Handin 4

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Question 1

Find p_c, v_c and T_c for the Van-der Waals fluid.

Answer: Given the Van-der Waals equation:

$$p = \frac{k_b T}{v - b} - \frac{a}{v^2}, \tag{1}$$

one rewrites this expression in the following manner:

$$v^3 - \left(b + \frac{k_b T}{p}\right) v^2 + \frac{a}{p} v - \frac{ab}{p} = 0.$$

At a critical point, all the critical constants are equal, and thus the above equation must have the form: $(v - v_c)^3 = 0$. Matching the terms to the new equation gives:

$$3v_c = b + \frac{k_b T_c}{p_c}, \quad 3v_c^2 = \frac{a}{p_c}, \quad v_c^3 = \frac{ab}{p_c}.$$

Rewriting the last equation gives: $p_c = ab/v_c^3$, and substituting this into the second equation gives: $v_c = 3b$. Substituting this into the first equation gives: $3v_c = b + \frac{k_b T_c}{p_c}$, and thus $T_c k_b = \frac{8a}{27b}$. Thus, the critical constants are given by:

$$p_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad T_c k_b = \frac{8a}{27b}.$$

Question 2

Rewrite the Van-der Waals equation in terms of reduced variables, $\tau = T/T_c$, $\nu = v/v_c$ and $\pi = p/p_c$.

Answer: Firstly, Van-der Waals equation is give by:

$$p = \frac{k_b T}{v - b} - \frac{a}{v^2},$$

we rewrite the reduced variables, such that the equation becomes:

$$\pi p_c = \frac{k_b \tau T_c}{\nu v_c - b} - \frac{a}{\nu^2 v_c^2}.$$

The critical constants are then given by:

$$p_c = \frac{a}{27b^2}, \quad v_c = 3b, \quad T_c k_b = \frac{8a}{27b},$$

and substituting these into the equation gives:

$$\begin{aligned} \pi \frac{a}{27b^2} &= \frac{8a}{27b} \frac{\tau}{\nu 3b - b} - \frac{a}{\nu^2 (3b)^2} \\ \implies \pi &= \frac{8\tau}{3\nu - 1} - \frac{3}{\nu^2}. \end{aligned}$$

Question 3

Expand the above equation in the vicinity of $\tau = \nu = \pi = 1$.

Answer: We rewrite the equation in terms of new variables $t = \tau - 1$ and $\phi = \nu - 1$,

$$\pi(\phi, t) = \frac{8(t+1)}{3(\phi+1)-1} - \frac{3}{(\phi+1)^2}.$$

Taylor expanding around the point $(\phi, t) = (0, 0)$ gives:

$$\begin{aligned}\pi(\phi, t) &= \frac{8(t+1)}{3\phi+2} - \frac{3}{(\phi+1)^2} \\ &= \pi(0,0) + \frac{\partial \pi}{\partial t}\Big|_{0,0} t + \frac{\partial \pi}{\partial \phi}\Big|_{0,0} \phi + \frac{1}{2}\frac{\partial \pi^2}{\partial t \partial \phi}\Big|_{0,0} t\phi + \frac{1}{2}\frac{\partial \pi^2}{\partial \phi^2}\Big|_{0,0} \phi^2 + \frac{1}{6}\frac{\partial \pi^3}{\partial \phi^3}\Big|_{0,0} \phi^3 + HOT \\ &= 1 + 4t - 6\phi t - \frac{3}{2}\phi^3 + HOT. \qquad (2)\end{aligned}$$

The higher order terms are not significant when close to the critical points.

Question 4

Using the above expression obtain the behavior of $v_g - v_l$ close to $T = T_c$. Here, v_g is the volume per particle when all gas, and v_l is the volume per particle when all liquid.

Answer: Using the expressions obtain above, we can say that v in itself is equivalent to ϕ, thus we seek ϕ_g and ϕ_l.

$$\begin{aligned} dp &= p_c \left[-6td\phi - \frac{9}{2}\phi^2 d\phi\right] \\ \implies 0 &= \int_{\phi_l}^{\phi_g} \phi \left(-6t - \frac{9}{2}\phi^2\right) d\phi. \end{aligned}$$

Using the fact that t is an odd function, we see that $\phi_g = -\phi_l$, and using eq (2), we have that:

$$\begin{aligned}\pi &= 1 + 4t - 6\phi_g t - \frac{3}{2}\phi_g^3 \\ &= 1 + 4t - 6\phi_l t - \frac{3}{2}\phi_l^3.\end{aligned}$$

Using the fact that $\phi_g = -\phi_l$, we obtain the two equations:

$$\begin{aligned}\pi &= 1 + 4t - 6\phi_g t - \frac{3}{2}\phi_g^3 \\ &= 1 + 4t + 6\phi_g t + \frac{3}{2}\phi_g^3.\end{aligned}$$

Subtracting the two equations gives:

$$0 = 12\phi_g t + 3\phi_g^3.$$

Assuming that $\phi_g \neq 0$, we divide by ϕ_g: and thus obtain:

$$\phi_g = 2\sqrt{-t}.$$

Since $\phi_g = -\phi_l$, we have that:

$$\left|\phi_g - \phi_l\right| = 2 \cdot \sqrt{-t} + 2\sqrt{-t} = 4\sqrt{1-\tau} = 4\sqrt{\frac{T_c - T}{T_c}}.$$

Question 5

Calculate the dependence off π on V on the critical isotherm.

Answer: The critical isotherm is given by $t = 0$, and thus we have that from eq (2):

$$\pi = 1 - \frac{3}{2}\phi^3.$$

Utilizing the fact that $\phi = \frac{V - V_c}{V_c}$, we have that:

$$\pi = 1 - \frac{3}{2}\phi^3 = 1 - \frac{3}{2}\left(\frac{V - V_c}{V_c}\right)^3.$$

Thus, on the critical isotherm, π has a cubic dependence on V. We can also do the inverse, thus we have that:

$$\phi^3 = 1 - \pi \implies \phi = \sqrt[3]{1 - \pi} = \frac{V - V_c}{V_c}.$$

Thus, the dependence off π on V is given by:

$$V = V_c + V_c\sqrt[3]{1 - \pi}.$$

Question 6

How does the latent heat of the transform scale close to T_c.

Answer: The latent heat ΔS is defined by:

$$\Delta S = T(v_g - v_l)\frac{dp}{dT}.$$

In the previous task, when close to the critical temperature, we found that $v_g - v_l \propto \sqrt{\frac{T_c - T}{T_c}}$, and thus we have that:

$$\Delta S = T \cdot 4\sqrt{\frac{T_c - T}{T_c}}\frac{dp}{dT}.$$

From eq (1), we compute $\frac{dp}{dT}$:

$$\frac{dp}{dT} = \frac{d}{dT}\left(\frac{k_b T}{v - b} - \frac{a}{v^2}\right) = \frac{k_b}{v - b}.$$

Therefore, the latent heat ΔS is given by, when in the vicinity of the critical temperature:

$$\Delta S = 4k_b T\sqrt{\frac{T_c - T}{T_c}}\frac{1}{v - b}.$$