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.

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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 $(\partial C_V/\partial V)_T = 0$).

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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 $p_a + p_b + p_c = 1$.

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