Due Apr. 11, Friday.

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 (20 points) Let α be the coefficient of thermal expansion, $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$, and κ_T, κ_S be (isothermal and adiabatic, respectively) compressibilities, $\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ and $\kappa_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$.

(a) Show the following general identities by using thermodynamic identities, Maxwell's relations, and the above identities in the previous problem.

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

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

C_P and C_V are heat capacities at constant pressure and constant volume, respectively.

(b) In the monatomic ideal gas case, find expressions for α, κ_T, and κ_S, in terms of n, V, and T. Then evaluate the right hand sides of the above two expressions, $C_P - C_V$ and C_P/C_V. Compare the results with those that you can derive directly from the well-known equation of state and the energy function for the monatomic ideal gas.

Problem 3 (20 points) In a Joule-Thomson process, a gas (or liquid) flows in an insulating cylinder, through a porous wall that separates two partitions of gas, by a pressure difference, within the cylinder. One partition is maintained at pressure P_1, while the other partition is maintained at pressure P_2. Due to the porous wall, the gas flows quasi-statically.

(a) Show that the enthalpy $H = E + PV$ is conserved in the process, as gas moves from one partition to another.

(b) Consider the case when the pressure difference is very small. Show that

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left(T\left(\frac{\partial V}{\partial T}\right)_P - V\right)$$

[Hint: the results of problem 1 should be helpful.]

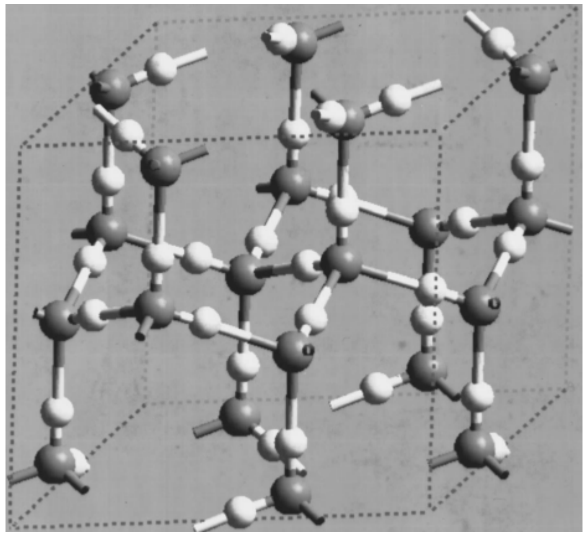
(c) Prove that the process is irreversible.

Problem 4 (20 points) Consider the possibility of negative temperatures. Use the maximum entropy principle to answer the following questions.

(a) Consider connecting two samples thermally (but not mechanically), where each sample can be maintained at a negative as well as positive temperature. Show that the heat flows from the small β sample to the large β sample, regardless of the sign of temperature. $\beta = 1/(k_B T)$.

(b) Show that it is impossible to build a Carnot engine operating between a negative temperature reservoir and a positive temperature reservoir.

Problem 5 (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 (barring the intervention of a different phase). Show that the entropy per hydrogen ion is (approximately) $\frac{1}{2}k_B \log\frac{3}{2}$. 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.]