Homework #8 Phys 711 Fall 2008

Don't hand in

1. Hand-in problem #2 in homework #7 modeled a diatomic molecule classically as two masses (spheres, for example) joined by a spring. This is a terrible model for a real molecule. Slight improvement comes about from assuming that the moment of inertia about the axis joining the spheres is small, or that the molecule is a rigid "dumbbell" at lower energies. A quantum-mechanical treatment is necessary, especially to capture the fact that different degrees of freedom come into play at different temperatures.

With this in mind, read the section "Gases with internal degrees of freedom" in chapter 8, on pages 225-234. Don't worry about the details (unless you want to!); just extract the main ideas.

Hand in

1. Study the statistical mechanics of N non-interacting, distinguishable "Fermi oscillators". These are quantum-mechanical oscillators defined by having only two energy states: zero and ε. Derive expressions for the entropy, pressure, chemical potential, and show that the specific heat at constant volume is

$$C_V = \frac{Nk\left(\beta\varepsilon\right)^2 e^{-\beta\varepsilon}}{\left(1+e^{-\beta\varepsilon}\right)^2}.$$

2. Now consider a similar single system with degenerate energy states. In particular, assume that the quantum states available are: (1) a group of g_1 equally likely states with a common energy ε, and (2) a group of g_2 equally likely states with a common energy $\varepsilon_2 > \varepsilon_1$.

a. Show that the entropy of the system is given by

$$S = -k\left[w_1 \ln\left(\frac{w_1}{g_1}\right) + w_2 \ln\left(\frac{w_2}{g_2}\right)\right],$$

where w_1 and w_2 are, respectively, the probabilities of the system being in a state belonging to group (1) or group (2), with $w_1 + w_2 = 1$.

b. Assuming that the probability of being in one particular state with energy ε_i is given by the canonical ensemble result, show that

$$S = k\left[\ln g_1 + \ln\left\{1+\left(g_2 / g_1\right)e^{-x}\right\} + \frac{x}{1+\left(g_1 / g_2\right)e^{x}}\right],$$

where $x = \left(\varepsilon_2 - \varepsilon_1\right)/kT$, which is assumed to be positive.

c. Verify the previous expression by deriving it from the partition function.

d. Check that as $T \to 0, S \to k \ln g_1.$ What about the third law of thermodynamics?