PHYS 813: Statistical Mechanics, Assignment 3

Due 3/13/08

1. Consider first a general system.

   (a) Show that the difference of the molar specific heats can be written as
   $$c_p - c_V = \frac{1}{N}\left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$$

   (b) Show that
   $$p + \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V$$

   (c) Using the results of (a) and (b), find the difference $c_p - c_V$ for a van der Waals gas fulfilling
   $$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$
   where v is the molar volume and a and b are constants.

   (d) Show that for $v \to \infty$ at constant p, one recovers the ideal gas result for the difference.

2. A van der Waals gas fulfilling
   $$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$
   where v is the molar volume and a and b are constants, undergoes an isothermal expansion from volume V_1 to volume V_2.

   (a) Calculate the change in Helmholtz free energy.

   (b) Calculate the change in internal energy.

3. Consider a Carnot engine filled with ideal gas.

   (a) Without an explicit consideration of the p–V dependence on the adiabatic segments, show that the sum of the work performed on these segements is zero.

(b) To confirm this result, use direct integration of the p–V dependence to find explicit expressions for the work on each of the adiabatic segments.

4. Consider a classical gas of hard spheres of diameter σ. Show that for such a gas the volume V in the ideal gas law should be replaced by $V - b$, where b is proportional to the number of particles N and to σ^3. Find the proportionality constant.

5. Consider a mixture of two ideal gases with different $\gamma = C_p/C_V$. Find the effective γ for the mixture.

6. The elasticity of a rubber band can be described by a "one-dimensional" model of a polymer involving $N + 1$ molecules linked together end-to-end. There are N such links, each of length d. The angle between successive links is equally likely to be 0 or π. Assume there are no interactions between the molecules.

   (a) Find the number of arrangements $g(N, m)$ that give an overall length $L = 2md$.

   (b) Show that for $m \ll N$, $g(N, m)$ can be written as

   $$g(N, m) = g(N, 0)\mathrm{e}^{-4m^2/N}.$$

   (c) Find the entropy of the system as a function of L for $N \gg 1$ and $L \ll Nd$.

   (d) Assume that the system is in equilibrium with a heat bath of temperature T. Using the expression derived in (c) and appropriate thermodynamic relations, find the external force required to maintain the length L.