Homework 4 (Due Thursday, February 9th)

1. (a) Show that the Van der Waals equation of state,

$$\left(P + \frac{an^2}{V^2}\right)(V - bn) = nRT$$

may be written as

$$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r$$

where $P_r = P/P_c$, $V_r = V/V_c$, $T_r = T/T_c$, and

$$T_c = \frac{8a}{27bR} \qquad P_c = \frac{a}{27b^2} \qquad V_c = 3bn$$

(b) Graph P_r versus V_r on a log-log scale for $T_r = 0.8$, 1.0 and 1.2. Have your plot extend up to $V_r = 10$. Don't just make a sketch by hand, use a computer.

2. (a) For a thermodynamic system, if we know P and C_V as functions of T and V, then all other quantities can be determined. Actually, knowing the equation of state gives us the volume dependence of the heat capacity[1]. Specifically,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Derive this identity; you will need a Maxwell relation. (b) Show that the heat capacity at constant volume, C_V for a Van der Waals gas is only a function of temperature (i.e., show that $(\partial C_V/\partial V)_T = 0$).

3. Consider a system which has only three states, labeled a, b and c; the probability of the system being in a particular state is p_a, p_b and p_c, respectively. The entropy is defined as

$$S = -k \sum_{i=a,b,c} p_i \ln p_i = -k[p_a \ln p_a + p_b \ln p_b + p_c \ln p_c]$$

Prove that the entropy is maximum when $p_a = p_b = p_c = 1/3$. Remember that the probabilities must satisfy the condition $p_a + p_b + p_c = 1$.

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[1] But we have to find the temperature dependance, if any, by other means

Solutions

1. (a) Writing $P = P_r P_c$, $V = V_r V_c$, and $T = T_r T_c$,

$$\left(P_r P_c + \frac{an^2}{V_r^2 V_c^2}\right)(V_r V_c - bn) = nRT_r T_c$$

or

$$\left(P_r \frac{P_c}{RT_c} + \frac{1}{V_r^2}\frac{an^2}{RV_c^2 T_c}\right)\left(V_r \frac{V_c}{n} - b\right) = T_c$$

or

$$\left(P_r \frac{1}{8b} + \frac{1}{V_r^2}\frac{3}{8b}\right)(3bV_r - b) = T_r$$

which gives the desired result by inspection.

(b) Your graph should look like Figure 1. One point of this exercise is that the cartoons that illustrate the isotherms as broad S-shaped curves are somewhat idealized. Remember that the minimum volume (where the pressure becomes infinite) is $V = b$, which is $V_r = 1/3$.

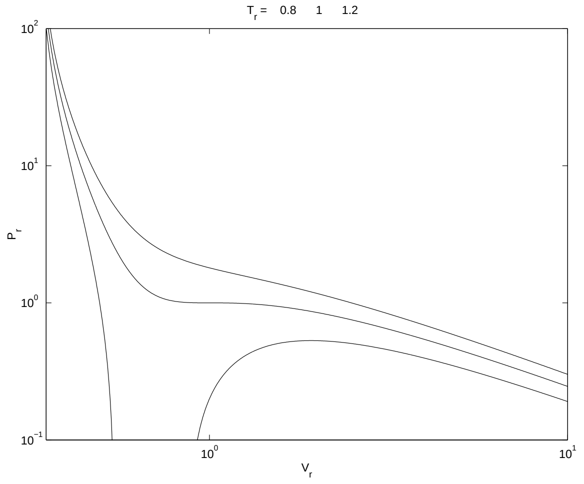

Figure 1: Isotherms for the van der Walls equation of state.

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2. (a) We first need to rearrange the derivatives as,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V} T \left(\frac{\partial S}{\partial T}\right)_V\right)_T = T\frac{\partial^2 S}{\partial V \partial T} = T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V$$

Using the Maxwell relation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

then

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)_V\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

(b) We now specifically use the Van der Waals equation of state (for one mole of gas),

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

so

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b} \qquad ; \qquad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

which establishes our desired result.

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3. We can write the entropy as

$$S = -k[p_a \ln p_a + p_b \ln p_b + (1-p_a-p_b)\ln(1-p_a-p_b)]$$

where we have used the constraint to set $p_c = 1-p_a-p_b$. To find the maximum entropy, we differentiate with respect to the probabilities, setting the derivative to zero. Explicitly, this is

$$\begin{aligned} \frac{\partial S}{\partial p_a} &= -k(\ln p_a + 1 - \ln(1-p_a-p_b) - 1) = 0 \\ \frac{\partial S}{\partial p_b} &= -k(\ln p_b + 1 - \ln(1-p_a-p_b) - 1) = 0 \end{aligned}$$

so

$$\begin{aligned} \ln p_a &= \ln(1-p_a-p_b) = \ln p_c \\ \ln p_b &= \ln(1-p_a-p_b) = \ln p_c \end{aligned}$$

thus $p_a = p_b = p_c$, that is, the states must be equally probable. Since the probabilities must sum to one, each must equal 1/3. Actually, we have only shown this to be an extremum but you can easily check that it is indeed a maximum since,

$$\begin{aligned} \frac{\partial^2 S}{\partial p_a^2} &= -k\left(\frac{1}{p_a} + \frac{1}{1-p_a-p_b}\right) \\ \frac{\partial^2 S}{\partial p_b^2} &= -k\left(\frac{1}{p_b} + \frac{1}{1-p_a-p_b}\right) \end{aligned}$$

which are clearly negative for $p_a = p_b = 1/3$.