PHYS 813: Statistical Mechanics, Assignment 1

Due 3/13/09

1. Consider three variables, x, y, and z, two of which are independent. Show that

   (a)

$$\left(\frac{\partial x}{\partial y}\right)_z = 1/\left(\frac{\partial y}{\partial x}\right)_z$$

   (b)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

2. The velocity of sound is given by

$$v_{\mathrm{s}} = \sqrt{\left(\frac{\partial p}{\partial \rho}\right)_{S,N}}$$

   where p, ρ, S, and N are the pressure, density, entropy, and number of moles of a fluid, respectively.

   (a) Consider first an ideal gas and show that v_{s} is given in this case by

$$v_{\mathrm{s}} = \sqrt{\frac{c+1}{c}\frac{RT}{M}} = \sqrt{\frac{c_p}{c_V}\frac{1}{\rho\kappa_T}}$$

   where R is the gas constant, T, M, c_p, c_V and κ_T are the temperature, molar mass, specific heat at constant pressure, specific heat at constant volume and the isothermal compressibility of the gas, respectively, and c is a constant equal to 3/2 for a monoatomic gas.

   (b) Now consider a general fluid and show that the expression for v_{s} is the same as the one for the ideal gas written in terms of c_p, c_V, and κ_T.

3. A substance has the following properties:

   (a) At a constant temperature T_0, the work done by it on expansion from a volume V_0 to V is

$$W = RT_0 \ln\frac{V}{V_0}$$

   (b) The entropy is given by

$$S = R\frac{V_0}{V}\left(\frac{T}{T_0}\right)^c$$

   where c is a constant equal to 3/2 for a monoatomic gas.

   Find (i) the expression for the Helmholtz free energy; (ii) the equation of state; (iii) the work done at an arbitrary constant temperature.

4. Show that for a van der Waals gas the heat capacity at constant volume, C_V, is a function of temperature alone. The equation of state for such gas is

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NRT$$

where p and N are the pressure and the number of moles of the gas, R is the gas constant, and a and b are constants characterizing a given gas. Show next that $C_V = cNR$, where c is a constant equal to $3/2$ for monoatomic gas, i.e., is the same as for ideal gas.

5. Calculate the internal energy U and the entropy S (relative to the values U_0 and S_0, respectively, in some reference state at $T = T_0$) of a monoatomic van der Waals gas as functions of temperature T and volume V. The equation of state for such gas is

$$\left(p + \frac{N^2 a}{V^2}\right)(V - Nb) = NRT$$

where p and N are the pressure and the number of moles of the gas, R is the gas constant, and a and b are constants characterizing a given gas. You may use without proof the fact that C_V is independent of V for a van der Waals gas.

6. The material constants are often connected by rigorous relations. Find such a relation between the isothermal compressibility κ_T, adiabatic compressibility κ_S, coefficient of thermal expansion at constant pressure α, and heat capacity at constant pressure C_p for a system with a fixed number of particles (you should express $\kappa_T - \kappa_S$ in terms of α, C_p, temperature T, and volume V). The coefficients are defined as follows:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T, \quad \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S, \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p, \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

   (a) Since the definitions include quantities S, V, T, and p, show that these quantities can be expressed as appropriate functions of each other by using only the postulates and basic definitions of thermodynamics.

   (b) Find a relation involving derivatives of all four quantities, preferably the derivatives from the definitions given above. Use rigorous mathematical reasoning (no "dividing of dy by dx").

   (c) Your expression will depend on at least one derivative not appearing in the definitions given above. Eliminate this derivative by using the "three derivatives" formula and a Maxwell's relation. Derive the particular Maxwell relation employed.

7. Similarly like in the problem above, but find a relation connecting κ_T, κ_S, C_p, and

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V.$$

8. One mole of a van der Waals gas obeying the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

where p, T, and v are the pressure, temperature, and molar volume of the gas, R is the gas constant, and a and b are constants characterizing this gas, has the molar internal energy $u = cT - a/v$, where c is a constant. Calculate the molar heat capacities c_V and c_p.

9. Consider two Carnot engines operating between the same given temperatures T_h and T_c and volumes V_{min} and V_{max}, one filled with a monoatomic and another with the same number of moles of a diatomic ideal gas.

   (a) Show that the conditions given define each engine uniquely.

   (b) Find the expression for the work in terms of given quantities.

   (c) Find the ratio of the works performed by the two engines. Which engine performs more work?

10. The fundamental relation in the entropy representation, $S = S(U, V, N_1, ..., N_r)$, where U is the internal energy, V is the volume, and N_i is the number of moles of substance i, can be replaced by the fundamental relation in the Helmholtz representation utilizing the Helmholtz potential $F = U - TS$, where T is temperature. For a single-component van der Waals fluid

$$S = NR\ln\frac{(V - Nb)N_0}{(V_0 - N_0b)N} + cNR\ln\frac{(U + N^2a/V)N_0}{(U_0 + N_0^2a/V_0)N} + \frac{N}{N_0}S_0,$$

where R is the gas constant, a, b, and c are constants characteristic of a given fluid, and the subscript "0" denotes quantities in a reference state. Find the fundamental relation for this fluid in the Helmholtz representation.