

## Homework F

PHY3513

Due: Wed. April 13, 2018

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1. The van der Waals equation of state provides a model for real gases. Another model for a real gas involves a perturbative expansion from Boyle's ideal gas law. For one mole of a real gas, instead of  $\frac{pV}{RT} = 1$  (ideal gas law),

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \dots$$

Here, as you can see, when the volume gets larger (the inter-atomic interaction gets weaker and the volume of molecules can be effectively ignored), the expression recovers the ideal gas law. The parameters  $B$ ,  $C$ , etc. are called virial coefficients and in general are temperature dependent. The temperature for  $B(T_B) = 0$  is called the Boyle temperature  $T_B$  since at this temperature the above equation approximately obeys Boyle's law ignoring the higher order corrections.

- (a) Express the van der Waals equation of state in the form of virial expansion.  
(a) What is the Boyle temperature for the van der Waals gas. Express it in terms of  $T_c$ .

2. (26.1)

3. (26.4) Use the cyclic relation.

4. (26.6)

5. Consider a van der Waals gas (1 mole) undergoing a Joule-Kelvin process. To have a cooling effect, the process has to be performed inside the inversion curve.

- (a) Show that the inversion curve for this system can be represented as

$$RT = \frac{2a(V-b)^2}{bV^2}.$$

- (b) Using the van der Waals equation one can convert the above inversion curve as

$$p = \frac{2a(V-3b/2)}{bV^2}.$$

From these two equations, find the maximum inversion temperature  $T_o$ . Express  $T_o$  in terms of the critical temperature  $T_c$ . How is  $T_o$  related to the Boyle temperature  $T_B$  obtained in Problem 1? Can you provide any physical interpretation why they are so closely related? (Inversion curve:  $\mu_{JK} = 0$ . The maximum inversion temperature occurs as  $p \rightarrow 0$ . Recall the shape of the inversion curve. You have two temperatures at  $p = 0$ .)

6. (27.1) Part (a): state type of expansion only. Part (b): do in full.

7. (27.2)

8. (27.5)

9. The figures below show the isotherms at two different temperatures and their corresponding paths in the P-T phase diagram of a van der Waals gas.

(a) Plot (sketch) the isothermal compressibility ( $\kappa_T$ ) following path **B** as a function of volume. It should exhibit correct behavior (relative size of  $\kappa_T$ ) at  $V_c$  (critical volume),  $V < V_c$  and  $V > V_c$ .

(b) Isothermal compression is performed following path **A** in Figure 2. Specify the region in volume that the system is thermodynamically unstable.

(c) Specify the region in volume that the liquid and gas phases coexist.

(d) Helmholtz free energy  $F$  is a function of  $T$  and  $V$ . What is the free energy difference between  $(T_1, V_1)$  and  $(T_1, V_4)$ ,  $\Delta F = F(T_1, V_1) - F(T_1, V_4)$ ? Express this in terms of specified volume and pressure in Figure 1.

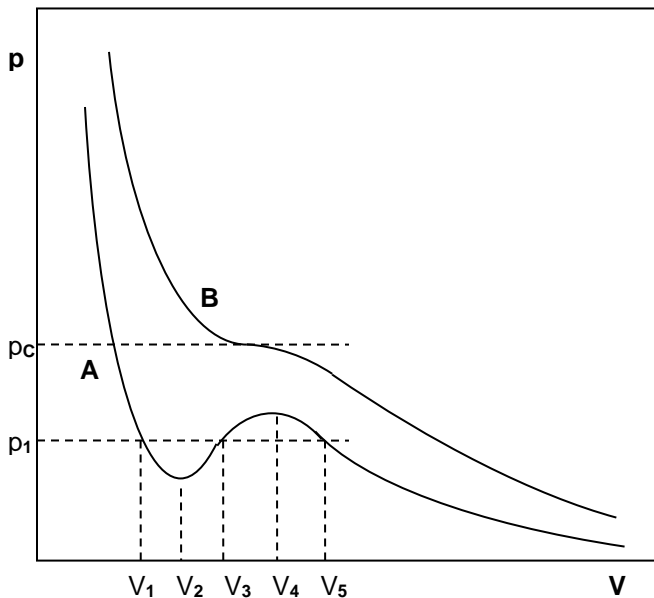


Figure 1

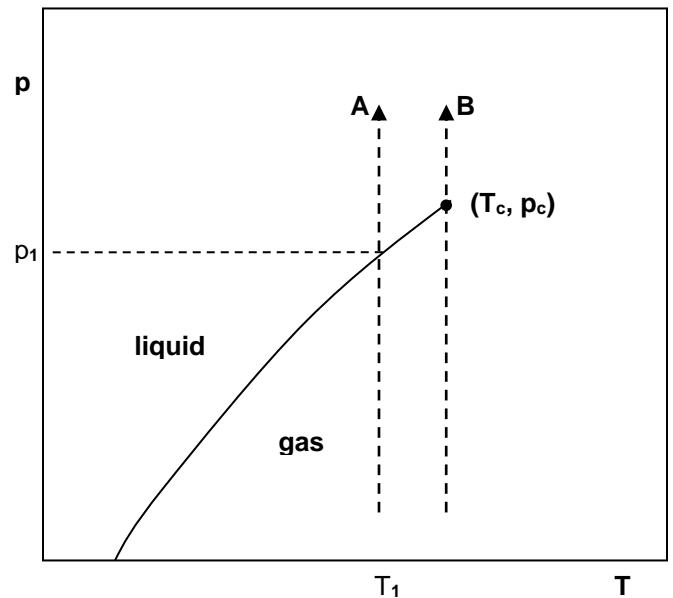


Figure 2