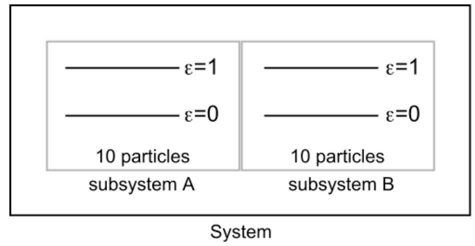
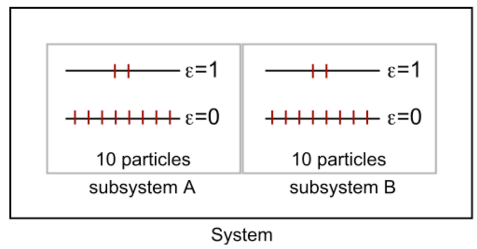
Core Course 2002
Homework Part II, Problem Set 3

1. a) For the two 10-particle, two-state subsystems discussed in class, suppose the total energy to be shared between the two objects (ie., of the system overall) is $U = U_A + U_B = 4$, what is the distribution of energies that gives the highest multiplicity?
In other words, the subsystems can exchange energy, but not particles (mass).



We want to maximize: $W_{Total} = W_A W_B$
By the symmetry of the system (same number of particles on each side) you can already guess that the distribution of energies will be the same on each side. So the answer is simple.



b) Assuming that the energy separation in this system is $3.83\text{x}10^{-21}$ J, what is the temperature of the above system?

Use the Boltzmann equation:

$$\frac{n_{\varepsilon=1}}{n_{\varepsilon=0}} = e^{-\frac{\Delta\varepsilon}{kT}} \qquad \ln\left(\frac{n_{\varepsilon=1}}{n_{\varepsilon=0}}\right) = -\frac{\Delta\varepsilon}{kT}$$

$$T = -\frac{\Delta\varepsilon}{k\ln\left(\frac{n_{\varepsilon=1}}{n_{\varepsilon=0}}\right)} = -\frac{3.83x10^{-21}J}{\left(1.38x10^{-23}JK^{-1}\right)\ln\left(\frac{2}{8}\right)} = 200K$$

c) Express the above energy separation in terms of J/mol of particles.

$$\left(3.83x10^{-21}J\right)\left(6.02x10^{23}mol^{-1}\right) = 2300J\ mol^{-1} = 2.30kJ\ mol^{-1}$$

d) Express the above energy separation in terms of kcal/mol. Compare that to the energies of the various spectroscopies on your hand out of last week.

$$\left(2.30kJ\ mol^{-1}\right)\left(\frac{kcal}{4.184kJ}\right) = 0.550kcal\ mol^{-1}$$

2. a) Consider an optical transition in the near-IR, at 800 nm. What is the ratio of excited to ground state population at room temperature (25° C)?

Use the Boltzmann equation:

$$\Delta\varepsilon = \frac{hc}{\lambda} = \frac{\left(6.626x10^{-34}\,J\,s\right)\left(2.998x10^{8}\,m\,s^{-1}\right)}{800nm}\frac{10^{9}\,nm}{m} = 2.48x10^{-19}\,J$$

$$\frac{n_{excited}}{n_{ground}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{2.48x10^{-19}J}{\left(1.381x10^{-23}J\,\mathrm{K}^{-1}\right)(25+273)K}} = e^{-60} = 6.7x10^{-27}$$

Just for fun:

$$\Delta E = N_0\Delta\varepsilon = 2.48x10^{-19}\,J\left(6.022x10^{23}\,mol^{-1}\right) = 1.50x10^{5}\,J\,mol^{-1} = 150kJ\,mol^{-1}$$

BIG!!

b) What is the ratio for that same transition at 77 K, at 10 K?

at 77 K: $\frac{n_{excited}}{n_{ground}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{2.48x10^{-19}J}{\left(1.381x10^{-23}J\,\mathrm{K}^{-1}\right)77K}} = e^{-233} = 0$

OK, my calculator doesn't go that low…

at 10 K: $\frac{n_{excited}}{n_{ground}} = e^{-\frac{\Delta\varepsilon}{kT}} = e^{-\frac{2.48x10^{-19}J}{\left(1.381x10^{-23}J\,\mathrm{K}^{-1}\right)10K}} = e^{-1800} = 0$

OK, my calculator doesn't go that low either…

3. You flip a coin 5 times and record the number of "heads."
   Computer W for each of the possible outcomes listed below. Which is most probable?

0 heads	$W = \frac{5!}{5!0!} = 1$
1 heads	$W = \frac{5!}{4!1!} = 5$
2 heads	$W = \frac{5!}{3!2!} = 10$ Most probable
3 heads	$W = \frac{5!}{2!3!} = 10$ (Equally) Most probable
4 heads	$W = \frac{5!}{1!4!} = 5$
5 heads	$W = \frac{5!}{0!5!} = 1$

As for which is most probable, you could have looked at the symmetry of the problem and guessed the answer without even doing the calculation….