Due Apr. 11, Thursday.

Problem 1 (10 points) Prove the following identities assuming that x, y, z form a set of constrained variables

$$f(x, y, z) = 0$$

We assume that f is solvable for any variable x, y or z.

(a) For w, an arbitrary function of any two independent variables out of x, y, z,

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w = \left(\frac{\partial x}{\partial z}\right)_w$$

(b)

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

(c) Euler's chain rule.

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

Problem 2 (10 points) Show that by using thermodynamic identities, Maxwell's relations, and the above rules that

$$C_P - C_V = \frac{TV\alpha^2}{\kappa_T}$$

$$\frac{C_P}{C_V} = \frac{\kappa_T}{\kappa_S}$$

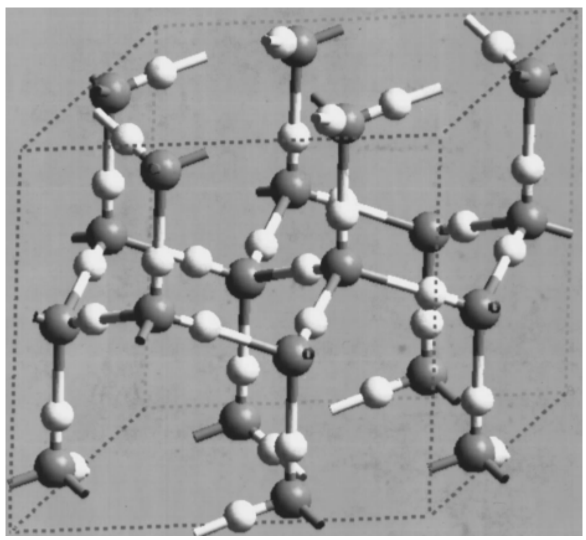
where C_P, C_V are heat capacities (at constant pressure and constant volume, respectively), α is the coefficient of thermal expansion, and κ_T, κ_S are (isothermal and adiabatic, respectively) compressibilities.

Problem 3 (20 points) Kardar 1.9 (check course web site for a copy of this problem)

Problem 4 (20 points) Kardar 1.10 (the same)

Problem 5 (10 points) Kardar 1.11 (the same)

Problem 6 (20 points) (ice and spin ice) It is known that in ice oxygen ions form crystals (in one – Ih – of the many crystalline phases) with a tetrahedral motif, but hydrogen ions are disordered.See the diagram below (gray = oxygen, white = hydrogen). This is due to the fact that the hydrogen to oxygen bond length is much like that in the water molecule, but that this bond length is much shorter than half of the oxygenoxygen bond length. One hydrogen ion is located along one oxygen-oxygen bond, but, because of the above reason, the hydrogen is much closer to one of the two oxygen ions than the other. We can say that the hydrogen ion "belongs to the first oxygen" when this happens. This asymmetry of the location of the hydrogen ion on the oxygen-oxygen bond is the source of disorder, and a residual entropy. Of course, the constraint for the ground state is that there must be only two hydrogen ions that belong to any given oxygen ion. These rules just described are usually referred to as the "ice rules." [To read more about this and the spin ice (which provides a particularly clean demonstration of the physics discussed here), see Ramirez et al., Nature vol. 399, 333 (1999) or any other information that you can collect (from the web?).] Show that for this problem, the residual entropy is truly finite, and so the entropy will not vanish at zero temperature. Show that the entropy per hydrogen ion is (approximately) $\frac{1}{2}k_B \log(3/2)$. Show that this residual entropy amounts to 1.69 J per mole per K.



[Hint: For approximate solution, use "the mean field approach." Within the mean field approach, focus on one water molecule only and consider all other water molecules "averaged out." It also helps to map the problem to a two dimensional square lattice.]