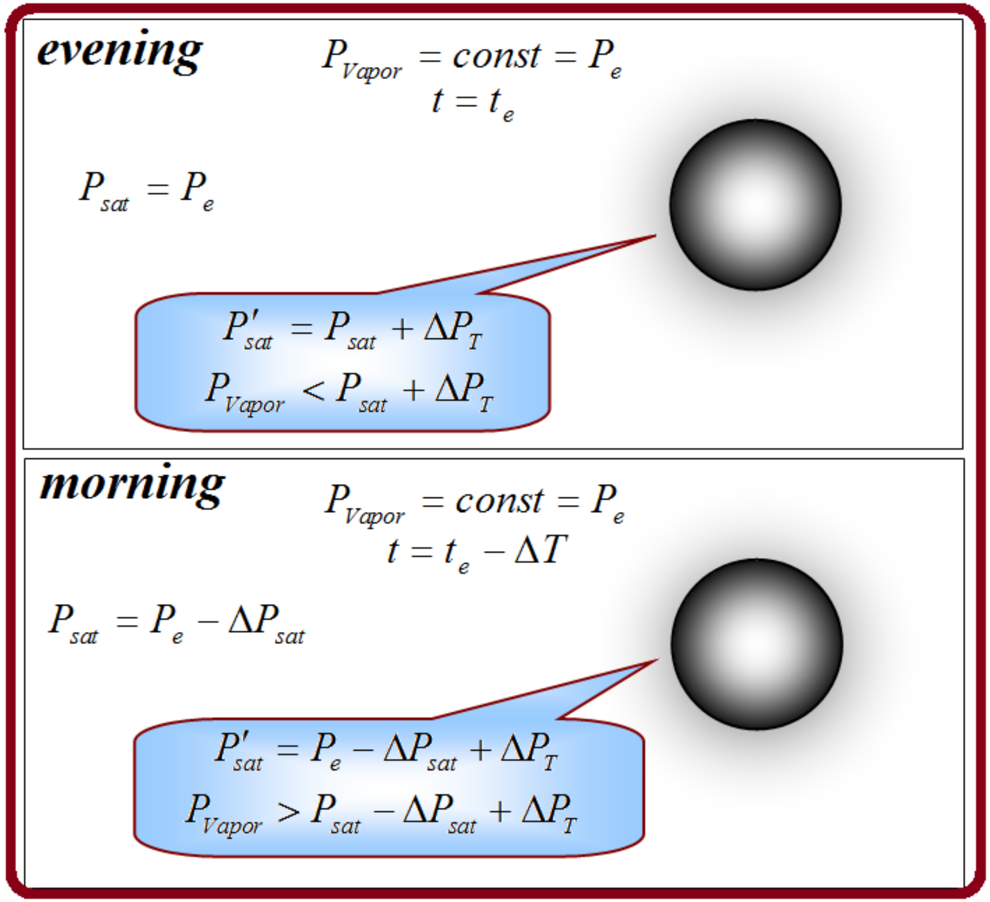
$$\Delta p_T = p_h - p_0 = \rho_S g h =$$

$$= \frac{2\sigma}{r}\frac{\rho_S}{\rho_L - \rho_S} \approx \frac{2\sigma}{r}\frac{\rho_S}{\rho_L}$$

# Question C4

**C4** Suppose that at the evening temperature of $t_e = 20°C$ the water vapor in the air was saturated, but in the morning the ambient temperature has fallen by a small amount of $\Delta t = 5{,}0°C$. Assuming that the vapor pressure has remained unchanged, estimate the minimum radius of droplets that can grow.

$$\boxed{|\Delta P_{sat}| \geq \Delta P_T}$$



***evening***

$$P_{Vapor} = const = P_e$$
$$t = t_e$$

$$P_{sat} = P_e$$

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

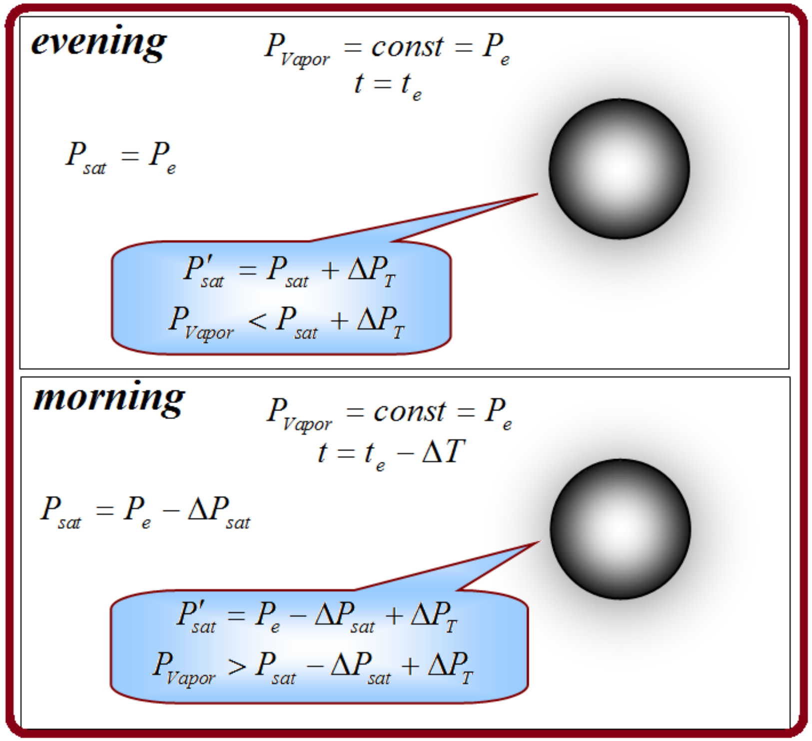
***morning***

$$P_{Vapor} = const = P_e$$
$$t = t_e - \Delta T$$

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

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

# Question C4



**evening**

$$P_{Vapor} = const = P_e$$

$$t = t_e$$

$$P_{sat} = P_e$$

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

$$P_{Vapor} < P_{sat} + \Delta P_T$$

**morning**

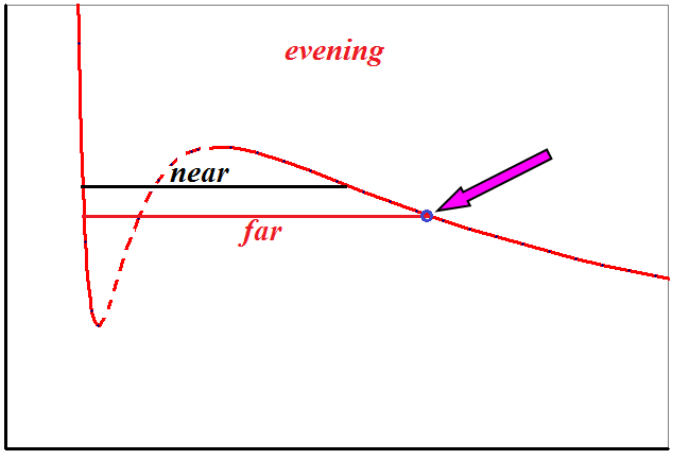
$$P_{Vapor} = const = P_e$$

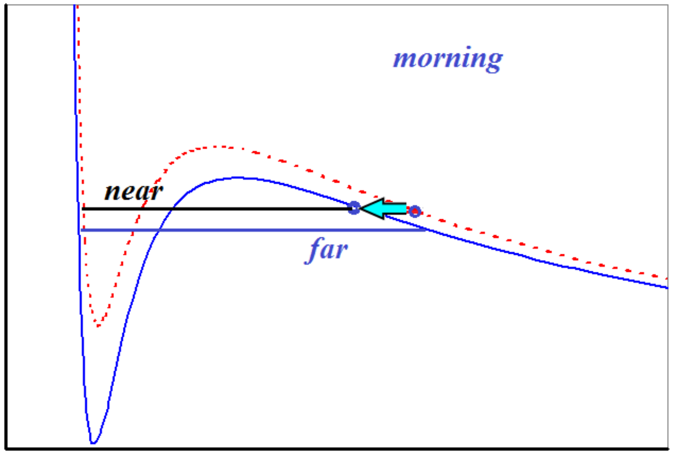
$$t = t_e - \Delta T$$

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

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

$$P_{Vapor} > P_{sat} - \Delta P_{sat} + \Delta P_T$$





# Question C4

$$\boxed{\left|\Delta P_{sat}\right| \geq \Delta P_T}$$

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

$$\rho_S = \frac{\mu P_e}{RT_e} \ll \rho_L$$

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

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

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

$$r = \frac{2\sigma b^2 T_e}{a\Delta T_e} = 1.45 \cdot 10^{-8}\,\mathrm{m}$$