PC2230 Thermodynamics and Statistical Mechanics, homework 5

Due Thursday, 30 Mar 11:59PM

Problems 6.5 (*20 marks*). Problem 6.9 (*20 marks*). Problem 6.18 (*20 marks).* 6.19 (20 marks), Problem 6.39 (*20 marks*). For (a), (b), (c) sub-questions, 20/3 = 6.66 each. Total 100 marks.

Problem 6.5. Imagine a particle that can be in only three states, with energies -0.05 eV, 0, and 0.05 eV. This particle is in equilibrium with a reservoir at 300 K.

(a) Calculate the partition function for this particle.

(b) Calculate the probability for this particle to be in each of the three states.

(c) Because the zero point for measuring energies is arbitrary, we could just as well say that the energies of the three states are 0, $+0.05$ eV, and $+0.10$ eV, respectively. Repeat parts (a) and (b) using these numbers. Explain what changes and what doesn't.

Problem 6.9. In the numerical example in the text, I calculated only the *ratio* of the probabilities of a hydrogen atom being in two different states. At such a low temperature the *absolute* probability of being in a first excited state is essentially the same as the relative probability compared to the ground state. Proving this rigorously, however, is a bit problematic, because a hydrogen atom has infinitely many states.

(a) Estimate the partition function for a hydrogen atom at 5800 K, by adding the Boltzmann factors for all the states shown explicitly in Figure 6.2. (For simplicity you may wish to take the ground state energy to be zero, and shift the other energies accordingly.)

(b) Show that if *all* bound states are included in the sum, then the partition function of a hydrogen atom is infinite, at any nonzero temperature. (See Appendix A for the full energy level structure of a hydrogen atom.)

(c) When a hydrogen atom is in energy level n, the approximate radius of the electron wavefunction is $a_0 n^2$, where a_0 is the Bohr radius, about 5×10^{-11} m. Going back to equation 6.3, argue that the $P\,dV$ term is *not* negligible for the very high-n states, and therefore that the result of part (a), not that of part (b), gives the physically relevant partition function for this problem. Discuss.

Problem 6.18. Prove that, for any system in equilibrium with a reservoir at temperature T, the average value of E^2 is

$$\overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}.$$

Then use this result and the results of the previous two problems to derive a formula for σ_E in terms of the heat capacity, $C = \partial \overline{E}/\partial T$. You should find

$$\sigma_E = kT\sqrt{C/k}.$$

Problem 6.19. Apply the result of Problem 6.18 to obtain a formula for the standard deviation of the energy of a system of N identical harmonic oscillators (such as in an Einstein solid), in the high-temperature limit. Divide by the average energy to obtain a measure of the *fractional* fluctuation in energy. Evaluate this fraction numerically for $N = 1$, 10^4, and 10^{20}. Discuss the results briefly.

Problem 6.39. A particle near earth's surface traveling faster than about 11 km/s has enough kinetic energy to completely escape from the earth, despite earth's gravitational pull. Molecules in the upper atmosphere that are moving faster than this will therefore escape if they do not suffer any collisions on the way out.

(a) The temperature of earth's upper atmosphere is actually quite high, around 1000 K. Calculate the probability of a nitrogen molecule at this temperature moving faster than 11 km/s, and comment on the result.

(b) Repeat the calculation for a hydrogen molecule (H_2) and for a helium atom, and discuss the implications.

(c) Escape speed from the moon's surface is only about 2.4 km/s. Explain why the moon has no atmosphere.