Homework 3

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February 14, 2014

Some problems in this homework deal with the quantum mechanical harmonic oscillator, or oscillator, for short. The essentials of what you need to know about its properties are given below.

The energy of an oscillator has the form $E_q = (q + 1/2)\hbar\omega$, where the quantum number q can take values $0, 1, 2, \cdots \infty$. In other words, the states form an equally spaced ladder with an energy spacing, between adjacent states, of $\hbar\omega$. The characteristic frequency of the oscillator is ω - different oscillators have different ω. We ignore the zero point energy of $\frac{\hbar\omega}{2}$ here. Thus if an oscillator has q quanta of energy it implies that its energy is $q\hbar\omega$.

1. Suppose you flip four fair coins. (a) Make a list of all the possible outcomes. (b) Make a list of all the different "configurations" and their probabilities. (c) Compute the multiplicity of each configuration using the combinatorial formula, and check that these results agree with what you got by brute-force counting.

2. Suppose you flip 50 fair coins. (a) How many possible outcomes (microstates) are there? (b) How many ways are there of getting exactly 25 heads and 25 tails? (c) What is the probability of getting exactly 25 heads and 25 tails? (d) What is the probability of getting exactly 30 heads and 20 tails? (e) What is the probability of getting exactly 40 heads and 10 tails? (f) What is the probability of getting 50 heads and no tails? (g) Plot a graph of the probability of getting n heads, as a function of n.

3. This is an illustration of Stirling's approximation for the factorial, $\ln(n!) = n \ln n - n$. Suppose you flip 1000 coins.
   (a) What is the probability of getting exactly 500 heads and 500 tails?
   (b) What is the probability of getting 502 heads and 498 tails?
   (c) What is the probability of getting 600 heads and 400 tails?

4. For a harmonic oscillator with each of the following values of N and q, list all of the possible microstates, count them, and verify the combinatorial formula ($W = \frac{(q+N-1)!}{q!(N-1)!}$). (a) $N = 3, q = 4$ (b) $N = 3, q = 5$ (c) $N = 3, q = 6$ (d) $N = 4, q = 2$ (e) $N = 4, q = 3$ (f) $N = 1, q =$ anything (g) $N =$ anything, $q = 1$.

5. Calculate the multiplicity of a sytem with 30 oscillators and 30 units of energy. (Do not attempt to list all the microstates.)

6. In a system with energy levels evenly spaced by 1.5×10^{-19} J at 500 K, n_0 is 1×10^{10}. What is n_1? What is n_1 at 175 K?

7. The ratio $n_j/n_i = 0.40$ for a system at 175 K. What is $\Delta e_{i,j}$ for this sytem? At 350K?

8. It was determined from spectroscopy that $n_j/n_i = 0.15$ and $\Delta e_{i,j} = 7.8 \times 10^{-21}$. (a) What is the temperature of the system? (b) If the temperature of the system was found to be 400 K, what would the observed n_j/n_i be?

9. This is an illustration of the effect of large numbers. It can be shown that for a system of n particles in a Boltzmann distribution with thermodynamic probability W_A, making a change that, on average, changes the population of levels by p percent of their original values, results in a new distribution with thermodynamic probability W_B such that

$$\frac{W_B}{W_A} \approx e^{-n\left(\frac{p}{100}\right)^2}$$

If Distribution A is the Boltzmann distribution at some temperature and Distribution B is a distribution differing by 0.001% from those of A, what is W_B/W_A if the system contains (a) 10,000 particles? (b) 0.5 mol particles? Perform the same calculation for A and B differing by 10^{-6}%, and 10^{-9}%. What conclusion do you draw from these results?

10. Consider a hypothetical atom that has just two states: a ground state with energy zero and an excited state with energy 2 eV. Draw a graph of the "partition function" for this sytem as a function of temperature, and evaluate it numerically at $T = 300$ K, 3000 K, and 300, 000K.

11. For each of the following processes deduce whether each of the quantities q, w, ΔU, ΔH is positive, zero, or negative. (a) Reversible melting of solid benzene at 1 atm and the normal melting point. (b) Reversible melting of ice at 1 atm and 0°C. (c) Reversible adiabatic expansion of a perfect gas. (d) Reversible isothermal expansion of a perfect gas. (e) Adiabatic expansion of a perfect gas into a vacuum. (f) Joule-Thomson adiabatic throttling of a perfect gas. (g) Reversible heating of a perfect gas at constant P. (h) Reversible cooling of a perfect gas at constant V.

12. The isothermal compressibility of lead is 2.3×10^{-6} atm^{-1}. A cube of lead of 10 cm length at 298K is inserted under 1000m of water where the temperature is 268K. Calculate the change in the volume of the cube given that the mean density of water is 1.03 g cm^{-3} and α_{Pb} is 8.61×10^{-5}.