Candidacy Exam Fall 1999

Thermodynamics

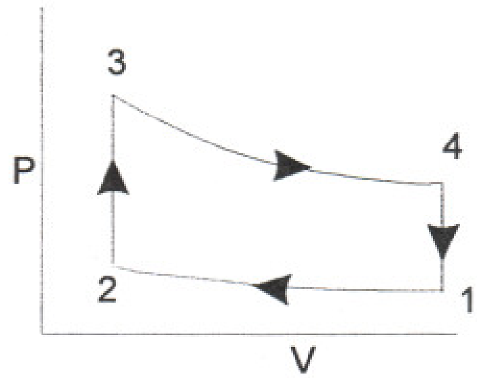
Do all problems

1. *(35 pts.)*

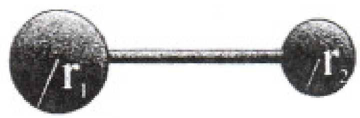
   20 pts. (a) Define the Helmholtz free energy A(T,V,N) and the Gibbs free energy G(T,P,N) based on the internal energy U(S,V,N). Write down the differential forms. Derive the Gibbs-Duhem relationship, $0=SdT-VdP+Nd\mu$, starting from A and starting from G.

   15 pts. (b) The coefficient of adiabatic thermal expansion is defined by $\beta_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{S,N}$. Show that $\beta_S = -\frac{c_v \kappa_T}{v T \beta}$, where c_v is the heat capacity at constant volume, κ_T is the isothermal compressibility, v is the number of particles per unit volume, and β is the thermal expansivity at constant pressure. Derive any Maxwell relations you need from the differential forms in (a).

2. *(30 pts.)* The cycle of a highly idealized gasoline engine can be approximated by the Otto cycle, at right. 1→2 and 3→4 are adiabatic compression and expansion, respectively, while 2→3 and 4→1 and are constant volume processes. Treat the working medium as an ideal gas with constant $\gamma = c_p/c_v$, where c_p and c_v are the heat capacity at constant pressure and volume respectively. Remember that along adiabatic paths in an ideal gas with γ constant, PV^γ=const.
   Define and compute the efficiency of this cycle for γ=1.4 and compression ratio $r = V_i/V_f = 10$.



3. *(35 pts.)* Two bubbles in solution are connected by a thin "straw" of negligible volume compared to the volume of the bubbles (see at right). The ambient pressure is P_a, the temperature is T, and the surface energy per unit area is γ.



   10 pts. (a) Show that the pressure inside a single spherical bubble of radius r_i is $P_i=P_a+2\gamma/r_i$.

   10 pts. (b) Is the configuration $r_1 = r_2$ in stable equilibrium? Argue why or why not, starting from a consideration of what happens when r_2 is slightly smaller than r_1.

   10 pts. (c) One could in principle use this system to determine γ by measuring r_1 and r_2 and then the final bubble radius r_f after one of the bubbles disappears entirely into the other. Relate γ to r_1, r_2, r_f and P_a. Assume that the gas inside the bubbles is ideal and that both the total mass within the bubbles and the temperature remain constant during this process.

   5 pts. (d) Comment on the result in the limits of large and small γ. For γ= 30mN/m (a typical value) and P_a~1 atm, at what order of radius would you want to try this way of determining γ (r~1 cm, 1mm, 1μm....?) Remember that 1 atm=10^5N/m^2.